Dimerization of α-Methyl-p-methylstyrene by Formic Acid and Structure of the Dimers Obtained

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Several reports have been published on the dimers of α-methyl-p-methylstyrene. Most of the papers deal with their production. Their constitution has attracted less notice. The dimers of the lower homolog, α-methylstyrene, have been studied more thoroughly. Because, however, the styrenes in question are analogous in regard to their polymerizing properties, there is good reason to consider also the reports on the dimers of α-methylstyrene when those of the higher homolog are being examined.

Errera [1] obtained an oily dimer distilling at 350° without decomposition by heating α-methyl-p-methylstyrene with hydrobromic acid (d. 1.59) at 190—200° in a sealed tube.

Klages [2] states that by heating dimethylphenylcarbinol with syrupy phosphoric acid to 120° an oily unsaturated dimer (that of α-methylstyrene), b. p. 302° was produced. For this he proposed the following structure:

$$C_6H_5C(CH_3) = CHCH_2CH(CH_3)C_6H_5$$

Tiffeneau [3] obtained a solid saturated dimer, m. p. 40°, by adding α-methyl-p-methylstyrene to cold concd. sulphuric acid. Similar reaction in which α-methylstyrene was employed yielded a dimer [4], m. p. 52°. For the latter product he proposed the structure of diphenyl-dimethylcyclobutane.

Staudinger and Breusch [5] reported in a paper on the polymerization of α-methylstyrene that the action of stannic chloride on α-methylstyrene yielded a solid dimer, m. p. 52°. They, too, assumed this product to be diphenyl-dimethylcyclobutane. On the other hand by using floridin, titanium tetrachloride or boron trichloride as catalysts, an oily unsaturated dimer was produced for which they proposed the structure:

$$C_6H_5C(CH_3) = CHCH_2(CH_3)CHC_6H_5$$
$$\text{or}\quad C_6H_5CH(CH_3)CH = CH(CH_3)CHC_6H_5$$
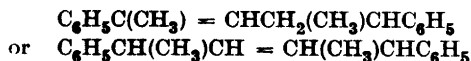
The latest reports on the constitution of the two dimers of α-methylstyrene are due to Bergmann, Taubadel and Weiss [6]. The cyclic saturated dimer was prepared by them according to Staudinger et al., and characterized as 1,1,3-trimethyl-3-phenylhydrindene. The oily unsaturated dimer produced by the Klages method was shown by the above authors on the basis of ozonization to be 2,4-diphenyl-4-methylpentene-2 in analogy with the unsaturated dimer of assym. diphenylethylene for which the corresponding structure was established already by Lebedew [7]. Furthermore, according to the authors the unsaturated dimer could be converted into the saturated one either with stannic chloride or aluminium chloride.

Puranen [8-10] has extensively studied the saturated dimer (dicymene) of α-methyl-p-methylstyrene. He obtained this dimer from cymene with nitrosyl sulphuric acid. According to his opinion cymene was hereby first oxidized to dimethyl-p-tolylcarbinol which then under the influence of concd. sulphuric acid was either directly condensed to the dimer or by elimination of water first converted to α-methyl-p-methylstyrene which subsequently dimerized. On the basis of experimental observations Puranen established for this dimer the structure 1,3,3,6-tetramethyl-1-p-tolylhydrindene in accord with the corresponding dimers of assym. diphenylethylene and α-methylstyrene.

In a treatise on the polymerization of α-methylstyrene Hersberger, Reid and Heiligmann [11], referring to the paper of Bergmann et al., used the formula 2,4-diphenyl-4-methylpentene-1 for the unsaturated dimer of α-methylstyrene in a polymerization reaction between the dimer and maleic anhydride. This is incorrect in so far as the formula deduced by Bergmann et al., is 2,4-diphenyl-4-methylpentene-2, not -1. The compound put forward by Hersberger et al., is not reported in literature.

Recently a method [12] has been patented for producing unsaturated dimers of α-alkyl styrenes (including α-methyl-p-methylstyrene and α-methylstyrene). According to the patent report the unsaturated dimers were obtained substantially free of cyclic saturated dimers by intimately contacting an α-alkyl styrene with sulphuric acid of 30 % to 65 % concentration at temperatures between 65 and 105° C. In the case of α-methylstyrene, by reaction at 21 to 27° C for 8 hours with 60 % sulphuric acid and a 400 % ratio of acid the yield of the unsaturated dimer was 100 %. In addition, by using 80 % sulphuric acid at 24 to 38° C. α-methylstyrene could be quantitatively converted into its cyclic saturated dimer, m. p. 52—54°. The increase both in acid concentration and reaction temperature was stated to promote the formation of the cyclic saturated dimer.

A still later report [13] in the patent literature deals with the production of a solid dimer from α-methyl-p-methylstyrene. Accordingly a »new» dimer was prepared from α-methyl-p-methylstyrene in yields of 90—95 % by treating this at 200—250° C with an activated diatomaceous earth (2—10 %), e. g. fuller's earth or floridin. The dimer obtained was a white crystalline solid, m. p. 40—41°. Because Tiffeneau [3] reported the melting point of his dimer to be 40° and Puranen [8] that of his 37.5—38.5° there is every probability that the compounds in question in all three cases are identical. Moreover, the invention relates to a similar method for producing the solid dimer from the liquid one, which latter was formed in the process described above at temperatures not exceeding 200° C. By treating this at 200—250° in the same manner as above it was converted in yields of 90—100 % into the solid form.

A conclusion based on the reports mentioned above reveals that both α-methyl-p-methylstyrene and α-methylstyrene have been converted into their solid saturated and liquid unsaturated dimers by methods using inorganic compounds mostly of acidic character as dimerizing catalysts. The structure of the solid dimer of both styrenes can be regarded as established. As to the liquid form, in the case of α-methylstyrene one constituent has been fully characterized. This, however, does not by any means exclude the presence of some isomer.

The dimerizing action of formic acid on aromatic ethylene derivatives is not unknown. In spite of considerable time spent on the study of the literature, only one publication concerning this was found. The report of Glichitch [14] describes the action of formic acid on the propenylphenols and phenolethers. It stated that anethole, by boiling with an equal weight of 90 % formic acid for 1 hour, was dimerized to metanethole. Moreover, under the same conditions isoeugenol, methylisoeugenol and isosafrole were converted to their dimers. On the basis of these experiments Glichitch deduced the conception that the dimerization under the influence of boiling formic acid would be characteristic for phenols and phenolethers possessing a propenyl side chain.

DIMERIZATION OF α-METHYL-p-METHYLSTYRENE BY FORMIC ACID

In the study described in this paper, the starting material used in majority of dimerization experiments was prepared by catalytic oxidation of cymene with air at 80—100° and by removal of the acids and higher boiling polymerization and condensation products as well as the bulk of the unchanged cymene from the oxidation product. The liquid thus obtained contained 62 % of dimethyl-p-tolylcarbinol and 35 % of p-methylacetophenone the rest being

primarily unchanged cymene still present. The intension was namely to study the possibilities for production of the dimers directly from the tertiary alcohol in presence of the ketone. At the same time some experiments were carried out by using for dimerization pure α-methyl-p-methylstyrene prepared by catalytic removal of water from the tertiary alcohol in the above mixture, followed by separating the α-methyl-p-methylstyrene formed from the ketone by fractional distillation.

In this connection it may be pointed out that the present study originated in experimenting with various methods for removing water from the tertiary alcohol in the above mixture. In these tests a method proposed by Eisenlohr and Schulz [15], too, was tried. They claimed that α-methyl-p-methylstyrene could be obtained by dissolving 20 g of dimethyl-p-tolylcarbinol in 50 g of 90 % formic acid and distilling the resulting mixture. However, the experiment carried out by using the mixture of the tertiary alcohol and the ketone instead of the pure alcohol gave not at all the styrene in question but its unsaturated dimer in a good yield.

After many trials it was found that the best way for producing α-methyl-p-methylstyrene from the above mixture was to distil this under diminished pressure through a catalyst tube filled with activated alumina and maintained at a proper temperature (see Experimental). The yield was 93 %. By using potassium bisulfate as dehydrating agent markedly more polymerization products were formed.

I. Dimerization experiments using the mixture of dimethyl-p-tolylcarbinol and p-methylacetophenone as starting material

A mixture of the starting material and formic acid was distilled first under atmospheric pressure until the acid was removed, then under diminished pressure for separating the dimer fraction from the ketone and higher polymers (see Experimental). In the dimer fraction the quantity of unsaturated dimer was determined by means of bromine titration.

Results from 9 experiments are reported in the following table (Table 1). For comparison a table (Table 2) of Hersberger et al.[12] concerning the dimerization of α-methylstyrene by sulphuric acid is included.

In the optimum cases (experiments 3 and 4 in Table 1) the formic acid method gave a yield of unsaturated dimer exceeding 80 %. The concentration of acid was 95 % and its quantity 20—33 % of that of the tertiary alcohol-ketone mixture used. Upon decreasing the quantity of the acid (experiments

Table 1. Dimerization experiments with the mixture of dimethyl-p-tolylcarbinol and p-methylacetophenone.

No.	Formic acid		Reaction products			
	Concentration	Quantity	Unconverted + monomer	Dimers		Trimers + polymers
				Unsat.	Sat.	
	%	%	%	%	%	%
1	95	133	4	26	47	23
2	95	67	7	66	8	19
3	95	33	6	84	0	10
4	95	20	12	81	0	7
5	95	13	59	37	0	4
6	95	7	80	18	0	2
7	70	29	34	61	0	5
8	95	133	0	5	73	22
9	95	67	8	79	1	12

Experiments 1—7 were done by distilling the reaction mixture directly.
Experiment 8 was done by refluxing the reaction mixture for 2 hours.
Experiment 9 was carried out at room temperature.
Unconverted among the reaction products was calculated as α-methyl-*p*-methylstyrene.

Table 2. Dimerization of α-methylstyrene by sulphuric acid. Hersberger, Hill and Heiligmann [12].

Sulphuric acid		Reaction		Per cent unconverted	Per cent unsat. dimer	Per cent sat. dimer
Concentration	Quantity	Temp. °F	Time h			
%	%					
30	400	170—190	4	60	40	0
40	400	170—190	4	57	43	0
50	400	122—180	6	0	99	1
60	400	122—180	6	0	98	2
60	3	150—180	6	88	12	0
60	6	150—180	6	80	20	0
60	100	150—180	6	23	75	2
70	400	180—190	6	0	10	90
50	400	70— 80	8	80	20	0
60	400	70— 80	8	0	100	0
70	400	75—100	8	0	90	10
80	400	75—100	5	0	0	100

5 and 6) plenty of undimerized α-methyl-*p*-methylstyrene was obtained. On the other hand when more acid was used, saturated dimer was formed in increasing quantity at the expense of the unsaturated one (see later the isomerization of the unsaturated dimer into the saturated one by formic acid). Prolongation of the reaction time had a similar effect (experiment 8). It is therefore possible to prepare also the saturated dimer directly from the tertiary alcohol-ketone mixture although in a considerably poorer yield owing to the formation of appreciable quantities of higher polymers as by-products.

If the results of the experiments 2 and 9 in Table 1 are compared with each other, it is seen that the increase in temperature had hardly any effect on the reactivity of the starting material but did have an effect on the ratio of the reaction products.

When the formic acid method is compared with the sulphuric acid method, it can be stated that for achieving the same yield of dimers an appreciably smaller amount of acid was sufficient in the former case. The reason, however, is not to be sought in the possibly different dimerizing actions of those acids. The main reason is that in the formic acid method the starting material for dimer (dimethyl-*p*-tolylcarbinol) forms with formic acid (also in the presence of *p*-methylacetophenone) a fully homogeneous mixture resulting in the best possible reaction conditions. Hereby the intimate contacting of the reactants, an important factor in the sulphuric acid method according to the patent report [12], becomes unnecessary.

From the technical standpoint the formic acid method is markedly simpler than the sulphuric acid method. In the former, distillation is the only operation and both the distillation of formic acid under atmospheric pressure and the fractionation of the reaction products under diminished pressure can be carried out in the same distillation apparatus. Formic acid can be recovered. It will be in diluted form owing to the cleavage of water from dimethyl-*p*-tolylcarbinol (the dilution in experiment 3 from 95 % to 78 %). In the sulphuric acid method according to the patent report [12] the following operations are to be taken into consideration:

1. Intimate contacting of the reactants at a defined temperature.
2. Separation of the dimer layer from the acid layer.
3. Neutralization of the dimer layer with a solution of a base.
4. Fractionation of the reaction products under diminished pressure.
The acid can be recovered in this method without dilution.

II. Dimerization experiments using α-methyl-*p*-methylstyrene as starting material

The α-methyl-*p*-methylstyrene employed was 98 % pure, prepared by catalytic dehydration of dimethyl-*p*-tolylcarbinol (see Experimental). Cymene was the principal impurity.

Because α-methyl-*p*-methylstyrene was insoluble in formic acid the situation in this respect was comparable with the dimerization of α-methylstyrene by sulphuric acid. Three experiments were carried out resulting in following data:

*Table 3. Dimerization of α-methyl-p-methylstyrene by formic acid.*

| No.	Formic acid		Reaction products			
	Concentration	Quantity	Unconverted	Dimers		Trimers + polymers
				Unsat.	Sat.	
	%	%	%	%	%	%
1	95	133	0	4	63	33
2	95	18	5	40	37	18
3	82	51	7	83	6	4

The results indicate that 95 % formic acid is too concentrated giving rise to a strong formation of polymers. In addition, because in this case no dilution of the acid takes place, the original concentration of acid can be taken smaller. The acid can be reused immediately after distillation. From the technical point of view this method is therefore simpler than the formic acid method using dimethyl-*p*-tolylcarbinol as starting material.

ISOMERIZATION OF THE UNSATURATED DIMER OF α-METHYL-*p*-METHYLSTYRENE INTO THE SATURATED DIMER

Trials were made with powdered aluminium chloride or formic acid as isomerizing agents. Both gave positive results. The latter, however, proved decisively simpler and better. Sulphuric acid was also used but only at a low temperature; the bulk of the dimer was then converted into a sulphonic acid. Aluminium chloride gave analogous results to those achieved by Bergmann *et al.* [6] in the case of the unsaturated dimer of α-methylstyrene. The reaction mechanism proposed by them was as follows:
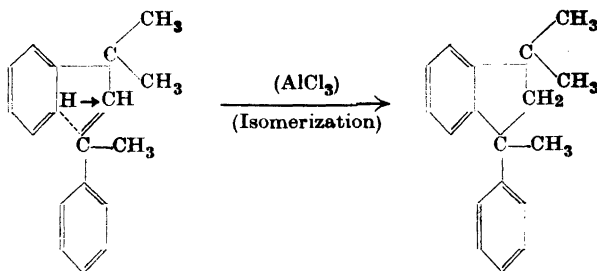
An analogous scheme may be true in the case of the unsaturated dimer of
α-methyl-*p*-methylstyrene. However, on the basis of the structures established
for it in this investigation (see later) the following possibility may be considered
just as probable, *viz.*:
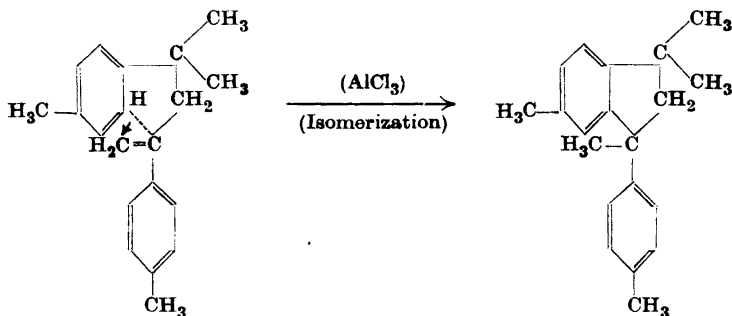
ESTABLISHMENT OF THE STRUCTURE OF THE DIMERIC α-METHYL-*p*-
METHYLSTYRENES OBTAINED BY FORMIC ACID

I. Solid, saturated dimer

The solid dimer obtained by formic acid from three different starting
materials, dimethyl-*p*-tolylcarbinol, α-methyl-*p*-methylstyrene and its liquid
dimer, was found to be the same compound in every case and identical with
the »dicymene» prepared from cymene according to the directions given by
Puranen [6]. This being the case the solid dimer must have the structure 1,3,3,6-
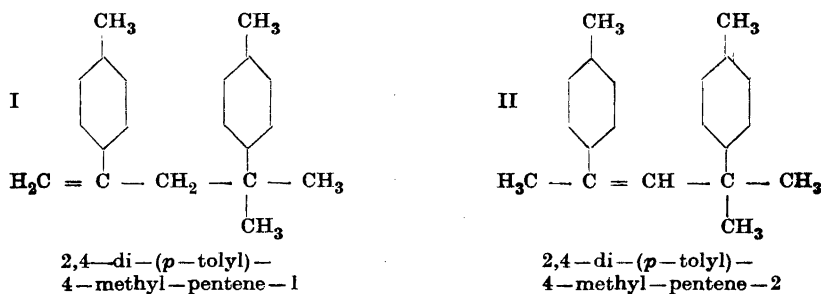tetramethyl-1-*p*-tolylhydrindene.

II. Liquid, unsaturated dimer

The structure of this dimer was established by ozonization. When the
ozonide had been decomposed with water the following products could be
identified:

1. Formaldehyde.
2. α-Oxo-γ-methyl-α,γ-di-p-tolyl-butane.
3. p-Methylacetophenone.
4. Dimethyl-p-tolylacetaldehyde.
5. Dimethyl-p-tolylacetic acid.
6. p-Toluic acid.

On the basis of these decomposition products the starting dimer must be a mixture of two isomeric hydrocarbons having the following formulas:
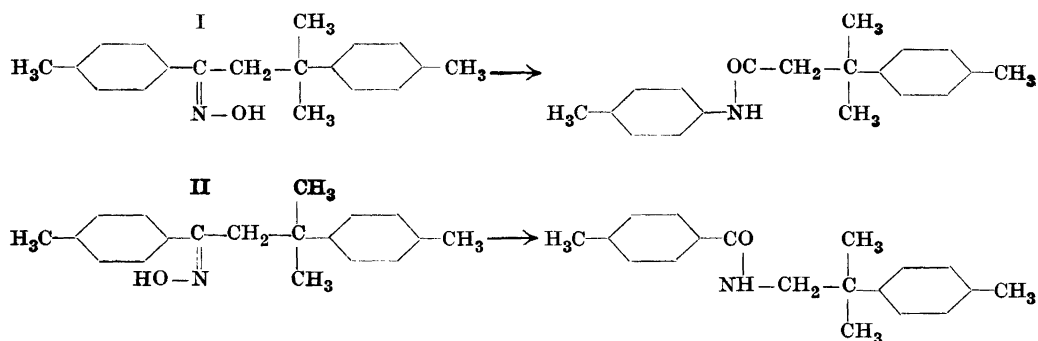

I
$H_2C = C - CH_2 - C - CH_3$
              |
              CH_3

2,4—di—(p—tolyl)—
4—methyl—pentene—1

II
$H_3C - C = CH - C - CH_3$
                    |
                    CH_3

2,4—di—(p—tolyl)—
4—methyl—pentene—2

The fragments of the former are formaldehyde and α-oxo-γ-methyl-α,γ-di-p-tolyl-butane, those of the latter p-methylacetophenone and dimethyl-p-tolyl-acetaldehyde. p-Toluic acid and dimethyl-p-tolylacetic acid are secondary products.

On the basis of the amounts of the two ketones the quantities of both isomers in the starting mixture were calculated. Accordingly, it was found to contain 66 % of the isomer I and 13 % of the isomer II. These are, however, to be considered as minimum values and only as approximative ones, because the secondary products are not taken into account. Based on the figures obtained the ratio of the isomers I and II in the mixture will be 5 : 1. Neither of these isomers has been previously reported in the literature. They couldn't be separated by fractional distillation since their boiling points are very close to each other.

Because α-oxo-γ-methyl-α-γ-di-p-tolyl-butane has not been previously reported in the literature, the structure of the higher boiling ketone isolated from the ozonization products had to be established. To that purpose the ability of the ketoximes to undergo the Beckmann rearrangement was made use of. By hydrolyzing the acid amides formed and identifying the hydrolysis products it should be possible to provide evidence of the structure of the original ketone.

According to Meisenheimer [16] the Beckmann rearrangement of α-oxo-γ-methyl-α,γ-di-p-tolyl-butane oximes (two possible stereoisomeric forms) into acid amides would proceed as follows:

I

$$H_3C-\!\!\!\left\langle\right\rangle\!\!\!-\underset{\underset{N-OH}{\|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\!\!-\!\!\!\left\langle\right\rangle\!\!\!-CH_3 \longrightarrow \quad H_3C-\!\!\!\left\langle\right\rangle\!\!\!-NH-\underset{}{\overset{}{OC}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\!\!-\!\!\!\left\langle\right\rangle\!\!\!-CH_3$$

II

$$H_3C-\!\!\!\left\langle\right\rangle\!\!\!-\underset{\underset{HO-N}{\|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\!\!-\!\!\!\left\langle\right\rangle\!\!\!-CH_3 \longrightarrow H_3C-\!\!\!\left\langle\right\rangle\!\!\!-CO-NH-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\!\!-\!\!\!\left\langle\right\rangle\!\!\!-CH_3$$

However, only one oxime of the ketone under investigation could be obtained and accordingly only one acid amide could be isolated from the rearrangement products. When the acid amide was hydrolyzed by a solution of potassium hydroxide in methanol, p-toluidine and an acid (m. p. 70.0—70.6°) were obtained as hydrolysis products. The latter was proved to be β-p-tolyl*iso*valeric acid (not previously reported) by synthesizing it in another way. Only minute amounts of p-toluic acid could be isolated from hydrolysis products giving, however, evidence for the existence of the other stereoisomeric oxime (II) expected.

At this point it may be mentioned that on carrying out the acid amide hydrolysis with 70 % sulphuric acid p-toluidine was certainly obtained in a good yield but the acid hardly at all. Instead of this, plenty of a neutral compound, m. p. 42—43°, was obtained. This was identified as 3,3,6-trimethylindanone-1 (not previously reported) afforded by the intermediate β-p-tolyl*iso*valeric acid through intramolecular water cleavage. The same compound could be prepared in a 80 % yield directly from β-p-tolyl*iso*valeric acid by means of concentrated sulphuric acid and also from the acid chloride by the usual method (Friedel-Crafts reaction).

The liquid dimer proved to correspond to its simplest aliphatic analogue, di*iso*butylene. Butlerow [17], Whitmore et al. [18-20] and Mc. Cubbin and Adkins [21] have shown that the dimer obtained from *iso*butylene by the sulphuric acid method consists of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2 in a ratio of 4 : 1.

It seems possible that the liquid dimer of α-methylstyrene investigated by Bergmann et al. [6] would also have a similar composition although they were

able to prove the existence of only one isomer, 2,4-diphenyl-4-methyl-pen-tene-2. The reason was that they isolated the ozonization products as the semicarbazones after a reaction time of 20 hours. In the present work, however, it turned out that the semicarbazone of α-oxo-γ-methyl-α,γ-di-*p*-tolyl-butane was formed very slowly. Only after two weeks did it begin to separate (see Experimental). This being the case it is to be thought that the corresponding ketone, α-oxo-γ-methyl-α,γ-diphenyl-butane, has escaped the notice of Bergmann *et al.*

DECOMPOSITION OF THE LIQUID DIMER OF α-METHYL-*p*-METHYL-STYRENE BY ATMOSPHERIC DISTILLATION

When the dimer was heated to its boiling point (about 330°) at atmospheric pressure, decomposition resulted. A light, colorless liquid, b. p. 176—189°, slowly distilled over. Its main constituents were proved to be *p*-cymene and α-methyl-*p*-methylstyrene. Accordingly the dimer had reconverted into its monomer. The dimer also decomposed in another way yielding *p*-cymene. The corresponding acetylenic fragment could not be identified. It was probably polymerized and remained in the tarry residue amounting to one half of the starting material.

EXPERIMENTAL

General dimerization method

75 g of the mixture of dimethyl-*p*-tolylcarbinol and *p*-methylacetophenone were placed in a 200 ml round-bottomed flask and formic acid was added (the acid used was a product of Schering-Kahlbaum, d. 1.22, about 95 %). At first a clear solution was formed. Depending on the acid quantity used, the solution got turbid either at room temperature or when heated to boiling, the resulting dimer separating as a distinct layer. The bulk of the formic acid was distilled off on an oil bath at atmospheric pressure by using a 40 cm high fractionating column filled with porcelain rings. The ketone and dimer fractions were distilled at diminished pressure. The residue consisted of trimers and higher polymers. *p*-Methylacetophenone remained unchanged throughout the process. The dimer fraction had a boiling point of 170−180° at 5 mm pressure; the boiling point of the saturated dimer was about 5° lower than that of the unsaturated one. The unsaturation of the dimer fraction was determined by means of bromine titration [22] and it was on this basis the quantities of the saturated and unsaturated dimers were calculated.

In experiments with α-methyl-*p*-methylstyrene the method employed was a similar one except that after the addition of formic acid, the mixture was refluxed for 1 hour owing to a smaller reaction velocity as a result of the insolubility of the hydrocarbon in the acid. Because the boiling acid layer was under the hydrocarbon layer, comparatively effective mixing was caused by refluxing.

Dimerization at room temperature

75 g of the tertiary alcohol-ketone mixture and 50 g of 95 % formic acid were mixed and placed immediately into a graduate. 50 minutes after the mixing, the solution became turbid and began to separate into two layers. Three hours from the beginning the boundary between the two layers had reached its lowest level. After the acid had been removed by neutralization, the layers were separated and analyzed. The dimer, ketone and acid were divided into the two layers as follows:

	Dimer layer	Acid layer
Dimer	95 %	5 %
Ketone	48 »	52 »
Acid	4 »	96 »

Production of α-methyl-*p*-methylstyrene from the tertiary alcohol-ketone mixture

435 g of the mixture (b. p. 96—111°/8 mm), containing 62 % of the tertiary alcohol, were vaporized *in vacuo* (13 mm). The vapors were passed through a Pyrex tube 60 cm long and 1 ½ cm in diameter, packed with coarse (6—8 mesh) granules of alumina and maintained at a temperature of 220—230°. The cooling system consisted of a spiral condenser followed by a suction flask kept in an ice-salt mixture. After the aqueous layer (28 g) had been removed, the distillate was dried with anhydrous sodium sulphate and fractionated at atmospheric pressure. 230 g (93 %) of α-methyl-*p*-methylstyrene, b. p. 189—191° and 128 g of *p*-methylacetophenone, b. p. 224—225°, were obtained.

Conversion of liquid dimer to solid dimer

1. *Isomerization with aluminium chloride*

9.5 g of the liquid dimer were dissolved in 10 ml of dichloroethane and 5 ml of a 5 % solution of aluminium chloride in dichloroethane were added with stirring. The mixture was allowed to stand for 2 hours. 3 g of a crystalline material, m. p. 38—39°, were isolated from the reaction product.

$C_{20}H_{24}$ Calc.   C 90.9   H 9.1   Mol. wt. 264
      Found   » 90.8   » 9.0   »   »   257

It was shown by mixed melting point to be identical with authentic 1,3,3,6-tetramethyl-1-*p*-tolylhydrindene.

2. *Isomerization with concentrated sulphuric acid*

150 ml of concd. sulphuric acid (d. 1.84) were allowed to act on 25 g of the liquid dimer for 3 days at — 5° and then for 14 days at room temperature. Only 2.5 g (10 %) of the solid dimer, m. p. 38—39° were obtained. In addition, 2.5 g of an unsaturated (one double bond) hydrocarbon, b. p. 98—100°/8 mm, mol. wt. 167, was isolated from the reaction product. The remainder was found to be sulphonated. Upon diluting with water and neutralizing with ammonia 20 g of an ammonium salt of a sulphonic acid could be isolated.

3. Isomerization with formic acid

40 g of the liquid dimer were refluxed with 52 g (130 %) of 95 % formic acid for 2 hours. When the formic acid had been distilled off at atmospheric pressure and the remainder had been fractionated *in vacuo*, 37 g (92 %) of a dimer fraction containing 95 % of the saturated dimer and 5 % of the unsaturated one were obtained. 8 % of the starting material had been further polymerized.

Structure of the liquid unsaturated dimer

After the liquid dimer had been fractionally distilled in vacuo, it was a colorless viscous oil, b. p. 181—186°/7 mm. As freshly prepared it was odorless but on longer standing an intense smell of formaldehyde became noticeable.

$$C_{20}H_{24} \quad \text{Calc.} \quad C\ 90.9 \quad H\ 9.1 \quad \text{Mol. wt. } 264$$
$$\text{Found} \quad \text{»}\ 91.0 \quad \text{»}\ 8.9 \quad \text{»} \quad \text{»}\ 248$$

The double bond determination by perbenzoic acid method gave 1.01 double bonds for one dimer molecule.

Ozonization of the unsaturated dimer

20.0 g of the dimer (b. p. 186—191°/8 mm) were dissolved in 200 ml of glacial acetic acid. Ozonized air containing about 2 % of ozone was passed through the solution until the double bonds had disappeared. The reaction vessel was cooled in cold water.

The solvent was evaporated *in vacuo* at room temperature by using a mercury vacuum pump. The residue was a viscous, yellow liquid.

The ozonide was decomposed by dropping it with stirring into a boiling mixture consisting of 150 ml of water, 5 g of zinc dust, 26 mg of silver nitrate and 17 mg of hydroquinone. Steam was then passed through the mixture until the volatile substances had come over. The steam distillate had a strong smell of formaldehyde. The resorcinol and Schiff tests for formaldehyde were positive. By iodometric titration the distillate contained 0.98 g of formaldehyde.

The steam distillate was extracted with ether and the ethereal extract shaken with saturated sodium bicarbonate solution to separate the acids formed. From the neutral extract, after evaporation of the solvent, the carbonyl compounds were isolated as the semicarbazones. 1.88 g of a crystalline precipitate were separated during 24 hours. Once crystallized from ethanol it melted at 204—205° and was shown by mixed melting point to be identical with authentic p-methylacetophenone semicarbazone.

The alcoholic mother liquor of the semicarbazone was steam distilled in order to remove the volatile compounds. Dilute sulphuric acid was added to the remainder and a second steam distillation carried out. This time a pleasent smelling oil giving a positive Schiff test for aldehydes passed over. It afforded 0.35 g of a semicarbazone, m. p. 171.5° when once crystallized from methanol. It gave no depression when mixed with authentic dimethyl-p-tolylacetaldehyde semicarbazone.

From the ozonization product non-volatile with steam, zinc dust was filtered off and washed with ether. The ethereal filtrate was shaken with saturated sodium bicarbonate solution to separate the acids. These were combined with the acids obtained from the

volatile part. Thus a total of 0.92 g of acids were obtained. After a distillation *in vacuo*
and a lengthy fractional crystallization the acid mixture could be divided into two parts:

I Part: 0.4 g, m. p. 179—180° when crystallized from benzene. It gave no depression
when mixed with authentic *p*-toluic acid.

$C_8H_8O_2$ Calc.   C 70.6   H 5.9   Neut. equiv. 136
           Found   » 70.6   » 5.8   »   »   136

II Part: 0.35 g, m. p. 80—81° after several recrystallizations from petrol ether. It
was shown by mixed melting point to be identical with authentic dimethyl-*p*-tolylacetic
acid.

After separation of the acids from the ozonization product non-volatile with steam,
the remainder was distilled in vacuo. Thereby 13.3 g of a yellow oil, b. p. 201—205°/7
mm passed over. This oil was considerably more viscous than the original dimer. It
had a pleasant although faint odor. It was scarcely volatile with steam. The Schiff test
for aldehydes was negative.

$C_{19}H_{22}O$ Calc.   C 85.7   H 8.3   Mol. wt. 266
           Found   » 85.7   » 8.2   »   »   253

a-Oxo-γ-methyl-a-γ-di-p-tolyl-butane semicarbazone

The semicarbazide acetate prepared by dry mixing of 0.84 g of semicarbazide hydro-
chloride and 0.74 g of potassium acetate was dissolved in 8 ml of ethanol. The potassium
chloride precipitated was filtered off. 2.0 g of the above ketone were added and the mixture
was allowed to stand at room temperature. It was only after 2 weeks that crystals began
to separate from the solution. 1.06 g of the semicarbazone were obtained which on
recrystallization from ethanol formed clusters of white needles, m. p. 173—174°.

Oximation of a-oxo-γ-methyl-a,γ-di-p-tolyl-butane

A mixture consisting of 6.44 g of the ketone, 1.86 g of hydroxylamine hydrochloride,
10 ml of abs. ethanol and 10 ml of pyridine was heated on a boiling water bath under
reflux for 2 hours. The solvents were distilled off in vacuo. The remainder afforded on
crystallization from ligroin 5.1 g of an oxime. On recrystallization from a mixture of
petrol ether and ether the oxime formed white needles, m. p. 124—125°. The other
stereoisomeric oxime could not be isolated by fractional crystallization.

$C_{19}H_{23}NO$ Calc.   C 81.1   H 8.2   N 4.97   Mol. wt. 281
           Found   » 81.2   » 8.0   » 4.92   »   »   276

Beckmann rearrangement of the oxime

2.3 g of the oxime were dissolved in 23 ml of abs. ether. Powdered phosphorus penta-
chloride was added until it did not disappear. 2.0 g of an acid amide were obtained.
When crystallized from ligroin it formed clusters of long, white needles, m. p. 128—129°.

$C_{19}H_{23}NO$ Calc.   C 81.1   H 8.2   N 4.97
           Found   » 80.8   » 8.0   » 5.02

By means of hydrolysis the acid amide was shown to be *β-p*-tolyl*iso*valeric acid *p*-toluidide.

Hydrolysis of the acid amide

1. With hydrochloric acid:

0.8 g of the acid amide and 16 ml of concentrated hydrochloric acid were refluxed for 2 hours. Only about 3 % of the amide were hydrolyzed.

2. With sulphuric acid:

A mixture of 0.77 g of the acid amide and 8 ml of 70 % sulphuric acid was refluxed for one-half hour. 0.04 g of an acid, m. p. about 70°, 0.24 g of an amine and 0.32 g of a neutral compound were obtained as reaction products.

The amine: On crystallization from petrol ether it formed large plates, m. p. 43 — 44°.

C_7H_9N	Calc.	C 78.5	H 8.4	N 13.03
	Found	» 78.5	» 8.3	» 13.10

It was shown by mixed melting point to be identical with authentic *p*-toluidine. The yield of *p*-toluidine on hydrolysis was 81 %.

The neutral compound: It crystallized from petrol ether in large plates, m. p. 42 — 43°.

$C_{12}H_{14}O$	Calc.	C 82.7	H 8.1	Mol. wt. 174	
	Found	» 82.5	» 8.1	»	» 167

It was shown by mixed melting point to be identical with 3,3,6-trimethylindanone-1 synthesized by the Friedel-Crafts reaction from *β-p*-tolyl*iso*valeric acid chloride. The compound formed a semicarbazone, m. p. 214 — 215° (with decomposition) when crystallized from ethanol. The yield of indanone on hydrolysis was 67 %.

3. With a solution of potassium hydroxide in methanol:

0.2 g of the acid amide and 10 ml of a 25 % solution of potassium hydroxide in pure methanol were kept in a sealed tube at 70° for 3 days. Only 10 % of the acid amide were hydrolyzed.

0.5 g of the acid amide (not recrystallized) and 20 ml of the potassium hydroxide solution mentioned above were kept in a sealed tube at 130° for 24 hours. 97 % of the amide were hydrolyzed. The yield of *p*-toluidine was 70 %. 0.32 g of an acid were obtained, m. p. 67 — 69° (crude product). On fractional crystallization minute amounts of *p*-toluic acid could be isolated. After three recrystallizations from petrol ether the main product was obtained as large, almost colorless crystals, m. p. 76.0 — 76.6°.

$C_{12}H_{16}O_2$	Calc.	C 75.0	H 8.4	Neut. equiv. 192	
	Found	» 74.9	» 8.3	»	» 192

The acid gave no depression in melting point when mixed with *β-p*-tolyl*iso*valeric acid. The yield of the acid on hydrolysis was 93 %.

6

Synthesis of β-p-tolylisovaleric acid

From the mixture of dimethyl-*p*-tolylcarbinol and *p*-methylacetophenone the latter was removed as the semicarbazone. The crude carbinol thus obtained was converted into dimethyl-*p*-tolylchloromethane by saturation with dry hydrogen chloride at a temperature below 0°. β-*p*-tolyli*so*valeric acid was prepared from this by the malonic ester synthesis according to the directions given by Hoffman [23] for producing the corresponding phenyl derivative. A dicarbonic acid was formed as an intermediate. This was first obtained as an oil which on long standing solidified to a mass of oily crystals. After two recrystallizations from benzene (the separation of the crystals took place very slowly) small hemispherical crystals were obtained, m. p. 131.5—132.5° (with decomposition).

$C_{13}H_{16}O_4$ Calc.   C 66.0   H 6.8   Neut. equiv. 118
                 Found   » 66.2   » 6.7   »   »   120

On the basis of its synthesis and the analytical figures obtained the dicarbonic acid must have the structure β-methyl-β-*p*-tolylpropane — a,a-dicarbonic acid (not previously reported in the literature).

The dicarbonic acid when heated at 200° afforded a monocarbonic acid which on crystallization from petrol ether was obtained as large, colorless crystals, m. p. 75.5—76.0°.

$C_{12}H_{16}O_2$ Calc.   C 75.0   H 8.4   Neut. equiv. 192
                 Found   ˃ 75.2   » 8.3   »   »   195

The yield of β-*p*-tolyli*so*valeric acid calculated from the weight of dimethyl-*p*-tolylchloromethane was 15 %. The main product was a-methyl-*p*-methylstyrene produced by elimination of hydrogen chloride from dimethyl-*p*-tolylchloromethane.

Synthesis of 3,3,6-trimethylindanone-1 from β-p-tolylisovaleric acid

A mixture of 0.5 g of β-*p*-tolyli*so*valeric acid and 2.5 g of concentrated sulphuric acid was kept on a boiling water bath for 3 hours. When cold, the reaction mixture was poured onto ice and extracted with ether. The ethereal extract was shaken with saturated sodium bicarbonate solution to remove the possibly unconverted acid. After evaporation of the ether the indanone was obtained in large, colorless plates, m. p. 42—43°, yield 80 %.

Synthesis of dimethyl-p-tolylacetaldehyde

The synthesis was carried out by known methods [24-26] by starting from *p*-methylacetophenone.

Synthesis of dimethyl-p-tolylacetic acid

The above aldehyde was oxidized to the corresponding acid by silver oxide according to Delépine and Bonnet [27]. On crystallization from petrol ether the acid was obtained as coarse crystals, m. p. 80.5—81.5°, yield 98 %.

$C_{11}H_{14}O_2$ Calc.   C 74.1   H 7.9   Neut. equiv. 178
                 Found   » 74.0   » 7.8   ˃   ˃   178

Rupe and Bürgin [28] reported the melting point of dimethyl-*p*-tolylacetic acid to be 70—71° »after previous sintering». Obviously the sample must have been impure because the melting point now found is 10° higher.

Decomposition of the unsaturated dimer by atmospheric distillation

The dimer (36 g) was heated to its boiling point in a distilling flask equipped with a 20 cm fractionating column. A light, colorless oil (17.8 g), b. p. 176—189°, slowly distilled over. According to bromine titration the unsaturation of the distillate was 33 % (calculated as *a*-methyl-*p*-methylstyrene).

Identification of the decomposition products

6.0 g of the above distillate were dissolved in 60 ml of chloroform and ozonized until the solution ceased to decolorise bromine.

The ozonide was decomposed by boiling with water. Formaldehyde and *p*-methylacetophenone (0.9 g) were found among decomposition products. The latter was isolated as the semicarbazone. Hereby the unsaturated part of the starting material was proved to be *a*-methyl-*p*-methylstyrene.

The mother liquor of the above semicarbazone afforded the saturated part of the starting material (3.0 g, b. p. 176—177°). On oxidation with $KMnO_4$ 1.1 g of the saturated compound yielded 0.4 g of hydroxycumic acid (m. p. alone and mixed with an authentic specimen 155—156°). Accordingly the saturated part was *p*-cymene.

SUMMARY

I. A method was worked out for production of the two dimers of α-methyl-*p*-methylstyrene either directly from the neutral liquid oxidation product of cymene (a mixture of dimethyl-*p*-tolylcarbinol and *p*-methylacetophenone) or from *a*-methyl-*p*-methylstyrene by using formic acid as a dimerizing agent. By this method it is possible in both cases to prepare a solid, saturated dimer and a liquid, unsaturated dimer separately. Further, by means of formic acid the liquid dimer can be isomerized into the solid one.

II. The structure of the liquid, unsaturated dimer of α-methyl-*p*-methylstyrene was established. In analogy with di*iso*butylene, the dimer was found a mixture of two isomeric hydrocarbons, 2,4-di-(*p*-tolyl)-4-methyl-pentene-1 and 2,4-di-(*p*-tolyl)-4-methyl-pentene-2 about in a 5 : 1 ratio.

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