Addition of Maleic Anhydride to α-Methyl-p-methylstyrene and some Related Compounds. I

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The conjugation of an aromatic double bond with an exocyclic one gives rise to a system capable of undergoing the diene synthesis. Particularly the styrene derivatives as the simplest types have been objects of investigation in this respect. However, their great tendency in general to polymerize and to form heteropolymers with maleic anhydride (or other philodienes) restricts their applicability as diene components. In the diene synthesis of this type either one or two molecules of maleic anhydride participate in the adduct formation. In the first case the primary addition product stabilizes through aromatization, in the second case one additional maleic anhydride molecule is added resulting in the formation of a stable bis-adduct. This latter case is known as the Wagner-Jauregg reaction.

On dealing with the addition of maleic anhydride to styrene and its nuclear — substituted derivatives, it can be stated that no reports about regular bis-adducts are to be seen in the literature except a preliminary one given by Alder and Schmitz-Josten [1]. According to these authors, by means of some unrevealed inhibitors the tendency of styrene to polymerization and heteropolymerization could be so far suppressed that a simple bis-adduct resulted. The following reaction mechanism was suggested:
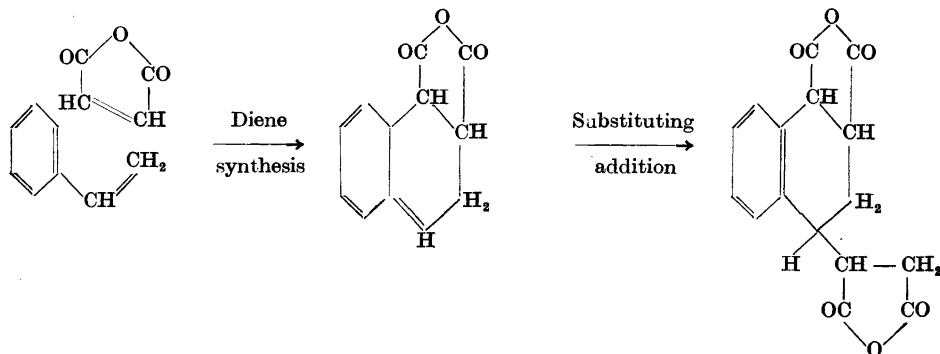
1,1-Diphenylethylene seems to be the favoured α-substituted styrene derivative to undergo the bis-adduct formation with maleic anhydride. Wagner-Jauregg [2], the discoverer of this reaction type, obtained this bis-adduct in good yield by simple heating the components together or in benzene solution. The reaction mechanism at first proposed by him was the following one:


(M. A. = maleic anhydride)
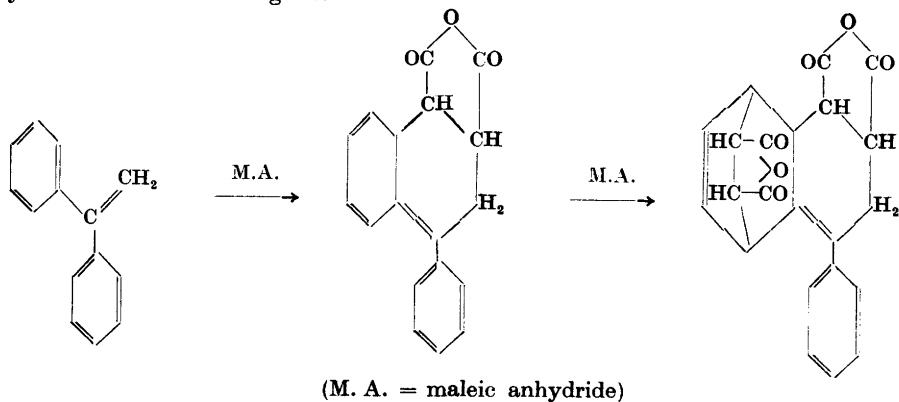
In spite of numerous observations in favour of the above structure of the bis-adduct he was not able to prove it decisively. Later he himself distrusted it and was inclined to accept a concept of substituting addition.

Bergmann *et al.*[3] prepared several new bis-adducts by condensing nuclear-substituted 1,1-diphenylethylenes with maleic anhydride. These authors accepted the above reaction mechanism without giving any conclusive arguments in its favour.

Other reports of α-substituted styrenes undergoing the bis-adduct formation with maleic anhydride are not to be seen in the literature.

Among the β-substituted styrene derivatives p-methoxypropenylbenzene (anethole) and o-methoxypropenylbenzene are the only ones that have been reported to form bis-adducts with maleic anhydride. By using dimethylaniline as polymerization inhibitor in the condensation of anethole with maleic anhydride Bruckner and Kovács [4,5] could repress the formation of heteropolymers and obtained a crystalline bis-adduct (m. p. 241°) with a 61 per cent yield. The following formula was given by them to this bis-adduct:
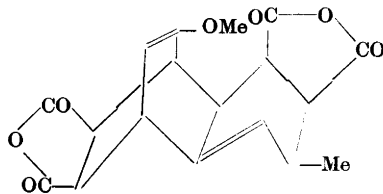
If the spatial arrangement is omitted, this formula is completely analogous to that proposed by Wagner-Jauregg to the corresponding 1,1-diphenylethylene adduct. In order to prove the existence and position of the double bond belonging to the bicyclo-octene ring in the above formula, the enol ether character of the methoxyl group was

made use of. The other double bond was demonstrated by hydrogen peroxide addition to a hydroxy lactone tricarboxylic acid obtained from the bis-adduct by saponification and lactonization resulting in the disappearance of the first double bond. The experimental observations made by Bruckner and Kovács may agree with the above structure, but that the bis-adduct in question must have just this structure, is, on the basis of the arguments put forward by these authors, rather difficult to become convinced of.

By using hydroquinone as inhibiting agent towards polymerization, Lora Tamayo [6] obtained a crystalline anethole — maleic anhydride bis-adduct (m. p. 232°), which he thaught to be identical with the Bruckner product. At first he accepted the structure proposed by Bruckner and Kovács. Because the ultra-violet absorption spectrum of this adduct proved to be of the same type as that of tetralin, Lora Tamayo later [7] took into account another possibility, a substituting addition of the second molecule of maleic anhydride to the intermediate. Accordingly the bis-adduct would have a tetrahydronaphthalene structure analogous to that suggested by Alder and Schmitz-Josten [1] for the corresponding styrene adduct.

A maleic anhydride bis-adduct of *o*-methoxypropenylbenzene is also reported by Lora Tamayo [8]. He suggested a tetrahydronaphthalene structure for this adduct too.

As a summary it can be stated, that two divergent opinions exist upon the mechanism of the Wagner-Jauregg reaction. All authors agree in the addition of the first molecule of maleic anhydride. The stabilization of the intermediate is thaught to proceed either through a second 1,4-addition of maleic anhydride resulting in the formation of a bicyclooctene ring (Bruckner and Kovács [4,5]) or through a substituting addition (Alder and Schmitz-Josten [1]). Both possibilities are put forward by Wagner-Jauregg [2] and Lora Tamayo [6,7]). The main argument in favour of the latter reaction mechanism has been the "saturated character" of the bis-adducts, a fact pointed out by almost all authors. The great tendency to resist catalytic hydrogenation and the negative double bond test with different reagents have been common features of these compounds. If both reaction mechanisms are possible by starting with the same styrene derivative, cannot be said at this time. So far only one bis-adduct of each styrene has been reported.

The purpose of the present investigation is:

1) to study, if α-substituted styrenes other than 1,1-diphenylethylene would react with maleic anhydride according to the Wagner-Jauregg reaction.

2) to elucidate the mechanism of the Wagner-Jauregg reaction by establishing the structure of one bis-adduct, if succeeded to obtain.

Most of the experiments for preparing bis-adducts were made with α-methyl-*p*-methylstyrene, a few ones with α-methylstyrene. For comparison some experiments were carried out with styrene.

I. Addition of maleic anhydride to α-methyl-*p*-methylstyrene

When α-methyl-*p*-methylstyrene was allowed to act on maleic anhydride, the reaction could take three different courses depending on the conditions:

3

1. *Heteropolymerization*

By warming the reactants together in a molecular ratio of 1 : 1 without solvents and inhibitors a heteropolymerization took place resulting in the formation of a clear, almost colorless, brittle resin with a fusion range of 105—120°. If more than one equivalent of maleic anhydride was used, the excess remained unconverted. The structure of the heteropolymer may be written, in analogy with that suggested by Hersberger et al [9]. for the corresponding heteropolymer of α-methylstyrene, as follows:
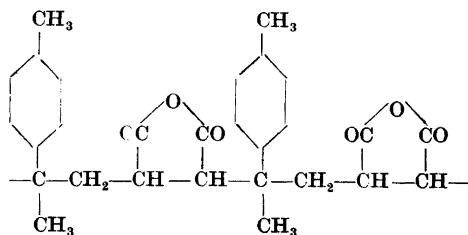
No more research was made within this field.

2. *Bis-adduct formation of α-methyl-p-methylstyrene with maleic anhydride*

In order to prevent the dimerization of α-methyl-p-methylstyrene and its heteropolymerization with maleic anhydride some inhibitor must be used. Dimethylaniline, the inhibitor used successfully by Bruckner and Kovács [4] in the case of anethole, was first experimented with. It proved to be effective in this case too. On the contrary hydroquinone, which according to Lora Tamayo [7] was usefull in respect of anethole, failed to prevent the dimerization of α-methyl-p-methylstyrene. Benzene and acetic anhydride were employed as solvents, the latter with better result. Besides, by starting with dimethyl-p-tolylcarbinol acetic anhydride acted also as a dehydration agent. The optimum temperature was 80°. The yield of the adduct was 40 per cent irrespective if α-methyl-p-methylstyrene or dimethyl-p-tolylcarbinol was used as starting material. The yield reported comprised only that part of the adduct that crystallized directly from the reaction mixture on cooling (cf. Bruckner and Kovács [4]).

Structure of the adduct: The adduct was obtained in the form of coarse, colorless prisms, m.p. 255—256° (dec.). When dissolved in glacial acetic acid the adduct did not absorb bromine, whereas its alkaline solution decolorized readily potassium permanganate. On the basis of analysis the compound

must be a maleic anhydride bis-adduct of monomeric α-methyl-*p*-methyl-styrene. A structural formula (III) analogous to that suggested by Wagner-Jauregg [2] for the corresponding bis-adduct of 1,1-diphenylethylene, was taken as working hypothesis.

For establishing the structure of the bis-adduct it was first aromatized by heating with sulfur according to Bergmann et al. [3]. The molecular formula of the yellow reaction product obtained in a yield of 66 per cent was proved by analysis to correspond that of a dimethylnaphthalene dicarboxylic acid anhydride. It was converted into the free dicarboxylic acid, the barium salt of which was decarboxylated. An oil resulted, which was identified as 1,6-dimethylnaphthalene (XIII). Because the expected aromatization product of the adduct, 1,6-dimethylnaphthalene-3,4-dicarboxylic acid anhydride (XI) is not reported in the literature, the position of the anhydride grouping had to be determined. It is done later.

For locating the double bonds (or one of them) ozonization as one of the most reliable methods in this respect was made use of. The amount of ozone absorbed by the adduct in ethyl acetate solution corresponded to one double bond in the molecule. Plenty of time was consumed with efforts to isolate the ozonide decomposition products (or product) obtained by various methods. A resinous matter always resulted, from which no single compounds could be separated, not even in the form of derivatives by means of carbonyl reagents.

The bis-adduct was now converted into the corresponding tetracarboxylic acid and the same ozonization experiments were repeated with this compound but unfortunately with the same result.

The next effort was made with the tetramethylester obtained from the above acid by diazomethane. The consumption of ozone corresponded exactly to one double bond. On decomposition of the ozonide by means of catalytic dehydrogenation, the hydrogen consumption was 80 per cent of that calculated for a mono-ozonide. A crystalline decomposition product resulted in high yield.

The molecular formula of the decomposition product corresponded to that of the tetramethylester added by two oxygen atoms. It formed dicarbonyl-derivatives with hydroxylamine and semicarbazide. The Schiff test for aldehydes was negative. Because, in addition, the same compound was obtained in another ozonization experiment, in which the decomposition of the ozonide was carried out by boiling with a dilute hydrogen peroxide solution, it must be a diketone. Assuming the tentative structure (III) of the bis-adduct to be correct, only one of the two double bonds would have been attacked by ozone resulting in the formation of the diketone (VI).

When the diketone obtained by ozonization was heated in a vacuum distillation apparatus at 220—230° (bath temperature), it decomposed smoothly and all except a little residue distilled slowly over. The distillate proved 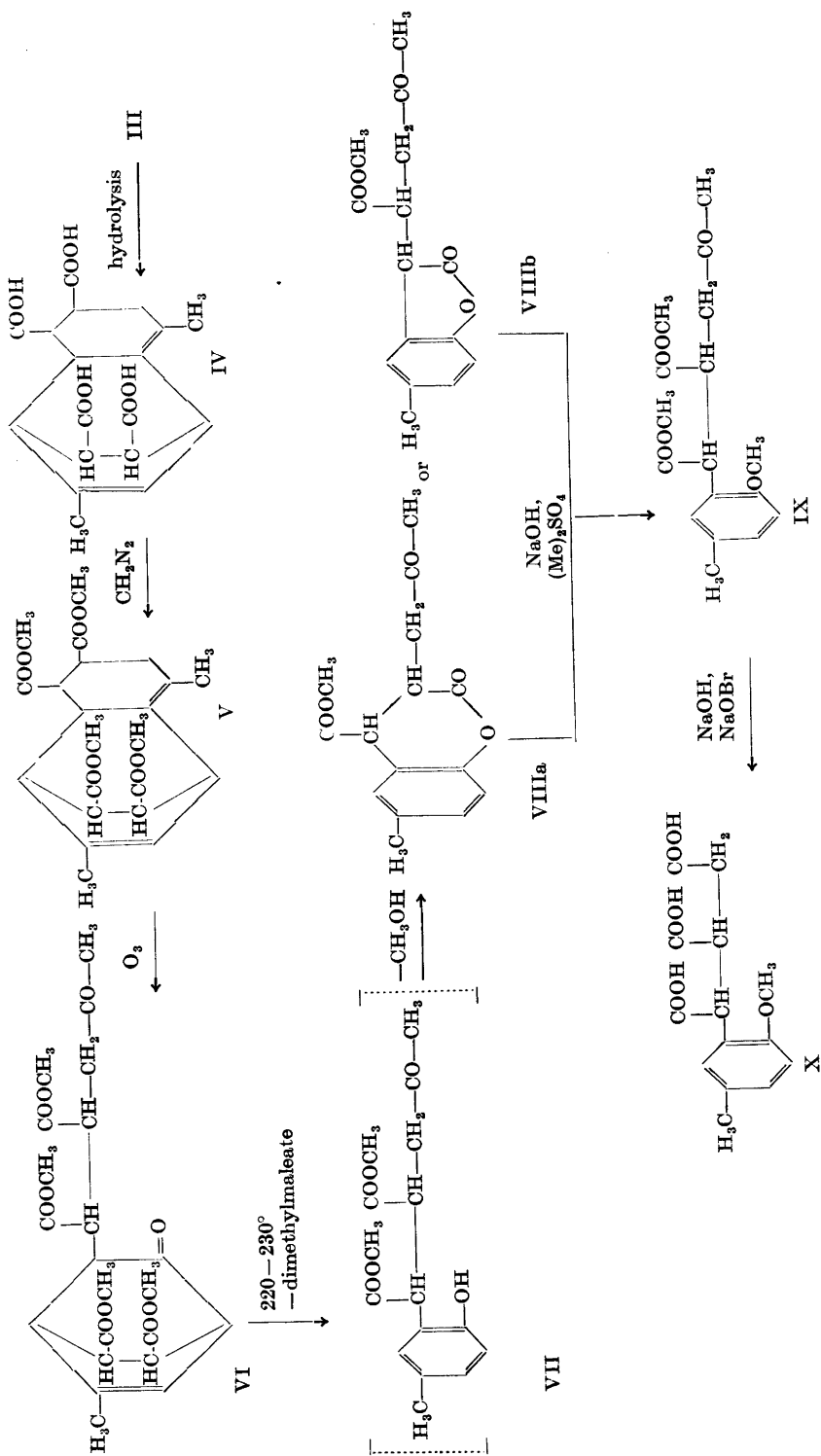to be a mixture, from which two compounds were isolated. One of them, an oil, was identified as dimethylmaleate (yield 73 per cent). The other was a crystalline solid, for which the molecular formula $C_{15}H_{16}O_5$ was obtained by analysis (yield 36 per cent). If dimethylmaleate ($C_6H_8O_4$) is thought to be cleaved off from the diketone ($C_{22}H_{28}O_{10}$), a residue of $C_{16}H_{20}O_6$ remains. This means that a compound with the formula CH_4O, *e.g.* methanol, would have been escaped during the decomposition. When in another experiment the vacuum distillation apparatus was provided with a trap cooled in liquid air, methanol really was caught in a yield of 74 per cent.

Considering the tentative structure (VI) of the diketone, the decomposition may be thought to proceed as presented in the reaction chart. The cleavage of methanol from the intermediate (VII) resulting in the formation of a dihydrocoumarin derivative (VIIIa) has an analogy in the behaviour of ethyl 2-hydroxyphenylpropionate reported by Pschorr and Einbeck [10].

That the decomposition product ($C_{15}H_{16}O_5$) must be one of the two products (VIIIa and VIIIb) is proved by the following consideration:

1) It dissolved quickly in dilute alkali by warming on a water bath. By methylating in this solvent with dimethyl sulphate an oil ($C_{17}H_{22}O_6$) was

(M. A. = maleic anhydride)

III

hydrolysis

COOH
COOH
HC—COOH
HC—COOH
CH₃

IV

CH₂N₂

COOCH₃ H₃C
COOCH₃
HC·COOCH₃
HC·COOCH₃
CH₃

V

O₃

COOCH₃ COOCH₃ H₃C
CH—CH₂—CO—CH₃
HC·COOCH₃
HC·COOCH₃=O

VI

220—230°
—dimethylmaleate

COOCH₃ COOCH₃
CH—CH₂—CO—CH₃
H₃C
OH

VII

—CH₃OH H₃C

COOCH₃
CH—CH₂—CO—CH₃ or H₃C
CO
O

VIIIa

COOCH₃
CH—CH₂—CO—CH₃
CO
O

VIIIb

NaOH,
(Me)₂SO₄

COOCH₃ COOCH₃
CH—CH—CH₂—CO—CH₃
OCH₃
H₃C

IX

NaOH,
NaOBr

COOH COOH COOH
CH—CH—CH₂
OCH₃
H₃C

X

obtained, which was proved to be a mixture of two isomers * of dimethyl α-(2-methoxy-5-methylphenyl)-β-acetonylsuccinate (IX) by mixed melting point of its semicarbazones (two isomers) with the corresponding ones of a synthetic sample. In addition, when the oil was saponified and the resulting acid treated with sodium hypobromite, carbon tetrabromide and an acid $(C_{14}H_{16}O_7)$ were obtained. The latter was identified by synthesis as α-(2-methoxy-5-methylphenyl)-tricarballylic acid (X).

2) When the decomposition product was hydrolyzed with a solution of potassium hydroxide in methanol, the solution acidified with concd. hydrochloric acid and the resulting free acid methylated by means of diazomethane, the starting material was recovered.

3) No free phenolic hydroxyl group could be present in the decomposition product, because its methanol solution did not decolorize an ethereal solution of diazomethane.

Which of the above two possibilities (VIIIa and VIIIb) is the correct one, is still uncertain, but the primary purpose of this work is not suffered by it.

Because the decomposition product contained only one carbonyl group (it formed a mono-semicarbazone), one of the two carbonyl groups of the diketone had disappeared during the heat treatment. It is clear that the carbonyl-oxygen of this latter had converted into a phenolic one with subsequent lactonization of the phenolic hydroxyl group. The aromatization of the diketone by mere cleavage of dimethyl maleate without any dehydrogenation is fully understood in this way.

By the formation of the above heat decomposition product from the diketone, the position of the dicarboxylic acid anhydride grouping in the sulfur dehydrogenation product of the bis-adduct is fixed too. Accordingly the sulfur dehydrogenation product must be 1,6-dimethylnaphthalene-3,4-dicarboxylic acid anhydride (XI) as expected. In addition, it must be the same maleic anhydride (or ester) molecule that has cleaved off in these two cases.

If the possible structure of the diketone is discussed in the light of the results obtained above, some conclusions may be drawn:

1) At least one ring must be present in the diketone molecule. If none, there would be owing to the molecular formula $(C_{22}H_{28}O_{10})$ three double bonds in an aliphatic compound. This is, however, impossible in reference to the saturated character of the diketone towards the common double-bond reagents.

2) The ring (or rings) must be carbocyclic, because the functions of all the oxygen atoms are strictly determined.

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* The existence of two isomers with a structural formula IX has to be ascribed to the presence of two dissimilar asymmetric carbon atoms in the molecule.

3) The ring (or one of them) must be a six-carbon ring on the basis of the following consideration: If in the compound (IX) the methoxyl group later introduced is thought to be hydrolyzed, a phenol results with the formula (VII). In this formula one molecule of maleic anhydride (as esterified) and the fragments of α-methyl-*p*-methylstyrene are still clearly to be seen. Because it is impossible to assume that the six-carbon ring of α-methyl-*p*-methylstyrene would have been ruptured during the maleic anhydride addition and reformed on the degradation process, this six-carbon ring skeleton must be present in the diketone.

4) By omitting the grouping that cleaves off as dimethyl maleate during the heat decomposition, the diketone must contain the following carbon skeleton (XIV):
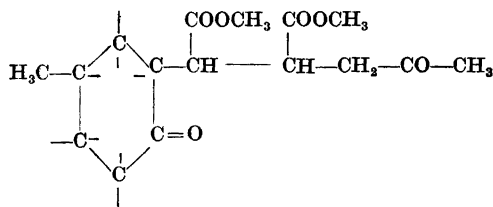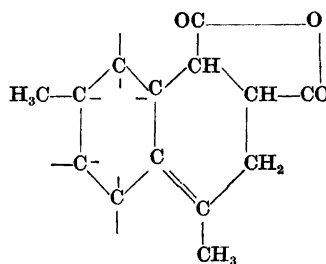
XIV   XV

How the omitted grouping is being thought to attach to the above skeleton (XIV), is still uncertain. If the diketone is monocyclic, the ring must contain two double bonds and a lateral chain consisting of the grouping $H_3COOC\text{-}CH\text{-}CH_2\text{-}COOCH_3$. Another possibility, which is to be preferred, is a bicyclo-octene structure represented by the formula VI.

Considering that the diketone has been obtained from the bis-adduct through reactions, the course of which is strictly determined, the above conclusions can be directly made use of in deducing the structure of the bis-adduct. Accordingly the bis-adduct must contain the skeletal structure XV. If this ring system is compared with the working hypothesis (formula III), it can be seen that the latter really is quite possible. The only thing impossible to explain at this stage is, why the other double bond in the formula III has not been attacked by ozone.

The research is being continued for establishing the definite structure of the bis-adduct.

3. *Dimerization of α-methyl-p-methylstyrene followed by bis-adduct formation of the resulting dimer with maleic anhydride*

If the mixture of α-methyl-*p*-methylstyrene and maleic anhydride in benzene solution was heated at 80°, large crystals slowly separated at the bottom of the reaction flask with simultaneous thickening of the liquid. It appeared that two processes, *viz.* adduct formation and heteropolymerization were going side by side. The molecular formula ($C_{28}H_{28}O_6$) found by analysis for the crystalline product corresponds to that calculated for a maleic anhydride bis-adduct of a dimeric α-methyl-*p*-methylstyrene. That this was really the case, was confirmed by reacting the unsaturated dimer of α-methyl-*p*-methylstyrene reported in a previous communication[11] with maleic anhydride. The same product was obtained, and this time in good yield (67 per cent). No corresponding report is to be seen in the literature. The same adduct could be prepared also from dimethyl-*p*-tolylcarbinol and maleic anhydride in the presence of formic acid (yield 70 per cent).

On the basis of the above observations it is quite clear that α-methyl-*p*-methylstyrene is at first dimerized owing to the action of maleic anhydride (or maleic acid) probably in the same way as by formic acid [11]. The dimer subsequently reacts with maleic anhydride according to the Wagner-Jauregg reaction.

On considering the possible structure of the reaction product it must be taken into account, that the unsaturated dimer of α-methyl-*p*-methylstyrene used above is a mixture of two isomers, *viz.* 2,4-di-(*p*-tolyl)-4-methyl-pentene -1 and 2,4-di-(*p*-tolyl)-4-methyl-pentene-2 in a ratio of 5:1. A question naturally arises, which of these two isomers participates in the adduct formation. It is hardly probable that any marked change would occur in the ratio of both isomers during the reaction with maleic anhydride, since the mixture of the isomers was obtained by means of formic acid under more drastic conditions. Thus considering the high yield of the adduct, the chief isomer component, 2,4-di-(*p*-tolyl)-4-methyl-pentene-1 must be the diene constituent of the bis-adduct. If the other isomer is also able to form a bis-adduct with maleic anhydride, is not known. Only one crystalline product could be isolated from the reaction mixture. As it may be seen, the above case is one additional example of α-substituted styrenes undergoing the Wagner-Jauregg reaction.

In order to cast some light upon the structure of the bis-adduct, it was ozonized in ethyl acetate solution. The amount of ozone absorbed and similarly that of hydrogen required for the catalytic hydrogenation of the ozonide both corresponded to one double bond. It was, however, impossible to isolate any crystalline decomposition product of the ozonide.

In addition, the bis-adduct was converted into the corresponding tetra-carboxylic acid ($C_{28}H_{32}O_8$) and the latter into its tetramethyl ester ($C_{32}H_{40}O_8$) A great similarity in behaviour was to be seen between these derivatives and the corresponding ones of the maleic anhydride bis-adduct of the monomeric α-methyl-p-methylstyrene. So it exists some reason to suggest for the bis-adduct of the dimer the following structural formula (XVI) in analogy with that proposed for the corresponding adduct of the monomer (III):
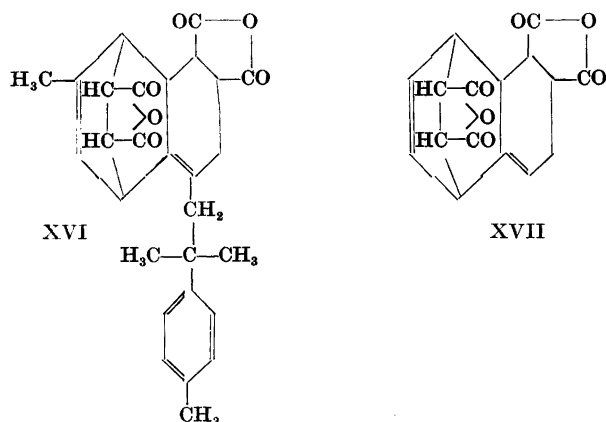
II. Addition of maleic anhydride to α-methylstyrene

By reacting α-methylstyrene with maleic anhydride in the presence of dimethylaniline under the same reaction conditions as in the case of α-methyl-p-methylstyrene, no bis-adduct could be isolated from the reaction mixture. This remarkable difference in these two homologous styrenes obviously has to be ascribed to the effect of p-substitution. This hypothesis is supported by the observation made by Hudson and Robinson [12] that in certain styrene derivatives an alkoxyl group in the p-position to the unsaturated side chain enhances the tendency to undergo a diene synthesis with maleic anhydride.

III. Addition of maleic anhydride to styrene

Some experiments were carried out in order to see, if it would be possible to prepare a regular maleic anhydride bis-adduct of styrene by the method used for obtaining that of α-methyl-p-methylstyrene. It turned out, however, that the Wagner-Jauregg reaction of styrene does not proceed as readily as that of α-methyl-p-methylstyrene. A black tar always resulted accompanied

by unchanged styrene and maleic anhydride. Only minute amounts (about 1 per cent) of a highly crystalline compound could be separated from the tar. Its molecular formula was stated by analysis to be $C_{16}H_{12}O_6$, so it must be the product pursued. It seems out, that a higher temperature is required for this reaction, but any increase in temperature is followed also by a greater tendency to polymerization.

In order to elucidate the structure of the above bis-adduct, so far only an aromatization with sulfur was carried out. It gave a light yellow compound, which was identified as naphthalene-1,2-dicarboxylic acid anhydride.

As it may be seen, the behaviour of this bis-adduct on heating with sulfur agrees with that of the corresponding adduct of α-methyl-p-methylstyrene. In addition, because these two compounds are formed under the same reaction conditions, it is quite possible that they have analogous structures. Accordingly the structural formula XVII is suggested for the maleic anhydride bis-adduct of styrene. If the bis-adduct obtained is identic with that reported by Alder and Schmitz-Josten [1], is still in doubt, because no constants of the latter are to be seen. The structure proposed by these authors for their product is represented in the beginning of the present paper.

EXPERIMENTAL

Heteropolymerization of α-methyl-p-methylstyrene with maleic anhydride

A mixture of 14.5 g (0.11 mole) of α-methyl-p-methylstyrene (b. p. 189 — 191°) and 10.8 g. (0.11 mole) of maleic anhydride was warmed on a water bath. At about 70° a vigorous reaction occurred the temperature rising to the boiling point of the liquid. After cooling, the reaction product was a clear, brittle, almost colorless resin with a fusion range of 105 — 120°.

Maleic anhydride bis-adduct of the monomeric α-methyl-p-methylstyrene

1) From α-methyl-p-methylstyrene and maleic anhydride:

A mixture of 5.0 g (0.038 mole) of α-methyl-p-methylstyrene, 7.4 g (0.076 mole) of maleic anhydride and 0.5 g of dimethylaniline dissolved in 10 ml of acetic anhydride was kept at 80° for 24 hours. Great, colorless crystals separated from the dark liquid already in the hot. After cooling, the crystalline product was separated and washed with cold acetic anhydride. The yield was 5.0 g (40 per cent), m. p. 252 — 254°. After recrystallization from 16 ml of acetic anhydride, 4.3 g of colorless prisms, m. p. 255 — 256° (dec.), were obtained. If the temperature was raised very slowly, a melting point of 250 — 251° (dec.) was recorded. The product was moderately soluble in boiling ethyl acetate, well in boiling acetic anhydride but only slightly in other usual solvents. From xylene it crystallized as small, white needles.

$C_{18}H_{16}O_6$	Calc.	C	65.9	H	4.9	Mol.wt.	328
	Found	»	65.7	»	4.9	» »	338

2) From dimethyl-*p*-tolylcarbinol and maleic anhydride:

A mixture of dimethyl-*p*-tolylcarbinol and *p*-methylacetophenone obtained by catalytic oxidation of cymene with air in liquid phase [11] was used as starting material. It contained 62 per cent of dimethyl-*p*-tolylcarbinol.

8.1 g of the above mixture (0.033 mole of dimethyl-*p*-tolylcarbinol), 9.7 g (0.099 mole) of maleic anhydride, 0.5 g of dimethylaniline and 15 ml of acetic anhydride were mixed and heated at 80° for 24 hours. After cooling, 4.4 g (40 per cent) of a crystalline compound, m. p. 252−3° were separated from the reaction mixture. It was proved to be identic with the previous product by mixed melting point.

Aromatization of the bis-adduct $C_{18}H_{16}O_6$

An intimate mixture of 5.0 g of the bis-adduct and 0.98 g (2 equiv.) of sulfur was heated at 220−30° for 1 ½ hours, after which the temperature was raised to 270−80° for 5 minutes. The black reaction product was extracted with boiling ethyl acetate and the solution concentrated. On cooling, black crystals separated, yield 2.76 g, m. p. 228 −231°. By subliming in vacuo at 210° (bath temperature) 2.28 g (66 per cent) of yellow needles, m. p. 235.5−6.5° were obtained.

$C_{14}H_{10}O_3$	Calc.	C	74.2	H	4.4
	Found	»	74.4	»	4.5

Hydrolysis of the aromatization product $C_{14}H_{10}O_3$

2.0 g of the yellow product obtained above were converted into the free acid by heating on a water bath with a solution of 1.4 g of sodium hydroxide in 25 ml of water until all had dissolved. After cooling, the solution was acidified with concd. hydrochloric acid. A microcrystalline, white compound precipitated, yield 2.1 g (97 per cent), m. p. 236−7°. On crystallization from methanol, coarse, light yellow, transparent crystals were obtained, the melting point being unaltered.

$C_{14}H_{12}O_4$	Calc.	C	68.7	H	4.9	Neut.equiv.	122
	Found	»	68.8	»	5.0	» »	125

Decarboxylation of the acid $C_{14}H_{12}O_4$

1.8 g of the acid were dissolved in 28 ml of 5 % sodium bicarbonate solution. By adding 2 g of barium chloride in 8 ml of water, the acid was precipitated as the barium salt, which was separated, washed with water and dried at 100°. It was mixed with half its weight of copper bronze and ground thoroughly. By heating the mixture on a sand bath in vacuo, 440 mg of a red oil distilled slowly over. It gave on fractionation in vacuo 240 mg (21 per cent) of an almost colorless oil, b. p. 135−8°/15 mm, the odor of which resembled that of naphthalene. The oil was proved to be 1,6-dimethylnaphthalene by mixed melting point of its picrate and trinitrobenzolate with authentic specimens *.

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* I am indebted to Dr. J. Gripenberg for these samples.

Hydrolysis of the bis-adduct $C_{18}H_{16}O_6$.

30.0 g of the bis-adduct were dissolved in a solution of 34 g of potassium hydroxide in 300 ml of water by heating on a water bath. After cooling, the solution was acidified by slowly adding 84 ml of cold, concd. hydrochloric acid with stirring and cooling. The solution remained clear during this operation but on standing colorless crystals soon begin to separate. After standing overnight, the crystals were filtrated off, washed with water and dried. The yield was 33 g (theoretical), m. p. about 200° (dec.). The acid crystallized from glacial acetic acid in colorless microcrystals, m. p. 210—15° (dec.) after sintering already at 200°.

$C_{18}H_{20}O_8$ Calc.   C   59.3   H   5.5   Neut.equiv.   91
              Found   »   59.7   »   5.6   »   »   91

The acid could not be titrated directly with 0.1 N sodium hydroxide. The neut.equiv. value reported above was obtained by a lactone titration.

If the alkaline solution was acidified with concd. hydrochloric acid in the hot and the solution concentrated on a water bath, another acid was obtained. Once crystallized from glacial acetic acid it formed colorless microcrystals, m. p. 307—8° (dec.).

$C_{18}H_{18}O_7$ Calc.   C   62.4   H   5.2
              Found   »   62.4   »   5.3

Accordingly it must be an anhydride-acid formed from the tetracarboxylic acid by the elimination of one molecule of water.

Methylation of the tetracarboxylic acid $C_{18}H_{20}O_8$ *by diazomethane*

30.0 g of the tetracarboxylic acid prepared above were dissolved in 120 ml of methanol and methylated with an ethereal solution of diazomethane by cooling. After concentration on a water bath, coarse, colorless crystals separated. The yield was 34.0 g (98 per cent), m. p. 120—2°. Once recrystallized from methanol, the compound formed large prisms, m. p. 121—3°.

$C_{22}H_{28}O_8$ Calc.   C   62.7   H   6.6
              Found   »   62.3   »   6.4

Ozonization of the bis-adduct $C_{18}H_{16}O_6$

5.0 g of the bis-adduct were dissolved in 250 ml of ethyl acetate. Ozonized oxygen containing 4.9 vol. $^0/_0$ of O_3 was passed through this solution with cooling. The amount of ozone absorbed corresponded to one double bond. The solvent was evaporated at room temperature in vacuo. The residue was a porous, light yellow resin. On decomposition of the ozonide no single products could be isolated.

Ozonization of the tetracarboxylic acid $C_{18}H_{20}O_8$

5.0 g of the tetracarboxylic acid were dissolved in 100 ml of glacial acetic acid and ozonized as above. The behaviour of the free acid on ozonization was similar to that of the anhydride (bis-adduct).

Ozonization of the tetramethyl ester $C_{22}H_{28}O_8$

Ozonized oxygen containing 4.9 vol. $^0/_0$ of ozone was passed through a solution of 10.0 g of the tetramethyl ester in 100 ml of chloroform by cooling in an ice-salt mixture. A wash bottle charged with potassium iodide solution was connected to the reaction bottle. The completion of the ozonization was sharply indicated by a sudden separation of iodine. At this moment an amount of ozone equivalent to one double bond had been absorbed. The solvent was evaporated at room temperature in vacuo. The residue was a porous, white resin.

The ozonide was dissolved in 100 ml of methanol and decomposed by catalytic hydrogenation with Adams' platinum oxide catalyst. In the beginning, the hydrogenation vessel was cooled with cold water. After 18 hours, the amount of hydrogen consumed was 80 per cent of that calculated for a mono-ozonide. Plenty of colorless crystals had separated during the hydrogenation. The crystals were dissolved by warming, the platinum catalyst was filtrated off and the filtrate concentrated on a water bath. On cooling, coarse crystals separated. The yield was 7.53 g (70 per cent), m. p. 151—4°. After recrystallization from 20 ml of methanol, 6.5 g of large, clear prisms were recovered, m. p. 153—4°. The compound gave a negative Schiff test for aldehydes.

$$C_{22}H_{28}O_{10} \quad \text{Calc.} \quad C \quad 58.3 \quad H \quad 6.2$$
$$\text{Found} \quad » \quad 58.2 \quad » \quad 6.3$$

In another experiment, where the decomposition of the ozonide was carried out by boiling with dilute hydrogen peroxide solution, the same compound was obtained in a yield of 24 per cent.

Semicarbazone: Colorless crystals from 50 % ethanol, m. p. 230—1° (dec.).

$$C_{24}H_{34}N_6O_{10} \quad \text{Calc.} \quad N \quad 14.8$$
$$\text{Found} \quad » \quad 14.5$$

Oxime: Small plates from ethanol, m. p. 211—3° (dec.).

$$C_{22}H_{30}N_2O_{10} \quad \text{Calc.} \quad N \quad 5.8$$
$$\text{Found} \quad » \quad 5.5$$

Decomposition of the ozonization product $C_{22}H_{28}O_{10}$ by heating

3.45 g of the ozonization product were placed in a Claisen flask and heated in a metal bath in vacuo. A trap cooled in liquid air for catching the readily volatile products was inserted between the receiver and the water pump. At 220—30° (bath temperature) a pale yellow, towards the end thickening oil distilled slowly over. A residue of only 0.14 g remained in the Claisen flask. The trap contained 0.18 g of a colorless, mobile liquid (solid at the temperature of liquid air), b. p. 65—70°. It was identified as methanol (yield 74 per cent) by mixed melting point of its 3,5-dinitrobenzoate with an authentic sample.

The viscous distillate (3.05 g) was fractionated in vacuo:

Fraction I, b.p. 60—3°/1mm, 0.805 g, a mobile, colorless oil.
» II, » 180—6°/1 » 1.715 » » viscous, yellowish oil.

When Fraction I was refluxed for 15 minutes with a small crystal of iodine it was almost quantitatively converted into a solid compound, which formed large plates from ether, m. p. 101 — 2°.

$$C_6H_8O_4 \quad \text{Calc.} \quad C \quad 50.0 \quad H \quad 5.6$$
$$\text{Found} \quad » \quad 50.2 \quad » \quad 5.7$$

This compound was identified as dimethyl fumarate by mixed melting point. In accordance, the oily compound (Fraction I) must be dimethyl maleate (yield 73 per cent).

Fraction II deposited on standing 0.76 g of colorless crystals, m. p. 94 — 108°. This substance turned out to be a mixture of two components with the same empirical formula. The higher-melting compound only could be isolated pure by fractional crystallization from methanol. It was obtained as small plates, m. p. 114 — 5°, which did not decolorize an ethereal solution of diazomethane.

$$C_{15}H_{16}O_5 \quad \text{Calc.} \quad C \quad 65.0 \quad H \quad 5.8$$
$$\text{Found} \quad » \quad 65.1 \quad » \quad 5.8$$

Semicarbazone: Clusters of small needles from ethanol, m. p. 197 — 8° (dec.).

$$C_{16}H_{19}N_3O_5 \quad \text{Calc.} \quad N \quad 12.6$$
$$\text{Found} \quad » \quad 12.8$$

Saponification of the decomposition product $C_{15}H_{16}O_5$

1.7 g of the crude decomposition product (m. p. 94 — 108°) were dissolved in 3 ml of methanol. A solution of 2.5 g of potassium hydroxide in 12 ml of water was added and the mixture refluxed for 6 hours. Methanol was evaporated and the residual solution acidified with 4 ml of concd. hydrochloric acid. The solution remained quite clear. It was extracted with ether. After evaporation of the solvent, a porous resin (1.7 g) was obtained, which could not be crystallized. It was very soluble in water.

Methylation of the saponification product with diazomethane

The resin (1.7 g) obtained above was dissolved in 15 ml of abs. ether and methylated with an ethereal solution of diazomethane. The solvent was evaporated and the residue triturated with methanol. Colorless crystals soon separated, yield 0.56 g, m. p. 92 — 114°. On fractional crystallization from methanol, 0.38 g of a compound, m. p. 114 — 5° were obtained. By mixed melting point it was proved to be identic with the higher-melting component of the starting material $C_{15}H_{16}O_5$.

In this connexion it may be mentioned that the uncrystallizable part (mother liquor) of the decomposition product, when saponified and methylated as above, yielded an appreciable amount of the isomer mixture $C_{15}H_{16}O_5$ in addition to the part that crystallized directly.

Methylation of the decomposition product $C_{15}H_{16}O_5$ by dimethyl sulfate in alkaline solution

0.8 g of the crude decomposition product (m. p. 94 — 108°) were heated with a solution of 0.5 g of sodium hydroxide in 2 ml of water on a water bath until all had dissolved (about 10 minutes). The methylation was carried out in the usual way with dimethyl

sulfate. A colorless, viscous oil, b. p. 182−192°/3 mm, was obtained, yield 0.7 g (75 per cent).

$C_{17}H_{22}O_6$ Calc.   C   63.2   H   6.8
                Found   »   63.0   »   6.8

Semicarbazones: A semicarbazone of the above oil was prepared in the customary manner. It proved to be a mixture that by fractional crystallization from ethanol could be divided into two isomers I and II, the latter being more readily soluble.

Isomer I, small plates, m. p. 183−5°.

$C_{18}H_{25}N_3O_6$ Calc.   N   11.1
                Found   »   11.2

Isomer II, microcrystalline, m. p. 157−160°.

$C_{18}H_{25}N_3O_6$ Calc.   N   11.1
                Found   »   11.0

These two semicarbazones gave no depression when mixed with the corresponding semicarbazones of dimethyl α-(2-methoxy-5-methylphenyl)-β-acetonyl-succinate prepared by synthesis (see later).

Hypobromite oxidation of the methylation product $C_{17}H_{22}O_6$

0.65 g of the oil (b. p. 182−92°/3 mm) obtained above were at first saponified by heating for 5 hours on a water bath with a solution of 0.44 g of sodium hydroxide in 4 ml of water. The resulted clear solution was cooled to room temperature. A cold solution of sodium hypobromite prepared at 0° by dissolving 1.5 g of sodium hydroxide and 2.0 g of bromine in 8.5 ml of water, was added during 10 minutes with stirring. The temperature rose hereby to about 35°. After the addition, the stirring was continued for 15 minutes. A clear, almost colorless solution resulted with some heavy particles at the bottom of the reaction vessel. The solid compound was filtrated off, yield 0.19 g, m. p. 86−9°. It was identified as carbon tetrabromide.

A few drops of acetone were added to the filtrate for destroying the excess of hypobromite. After removing all neutral matter by ether extraction, the alkaline solution was acidified with concd. hydrochloric acid and extracted with ether. After evaporation of the solvent, a brownish syrup remained. When it was triturated with cold ether, small crystals slowly separated. They were filtrated off and washed with ether. The yield was 74 mg, m. p. 157−60°. After recrystallization from a mixture of benzene and acetone, microscopical needles were obtained, m. p. 165−7°.

$C_{14}H_{16}O_7$ Calc.   C   56.8   H   5.4
               Found   »   57.0   »   5.6

This compound was identified as α-(2-methoxy-5-methylphenyl)-tricarballylic acid by mixed melting point with a sample prepared by synthesis (see later).

Trimethyl ester: It was obtained in the customary manner with diazomethane. It crystallized from dilute methanol as long needles, m. p. 73−5°. It gave no depression when mixed with the methyl ester of the synthetic acid (see later).

Synthesis of dimethyl α-(2-methoxy-5-methylphenyl)-β-acetonylsuccinate

2-Methoxy-5-methylbenzaldehyde cyanohydrin: By starting from *p*-cresol, this was converted by known methods into 2-methoxy-5-methylbenzaldehyde, from which the corresponding cyanohydrin was obtained according to a method used by Levine et al.[13] for the preparation of *o*-methoxybenzaldehyde cyanohydrin. Coarse crystals from benzene, m. p. 57 − 9°, yield 95 per cent.

$$C_{10}H_{11}NO_2 \quad \text{Calc.} \quad C \quad 67.8 \quad H \quad 6.2 \quad N \quad 7.9$$
$$\text{Found} \quad \text{»} \quad 68.1 \quad \text{»} \quad 6.2 \quad \text{»} \quad 7.6$$

2-Methoxy-5-methylmandelic acid: 100 g of 2-methoxy-5-methylbenzaldehyde cyanohydrin were placed in a porcelain dish and 100 ml of concd. hydrochloric acid (d. 1.19) were added. The hydrolysis was allowed to proceed in the cold for 14 hours. The mixture was concentrated by heating for 6 hours on a water bath. When cold, the residue was triturated with ether and the unsoluble part consisting of ammonium chloride was filtrated off. The yield of ammonium chloride on hydrolysis was 93 per cent.

The ethereal filtrate was shaken with a saturated sodium bicarbonate solution for removing any unhydrolyzed cyanohydrin (7 g). The bicarbonate solution was washed several times with ether and acidified with concd. hydrochloric acid. A colorless oil separated. It was taken in ether. The ethereal extract was washed three times with water and the solvent was evaporated. The residue was a viscous oil, which did not crystallize on standing.

In order to purify the crude acid, it was converted into the methyl ester by means of diazomethane. The reaction product was fractionated in vacuo. Only 38 g of a yellowish oil distilled over, b. p. 170°/12 mm. The bulk of the methylation product remained in the distilling flask as a red resin. The distillate in the receiver solidified almost immediately, m. p. 85 − 9°. It crystallized from methanol in colorless plates, m. p. 89 − 91°.

$$C_{11}H_{14}O_4 \quad \text{Calc.} \quad C \quad 62.8 \quad H \quad 6.7$$
$$\text{Found} \quad \text{»} \quad 62.7 \quad \text{»} \quad 6.7$$

36.9 g of the methyl ester were saponified by refluxing for 5 hours with a solution of 8 g of sodium hydroxide in 80 ml of water. After cooling, the resulted solution was extracted with ether for removing any unhydrolyzed ester. The alkaline solution was acidified with dilute hydrochloric acid. An oil separated which was taken in ether. After evaporation of the solvent, the remainder (38 g) solidified on long standing. It crystallized from benzene in tiny needles, m. p. 105 − 6°. The yield was 34 g (31 per cent calculated from the cyanohydrin, 98 per cent calculated from the methyl ester). The melting point of 2-methoxy-5-methylmandelic acid prepared by Kindler et al.[14] by catalytic hydrogenation of the corresponding phenylglyoxylic acid, was 106°.

Ethyl (2-methoxy-5-methylphenyl)-bromoacetate: 23 g of powdered 2-methoxy-5-methylmandelic acid were placed in a 150-ml round-bottomed flask provided with a reflux condenser. 107 g of powdered phosphorus pentabromide were added gradually through the condenser. A vigorous reaction occurred. Finally the reaction flask was heated on a water bath until the evolution of hydrogen bromide had ceased. After cooling, 150 ml of abs. ethanol were added in small portions through the condenser. A violent reaction followed. At last the reaction mixture was heated on a water bath for a short

while, after which the ethyl bromide formed and a part of ethanol were distilled off. After cooling, the residue was poured into water. A brown, heavy oil separated. It was taken in ether. The ethereal solution was washed once with dilute sodium carbonate solution and several times with water. Ether was evaporated and the residue distilled in vacuo. 24 g of a pale yellow oil, b. p. 135 — 6° /2mm were obtained. In spite of the narrow boiling range, the oil was a mixture containing along with the ester expected plenty of ethyl 2-methoxy 5-methylmandelate. A lot of 10 g of this oil was used for the preparation of the following compound. The remainder (14 g) on long standing deposited crystals, which were filtrated off. The yield was 5.9 g (30 per cent), m. p. 53 — 6°. On recrystallization from ethanol great, colorless prisms were obtained, m. p. 57 — 8°.

$$C_{12}H_{15}BrO_3 \qquad \text{Calc.} \quad C \quad 50.2 \quad H \quad 5.2 \quad Br \quad 27.8$$
$$\text{Found} \quad » \quad 49.9 \quad » \quad 5.4 \quad » \quad 28.1$$

Dimethyl α-(2-methoxy-5-methylphenyl)-β-acetonylsuccinate: 0.8 g of sodium were dissolved in 10 ml of abs. ethanol. 7.5 g of diethyl acetonylmalonate prepared according to Gault and Salomon [15] and 10.0 g of crude ethyl (2-methoxy-5-methylphenyl)-bromoacetate (see before) were added. The mixture was heated for 3 hours on a water bath, after which the reaction product was poured into water and extracted with ether. The ethereal solution was washed once with dilute hydrochlorid acid and several times with water. After evaporation of the solvent, a red, viscous oil (13.4 g) remained, which did not crystallize on standing.

The above condensation product was saponified by refluxing for 3 hours with a solution of 10.6 g of potassium hydroxide in 21 ml of water. The free acid was separated in the usual way. It was a red, viscous oil (10.9 g), which could not be crystallized.

The decarboxylation of the malonic acid derivative obtained above was carried out by refluxing for 3 hours with dilute sulfuric acid (1 ml of concd. sulfuric acid in 17 ml of water). By treating in the customary manner, the reaction mixture yielded 9.3 g of a red, resinous acid, which did not crystallize on standing.

The acid (9.3 g) was converted into the methyl ester by refluxing for 4 hours with a mixture of 4 ml of concd. sulfuric acid and 100 ml of methanol. The ester formed was separated as usually and fractionated in vacuo:

Fraction   I, b.p. 160 — 200°/14 mm, 2.6 g
»   II,   »   210 — 220°/14   »   3.4 »

Fraction II was assumed to contain the product expected. For purifying, it was converted into a semicarbazone, yield 2.4 g, m. p. 156 — 62°. By repeated fractional crystallization the semicarbazone was divided into two isomeric compounds:
Isomer   I, small plates, 0.92 g, m. p. 184 — 5°.

$$C_{18}H_{25}N_3O_6 \qquad \text{Calc.} \quad N \quad 11.1$$
$$\text{Found} \quad » \quad 10.9$$

Isomer II, microcrystalline, 1.21 g, m. p. 158 — 60°.

$$C_{18}H_{25}N_3O_6 \qquad \text{Calc.} \quad N \quad 11.1$$
$$\text{Found} \quad » \quad 10.8$$

In order to obtain the corresponding carbonyl compounds, the semicarbazones were hydrolyzed separately by heating with a concd. oxalic acid solution on a water bath.

Isomer I, a colorless, viscous oil, b.p. 179—81°/3 mm.

$C_{17}H_{22}O_6$ Calc.   C   63.2   H   6.8
          Found   »   62.9   »   7.0

Isomer II, a colorless, viscous oil, b.p. 188—90°/3 mm.

$C_{17}H_{22}O_6$ Calc.   C   63.2   H   6.8
          Found   »   63.0   »   6.8

The corresponding free acids were also prepared by saponification of the above esters. Both acids were non-crystallizable resins.

Synthesis of α-(2-methoxy-5-methylphenyl)-tricarballylic acid

Ethyl 2-methoxy-5-methylphenylacetate: It was prepared according to known methods by starting from *p*-tolyl methyl ether. This was converted into 2-methoxy-5-methyl-benzyl chloride, from which 2-methoxy-5-methylphenylacetic acid was obtained through the corresponding cyanide. The acid was esterified in the customary manner with ethanol.

α-(2-Methoxy-5-methylphenyl)-tricarballylic acid: The condensation of the above ethyl ester (b. p. 136—8°/5 mm) with diethylmaleate was carried out in analogy with the directions given by Borsche and Schmidt [16] for the preparation of α-phenyltricarballylic acid. The ester obtained was a pleasant-smelling, viscous, colorless liquid, b. p. 217—8°/5 mm. The yield was 58 per cent.

$C_{20}H_{28}O_7$ Calc.   C   63.1   H   7.4
          Found   »   63.1   »   7.3

The free acid was obtained from the ethyl ester by hydrolysis (yield 54 per cent). It crystallized from a mixture of benzene and acetone in microscopical needles, m. p. 167°.

$C_{14}H_{16}O_7$ Calc.   C   56.8   H   5.4
          Found   »   56.8   »   5.6

Trimethyl ester: It was prepared from the acid by diazomethane. It crystallized from dilute methanol in long needles, m. p. 74—6°.

Maleic anhydride bis-adduct of the dimeric α-methyl-p-methylstyrene

1) From α-methyl-*p*-methylstyrene and maleic anhydride:

A mixture of 2.3 g of α-methyl-*p*-methylstyrene and 1.7 g of maleic anhydride in 2 ml of benzene was heated for 24 hours at 80°. Large, colorless crystals separated slowly at the walls of the reaction vessel with simultaneous thickening of the liquid part. After cooling, the crystalline product was separated and washed with acetone. The yield was 0.8 g, m. p. 220—30°. The compound was well soluble in hot acetic anhydride, moderately in hot ethyl acetate, slightly in other common organic solvents. It crystallized from ethyl acetate in semispherical clusters of small needles, m. p. 231—3°.

$C_{28}H_{28}O_6$ Calc.   C   73.0   H   6.1   Mol.wt.   460
          Found   »   72.9   »   5.9   »   »   435

It showed no depression when mixed with the bis-adduct obtained from the unsaturated dimer of α-methyl-*p*-methylstyrene and maleic anhydride. In order to obtain a better yield of the bis-adduct by starting from the monomeric α-methyl-*p*-methylstyrene and maleic anhydride, it is advisable to proceed in analogy with the third method (see later).

2) From the unsaturated dimer of α-methyl-*p*-methylstyrene and maleic anhydride:

A mixture of 15.0 g (0.057 mole) of the dimer [11] (b. p. 181—6°/7 mm) and 16.7 g (0.171 mole) of maleic anhydride was heated for 24 hours on a boiling water bath. Plenty of coarse crystals had separated. The liquid part was removed from the hot reaction product by suction. It was mainly maleic anhydride with some unconverted dimer as the upper layer. The crystals were washed with ether. The yield was 17.6 g (67 per cent), m. p. 225—31°. After recrystallization from 35 ml of acetic anhydride, 14.8 g of large, colorless prisms, m. p. 231—3°, were obtained.

3) From dimethyl-*p*-tolylcarbinol and maleic anhydride:

8.1 g of the mixture of dimethyl-*p*-tolylcarbinol and *p*-methylacetophenone (see the corresponding preparation of the maleic anhydride bisadduct of the monomeric α-methyl-*p*-methylstyrene), 16.4 g of maleic anhydride and 5.0 ml of 95 % formic acid were mixed and allowed to stand for 72 hours at room temperature. The crystalline reaction product was separated and washed with ether. The yield was 5.4 g (70 per cent), m. p. 230—2°.

Hydrolysis of the bis-adduct $C_{28}H_{28}O_6$

10.0 g of the bis-adduct were heated on a water bath with a solution of 8 g of potassium hydroxide in 200 ml of water until all had dissolved. After cooling, the solution was acidified with concd. hydrochloric acid. A white gum separated. This was very soluble in ether but when extracted with this solvent, it began after a while to separate as small, white crystals. After standing overnight, these were filtrated off and washed with ether. On drying in a vacuum desiccator, the product decreased continuously in weight. Only after keeping for some hours at 100° the weight became constant. The yield was 10.7 g (98 per cent), m. p. 210—5° (dec.) after previous sintering.

$$C_{28}H_{32}O_8 \quad \text{Calc.} \quad C \quad 67.6 \quad H \quad 6.4 \quad \text{Neut.equiv.} \quad 124$$
$$\text{Found} \quad » \quad 67.5 \quad » \quad 6.3 \quad » \quad » \quad 127$$

On direct titration of the acid in ethanol solution with 0.5 N sodium hydroxide, no sharp end point could be observed. The value reported above was obtained by a lactone titration.

Methylation of the tetracarboxylic acid $C_{28}H_{32}O_8$ by diazomethane

5.0 g of the above tetracarboxylic acid were dissolved in 20 ml of methanol and methylated by an ethereal solution of diazomethane. Ether and the bulk of methanol were distilled off. On long standing, the remainder deposited a compact layer of crystals at the bottom of the flask. After filtering and washing with methanol, 5.1 g (92 per cent) of a crystal pulver was obtained, m. p. 118—21°. It crystallized from methanol as a white, fine-grained pulver, m. p. 120—3°.

$$C_{32}H_{40}O_8 \quad \text{Calc.} \quad C \quad 69.5 \quad H \quad 7.2$$
$$\text{Found} \quad » \quad 69.9 \quad » \quad 7.3$$

Ozonization of the bis-adduct $C_{28}H_{28}O_6$

7.0 g of the bis-adduct were dissolved in 280 ml of ethyl acetate and ozonized with cooling in an ice-salt mixture. The amount of ozone absorbed by the bis-adduct corresponded to one double bond. About 200 ml of the solvent were evaporated at room temperature in vacuo. The ozonide in the remaining solution was decomposed by catalytic hydrogenation. The hydrogen consumption was about 90 per cent of that calculated for a mono-ozonide. After removing the catalyst and evaporating the solvent, the decomposition product was obtained as a porous resin.

In another experiment the tetracarboxylic acid $C_{28}H_{32}O_8$ was ozonized according to the same method. No definit ozonization products could be isolated in either case.

Maleic anhydride bis-adduct of styrene

A mixture of 5.0 g (0.048 mole) of styrene (prepared by dehydration of β- phenylethyl alcohol), 14.2 g (0.145 mole) of maleic anhydride, 0.5 g of dimethylaniline and 10 ml of acetic anhydride was heated for 24 hours at 80°. On long standing in an open Erlenmeyer flask at room temperature, crystals separated from the dark liquid. They were filtrated off and washed with cold acetic anhydride. Upon treating with water, almost all dissolved (maleic acid). Only a little, crystalline residue (0.17 g) remained, m. p. 252—5° (dec.). It crystallized from acetic anhydride in clusters of small, colorless needles, m. p. 254—6° (dec.).

$$C_{16}H_{12}O_6 \quad \text{Calc.} \quad \text{C} \quad 64.0 \quad \text{H} \quad 4.0$$
$$\text{Found} \quad » \quad 63.9 \quad » \quad 4.0$$

Aromatization of the bis-adduct $C_{16}H_{12}O_6$

The maleic anhydride bis-adduct of styrene was aromatized in the same way as that of a-methyl-p-methylstyrene. By starting with 0.29 g of the bis-adduct, 0.13 g (67 per cent) of dark crystals, m. p. 155—60°, were obtained. After sublimation in vacuo and subsequent crystallization from xylene, the product was obtained in pale yellow needles, m. p. 166—7°.

$$C_{12}H_6O_3 \quad \text{Calc.} \quad \text{C} \quad 72.7 \quad \text{H} \quad 3.0$$
$$\text{Found} \quad » \quad 72.6 \quad » \quad 3.1$$

The compound showed no depression when mixed with authentic naphthalene-1,2-dicarboxylic acid anhydride.

SUMMARY

I. a-Methyl-p-methylstyrene as well as one of its dimers, viz. 2,4-di-(p-tolyl)-4-methylpentene-1, were stated to form, each one separately, a bis-adduct with maleic anhydride in a good yield (40 and 70 per cent respectively). It was also possible to prepare a maleic anhydride bis-adduct of styrene, although in a poor yield. On the contrary, a-methylstyrene failed to give a bis-adduct under the same reaction conditions.

II. Depending on the reaction conditions, the action of maleic anhydride on α-methyl-*p*-methylstyrene can lead to three different end products: 1) a heteropolymer, 2) a maleic anhydride bis-adduct of the monomeric α-methyl-*p*-methylstyrene and 3) that of the dimeric α-methyl-*p*-methylstyrene.

III. The structure of the maleic anhydride bis-adduct of the monomeric α-methyl-*p*-methylstyrene has been examined by means of ozonization. The results obtained agree with a formula deduceable from α-methyl-*p*-methyl-styrene through two successive 1,4-additions of maleic anhydride (formula III). A reaction mechanism involving a diene synthesis followed by a sub-stituting addition, which would lead to a tetralin berivative, has been excluded.

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