

Studies on Peroxy Compounds XI *

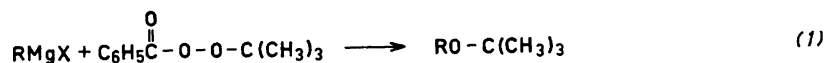
The Introduction of the *t*-Butoxy- and Benzoyloxy Groups into Malonic Esters — a Novel Method for the Preparation of Tartronates

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In contrast to reactions in alcoholic solutions, the sodium derivative of diethyl malonate in benzene gives with *t*-butyl peracetate, diethyl *O-t*-butyl tartronate and with benzoyl peroxide, diethyl *O*-benzoyl tartronate together with small amounts of diethyl dibenzoyloxy malonate. Substituted sodium malonates give no *O-t*-butyl tartronates with peresters but with benzoyl peroxide, the corresponding benzoyl tartronates are formed smoothly. A representative series of alkyl, aryl, aralkyl and chloro-substituted diethyl malonates have been shown to give high yields of benzoyl tartronates which, in a few cases, have been characterized as diethyl tartronates and tartroic acids.

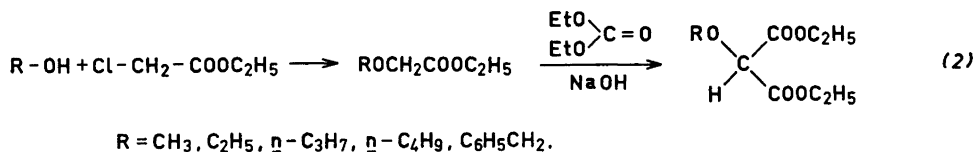
In a recent investigation¹ of the reactions between Grignard reagents and peroxy compounds, it was found that in the case of *t*-butyl perbenzoate the oxygen-oxygen bond is ruptured, thus affording a novel and convenient method for the preparation of *t*-butyl ethers, according to the following scheme:



Similarly, when benzoyl peroxide was allowed to react with Grignard reagents, the oxygen-oxygen bond seems to be initially ruptured. As a logical continuation of this investigation, we felt that instead of using organo-metallics, enolates or more precisely the sodium derivative of so called active methylene compounds, ought to be investigated. The *t*-butoxy group would thus be introduced into malonates to give *O-t*-butyl tartronates, in an analogous

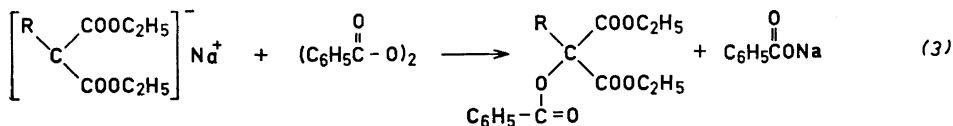
* Part X. Lawesson, S.-O. and Berglund, C. *Angew. Chem.* 73 (1961) 65.

way to the ether synthesis (eqn. 1). Such types of compounds cannot be prepared by reacting a sodium alkoxide with diethyl bromomalonate, since this gives tetraethyl ethanecarboxylate instead. However, simple diethyl *n*-alkyl tartronates have been prepared in recent years by the following method²⁻⁴:



We have found that by reacting *t*-butyl peracetate with the sodium compound of diethyl malonate, diethyl *O-t*-butyl tartronate was obtained in 27 % yield⁵, in addition to tar and polymeric products. Under similar conditions, *t*-butyl perbenzoate gave only ill-defined products. We also tried this reaction with substituted malonic esters but no reaction product could be isolated. Thus, attempts at introducing the *t*-butoxy group into diethyl malonate under the described conditions do not seem to hold much promise nor are they applicable to preparative purposes. When we used ethanol as solvent, the malonate was always recovered unchanged, and ethyl benzoate was isolated, indicating that the peroxy compound reacted faster with the sodium alcoholate than with the sodium malonate. Milas *et al.*⁶ similarly obtained methyl benzoate and *t*-butyl hydroperoxide when *t*-butyl perbenzoate was treated with sodium methoxide.

Since the reactions between *t*-butyl peracetate (perbenzoate) and sodium compounds of malonates were sluggish, we turned our attention to benzoyl peroxide. It has long been known that when benzoyl peroxide is treated with sodium alkoxide in ethanol, perbenzoic acid is formed; because of this, and also due to certain preliminary experiments, ethanol was considered unsuitable as the reaction medium. Tetrahydrofuran was not used as solvent because benzoyl peroxide underwent induced decomposition in it. Since benzene was found to be a convenient solvent, it was used in all subsequent experiments. We found that the oxygen-oxygen bond in benzoyl peroxide is split by the sodium compound according to the following⁷:



In an earlier work⁸ with ethyl benzoylacetate the same observation had also been made.

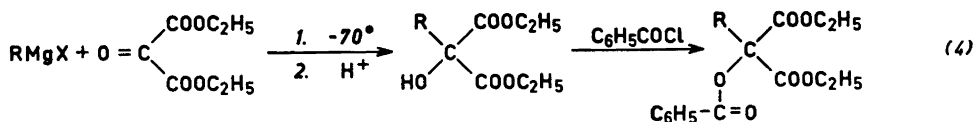
The benzoyl tartronic esters were prepared from benzoyl peroxide and the sodium derivative of malonic ester as follows. Sodium hydride and malonic ester were warmed together in benzene, the solution cooled to 0—4° and treated dropwise with benzoyl peroxide in benzene; after stirring overnight, the ben-

zoic acid was extracted with alkali, the benzene distilled off and the residue fractionated. The malonate is always used in excess, hence generally no peroxide is left at the end of the reaction. When necessary, unreacted peroxides are destroyed by treatment with sodium iodide in glacial acetic acid containing catalytic amounts of ferrous salt.

The O-benzoyl tartronates are stable compounds which, when stored for 1—2 years in closed vials, do not seem to decompose. They occur as very viscous liquids and might be suitable as plastizisers. When heated with glacial acetic acid, no exchange of acyloxy groups was observed, nor was any other reaction detected.

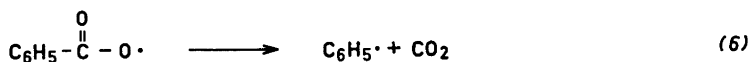
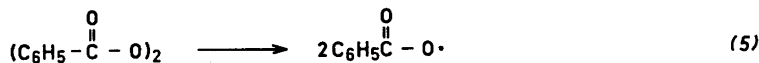
A single attempt to react benzoyl peroxide with ethoxymagnesium malonate in ether, according to Lund, was unsuccessful. Whereas no tartronate was detected, some decomposition of the benzoyl peroxide was observed.

Acyloxy compounds of malonates have been prepared earlier. Conrad and Brückner⁹ reacted diethyl bromomalonate with potassium acetate in absolute ethanol and obtained diethyl acetyl tartronate. Dimroth and Schweizer¹⁰ found that when diethyl malonate is treated with lead tetraacetate, the acetoxy group is easily introduced. Diethyl benzoyl tartronate was first prepared by Jackson and Phinney¹¹ by heating diethyl tartronate with benzoyl chloride under pressure. These authors gave no analytical data as they had difficulties with the final purification. Cope and Field¹², during an investigation on the reactions of Grignard reagents with diethyl mesoxalate according to eqn. 4, have also prepared diethyl O-benzoyl-1-naphthyl tartronate from diethyl 1-naphthyl tartronate according to Jackson and Phinney's method.

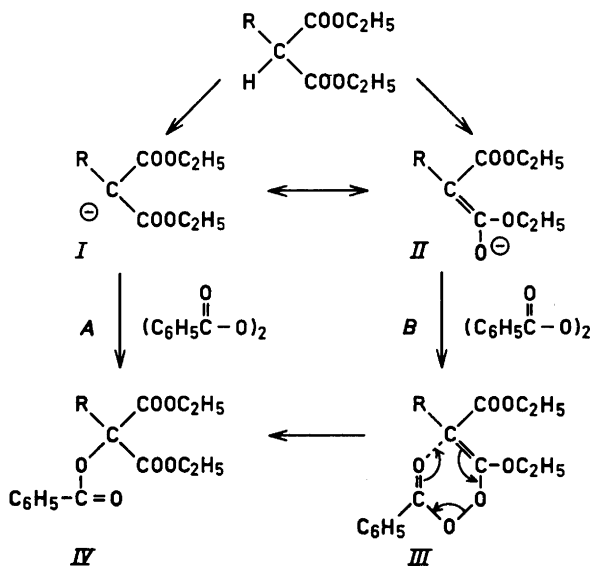


We have prepared diethyl O-benzoyl 1-naphthyl tartronate in almost quantitative yields according to eqn. 3 (R = 1-naphthyl). Although elementary analyses and molecular weight determinations were theoretical, we found a slightly higher melting point than did Cope and Field, and the mixed melting point with their compound showed a small depression. The infrared spectrum showed minor differences, too. We believe that Cope's and our compounds are identical but that crystal effects for instance might account for the differences observed.

We have prepared a series of benzoyl tartronates with various substituents and it was observed that good yields of the corresponding tartronates were obtained almost irrespective of the size of the substituent. Unlike the case with substituted diethyl malonate, the reaction between the unsubstituted compound and benzoyl peroxide seemed at first to be anomalous. Carbon dioxide was evolved and quantitative yields of benzoic acid were not isolated, indicating that in this case a free-radical reaction might be taking place. It is well-known that the scission of benzoyl peroxide is a two-step process and if a free-radical mechanism is involved a sequence of reactions could be



easily postulated. However, eventually we found that if redistilled diethyl malonate and twice recrystallized benzoyl peroxide were used, no gas evolution occurs and quantitative yields of benzoic acid are isolated. Both the mono-substituted malonate (main product) and the disubstituted one are produced. Since no gas was evolved when the sodium derivative of substituted malonates reacts with benzoyl peroxide, a conventional free-radical mechanism involving the benzoyloxy radical might be questioned. The reaction may instead be formulated in the following way:

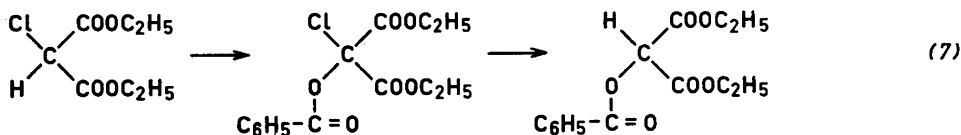


It is known from the work by Walling and especially by Denney that reactions of nucleophiles (phosphines¹³, phenoles¹⁴, amines¹⁵) proceed by initial displacement on one of the peroxide oxygens, the oxygen-oxygen bond being the weakest in the molecule. We believe that either form of the malonate, I or II (Scheme 1) will react according to route A or B. In route A the carbanion I will attack the oxygen-oxygen bond directly, giving the tartronate IV. The transition state III in route B might be formed by a nucleophilic attack of the enolate II on the oxygen-oxygen bond and is an unstable preester which then forms the tartronate IV by an intramolecular rearrangement.

Finally it must be stressed that from a mechanistic point of view a benzoyloxy radical is not eliminated but as this question may not be answered without a study with isotopic benzoyl peroxide (carbonyl ^{18}O), this matter will be reserved for a further publication.

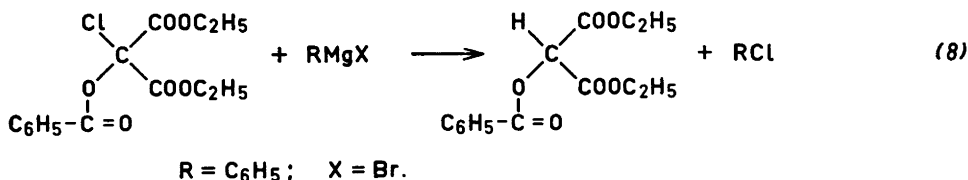
Besides the alkyl and aryl substituted malonic esters we have also investigated some other compounds in this series. Tricarbethoxymethane reacted violently with sodium hydride in benzene and gave a sodium derivative which, with benzoyl peroxide, gave the corresponding benzoate. Diethyl benzoyl malonate did not react with sodium hydride in benzene. The sodium hydride became deactivated, possibly due to the hydride being covered with a layer of the initially formed sodium compound. Diethyl O-benzoyl tartronate reacted rapidly with sodium hydride but when treated with benzoyl peroxide, only an ill-defined thick oil was initially isolated in low yield. After some time diethyl dibenzoyloxy malonate crystallized out. When the above mentioned sodium tartronate was allowed to react with benzoyl chloride, however, the benzoyl group was introduced in high yield.

Because of the difficulties at first encountered with the unsubstituted malonates, which, if not absolutely pure, caused induced decomposition of the peroxide, resulting in undesirable side-reactions and reduced yields, we tried working with diethyl chloro malonate, intending to prepare the tartronates according to the following scheme:

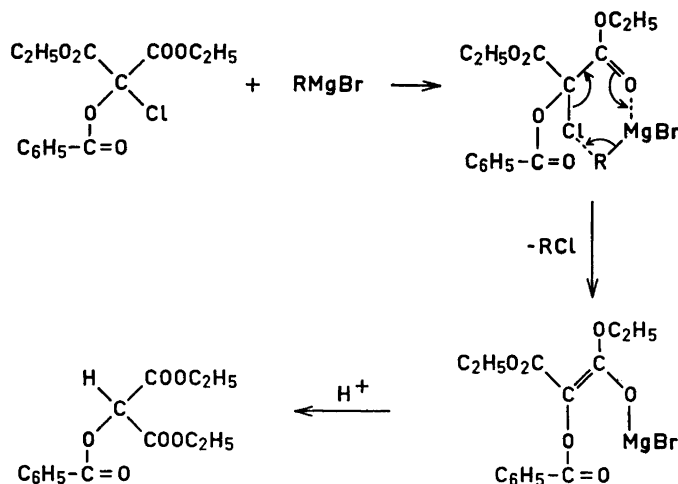


Diethyl chloromalonate reacted rapidly with sodium hydride without any dechlorination and the reaction with benzoyl peroxide ran smoothly to give the corresponding O-benzoyl tartronate in high yield. Elimination of chlorine from mono-chloro and dichloro malonates with Grignard reagents has been tried earlier^{16,17} but with little success. We found, however, that a Grignard reagent is very convenient in our case as it neither attacked the ester group nor did it cause other side-reactions, possibly because addition to the carbonyl group occurs very slowly or because of steric hindrance. When phenylmagnesium bromide was used, chlorobenzene was isolated according to eqn. 8.

It is known that in the case of 1-halosubstituted ketones, the elimination proceeds through an intermediate enolate and it is possible that the halogen



elimination in this case also proceeds *via* a somewhat similar mechanism involving a six-membered ring as an intermediate according to scheme 2.



Scheme 2.

In order to characterize these new benzoyl tartronates further and to explore the possibilities of using this method for the preparation of tartronates and tartronic acids, we investigated the hydrolysis of some of these compounds.

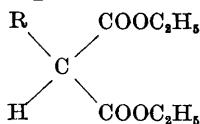
Acids and bases are unsuitable for the hydrolysis of O-benzoyl tartronates since mixtures of acids are formed which are difficult to separate. However, by alcoholysis reesterification will take place and ethyl benzoate is easily distilled off from the tartronate. In some cases the tartronate was isolated and shown to be an authentic hydroxy malonate. The tartronic acids were easily prepared from the tartronate (which usually were not isolated) by acid hydrolysis. Decarboxylation occurred when diethyl O-benzoyl phenyl tartronate was alcoholized and then hydrolyzed, giving mandelic acid as the sole product. From the work of Cope and McElvain¹⁸ it is known that alcoholic sodium ethoxide smoothly cleaves dialkylated malonic esters into the substituted acetic ester according to two possible routes. In our case, however, we cannot as yet say by which mechanism is the cleavage of the benzoyl tartronates effected by the ethoxide ion.

EXPERIMENTAL

The reactions between benzoyl peroxide and the sodium derivative of malonates were carried out in an atmosphere from which moisture was rigidly excluded. Benzoyl peroxide was recrystallized at low temperature from methanol and chloroform. *t*-Butylperacetate (Lupersol \neq 7) was supplied by Lucidol Division, Wallace and Tiernan, Inc., Buffalo, N.Y. and used without further purification. The experiments with Grignard reagents were carried out in nitrogen, and pure magnesium (Dow) was used. The sodium hydride (Kebo) was the ordinary laboratory reagent. The gas generated during the reaction was collected over saturated aqueous sodium chloride, saturated with carbon dioxide.

The infra-red spectra were recorded on a Perkin-Elmer Model 21, double beam spectrophotometer. The analyses were made by Dr. Alfred Bernhardt, Mülheim (Ruhr) and at The Analytical Department of Uppsala University. Boiling and melting points are uncorrected.

Starting material. Commercial diethyl malonate was used after distillation ($n_D^{20} = 1.4143$).



R	B.p.°C	mm Hg	n_D^{20}
CH ₃ ¹⁹	96	15	1.4178
C ₂ H ₅ ²⁰	97	15	1.4178
<i>n</i> -C ₃ H ₇ ²¹	100	10	1.4219
allyl ²²	117	10	1.4349
<i>n</i> -C ₄ H ₉ ²³	113	12	1.4243
<i>i</i> -C ₄ H ₉ ²⁴	112–114	12	1.4223
C ₆ H ₅ CH ₂ ²⁵	169	12	1.4869
C ₆ H ₅ ²⁶	160	10	1.4918
1-C ₁₀ H ₈ ²⁷	59–60*	—	—
Cl ²⁸	118	16	1.4247
—COOC ₂ H ₅ ²⁹	130	10	1.4297

* M.p.

The substituted malonates (R = ethyl, allyl, *n*-propyl, *n*-butyl, *isobutyl*, benzyl) were prepared by alkylation of diethyl malonate in the usual way. The methyl, phenyl and 1-naphthyl derivatives were prepared *via* the corresponding ethoxalyl derivative; diethyl chloromalonate²⁸ was prepared by chlorinating diethyl malonate with sulphuryl chloride. Tricarboethoxymethane²⁹ was prepared from sodium malonate and ethyl chloroformate and diethyl oxomalonate³⁰, b.p. 103–108°C/15 mm Hg, $n_D^{20} = 1.4195$, from diethyl malonate and oxides of nitrogen.

Preparation of diethyl O-t-butyl tartronate. 5 g of sodium hydride was placed into a three-necked flask fitted with stirrer, reflux condenser and a dropping funnel and covered with 800 ml of benzene. 0.15 mole of *t*-butyl peracetate in benzene was added and heat was applied for a few minutes until the exothermic reaction started. After 90 min, when the reaction seemed to cease, the clear, yellow solution was heated for 8 h at 60°C. Peroxide test: neg. The solution was poured into water, the organic phase separated, the aqueous phase extracted twice with ether and the combined extracts washed neutral with water and finally dried over sodium sulphate. Distillation gave a fore-run of diethyl malonate and a fraction with b.p. 68–70°/0.2 mm Hg. Redistillation gave the pure compound b.p. 67–68°/0.2 mm Hg, $n_D^{20} = 1.4298$. Yield 9.4 g (27%). (Found: C 56.93; H 8.78. Calc. C 56.88; H 8.68).

Preparation of 5-t-butoxy barbituric acid. 2 g of diethyl *t*-butyl tartronate ($n_D^{20} = 1.4290$) and 0.73 g of urea in 25 ml of ethanol was refluxed gently for 3 h with sodium alcoholate in alcohol. The solution was then poured into 25 ml of water, extracted with benzene and the aqueous phase acidified. White, fine crystals began to precipitate out. After standing the mixture in a refrigerator for some time, the product was separated, washed with water and benzene and dried in air. M.p. 187–189°C. (Found: C 47.96; H 6.04. Calc. C 47.99; H 6.04).

Diethyl O-benzoyl tartronate. 3.6 g (0.15 mole) of sodium hydride was covered with 300 ml of benzene and treated with 24 g (0.15 mole) of diethyl malonate, to give a yellow

porridge-like mixture of the sodium derivative. 24.2 g (0.1 mole) of benzoyl peroxide in 200 ml of dry benzene was added during 60 min to the sodium diethyl malonate, cooled to 0–4°. After standing overnight, the mixture was poured into cold water and acidified with hydrochloric acid. The benzene layer was separated and the aqueous phase extracted several times with ether. The combined organic layers were extracted with sodium hydroxide solution to remove benzoic acid, washed neutral with water and dried over sodium sulphate. 12 g of benzoic acid were recovered from the acidified alkali extract. The solvents were distilled off and the residue was fractionated. A fore-run of diethyl malonate (6 g) was followed by the main fraction, b.p. 145°/0.5 mm Hg, $n_D^{20} = 1.4890$. Weight 15.5 g. Yield 55 %. The tartronate solidified when treated with light petroleum. Recrystallisation from pet. ether and ether gave crystalline plates, m.p. 57–58°C. (Found: C 60.36; H 5.80. Calc. for $C_{14}H_{18}O_6$: C 59.99; H 5.75).

In one experiment, diethyl dibenzoyloxy malonate was isolated in 7 % yield. B.p. 170–180°C/0.1 mm Hg. M.p. 118–121°C (from pet. ether + ether). Found: C 63.25; H 5.10. Calc. for $C_{20}H_{20}O_8$: C 62.99; H 5.04).

Diethyl dibenzoyloxy malonate was also obtained when 0.1 mole of diethyl O-benzoyl tartronate in 150 ml of benzene was treated with 2.4 g of sodium hydride followed by the addition of 18 g of benzoyl peroxide (in 200 ml of benzene) in the usual way. Only 5 g of benzoic acid was isolated. When the organic phase was worked-up in the usual manner, a thick, viscous oil was initially obtained which, after storing in the cold, afforded 2.2 g of white crystals identical in every respect to authentic diethyl dibenzoyloxy malonate.

Dimethyl O-benzoyl tartronate. 0.1 mole of sodium dimethyl malonate in 150–200 ml of benzene was treated at 0°C with 0.075 mole of benzoyl peroxide in benzene. B.p. (of the tartronate) 133°/0.2 mm Hg. M.p. 45–47°C (from pet. ether). Weight 17.2 g. Yield 68 % (Found: C 57.40; H 4.80. Calc. for $C_{12}H_{12}O_6$: C 57.14; H 4.80).

Diethyl O-benzoyl methyl tartronate. This was prepared from 0.15 mole of methyl sodium diethyl malonate in 200 ml of benzene, and 0.1 mole of benzoyl peroxide in 150–200 ml of benzene, as described above. No gas was evolved. The product distilled at 143–146°/0.6 mm Hg. $n_D^{20} = 1.4893$. Weight 26.6 g. Yield 90 %. (Found: C 64.70; H 6.48. Calc. for $C_{15}H_{18}O_6$: C 64.73; H 6.52).

Diethyl O-benzoyl ethyl tartronate. Prepared from 0.15 mole of ethyl sodium diethyl malonate and 0.1 mole of benzoyl peroxide. No gas was evolved. A thick colourless oil of b.p. 137°/0.15 mm Hg, $n_D^{20} = 1.4890$ was obtained. Weight 23.2 g. Yield 75 %. Found: C 62.23; H 6.50. Calc. for $C_{14}H_{20}O_6$: C 62.32; H 6.54).

Diethyl O-benzoyl n-propyl tartronate. Prepared from 0.15 mole of the appropriate sodium compound and 0.1 mole of benzoyl peroxide. No gas was evolved. A viscous oil of b.p. 136–138°/0.15 mm Hg $n_D^{20} = 1.4880$ was obtained. Weight 26.8 g. Yield 83 %. (Found: C 63.25; H 6.62. Calc. for $C_{17}H_{22}O_6$: C 63.34; H 6.88).

Diethyl O-benzoyl allyl tartronate. Prepared from 0.21 mole of diethyl allyl malonate and 0.175 mole of benzoyl peroxide. No gas was evolved. Quantitative yields of benzoic acid were isolated. A colourless thick oil of b.p. 145°/0.5 mm Hg, $n_D^{20} = 1.4959$, was obtained. Weight 31.4 g. Yield 56 %. (Found: C 63.65; H 6.28. Calc. for $C_{17}H_{21}O_6$: C 63.74; H 6.29).

Diethyl O-benzoyl n-butyl tartronate. Prepared from 0.15 mole of diethyl n-butyl malonate and 0.1 mole of benzoyl peroxide. (The sodium derivative was soluble in benzene.) A viscous oil of b.p. 140°/0.15 mm Hg, $n_D^{20} = 1.4870$, was obtained. Weight: 28.9 g. Yield 86 %. (Found: C 64.22; H 7.28. Calc. for $C_{18}H_{24}O_6$: C 64.27; H 7.19).

Diethyl O-benzoyl isobutyl tartronate. From 0.1 mole of diethyl isobutyl malonate (its sodium derivative is soluble in benzene) and 0.1 mole of benzoyl peroxide. No gas was evolved. The product [has] b.p. 128–130°/0.1 mm Hg, $n_D^{20} = 1.4873$. Weight 19 g. Yield 56 %. (Found: C 67.22; H 7.28. Calc. for $C_{18}H_{24}O_6$: C 67.27; H 7.19).

Diethyl O-benzoyl phenyl tartronate. Prepared from 0.15 mole of diethyl phenyl malonate and 0.1 mole of benzoyl peroxide. Quantitative yields of benzoic acid were isolated. No gas was evolved. B.p. 184°/0.12 mm Hg, m.p. 80–81°C (from pet. ether). Weight 29.3 g. Yield 82 %. (Found: C 67.57; H 5.59. Calc. for $C_{20}H_{20}O_6$: C 67.40; H 5.66).

Diethyl O-benzoyl 1-naphthyl tartronate. Prepared from 0.1 mole of the appropriate malonate and 0.075 mole of benzoyl peroxide. No gas was evolved. Quantitative yields of benzoic acid were isolated. Needles of m.p. 116–117.5° (from pet. ether) were obtained. Mixed m.p. 111–113°C*. Weight 29.6 g. Yield 97%. (Found: C 70.92; H 5.51; mol. wt. 398. Calc. for $C_{24}H_{22}O_6$: C 70.92; H 5.46; mol. wt. 406.4).

Diethyl O-benzoyl benzyl tartronate. Prepared from 0.25 mole of diethyl benzyl malonate and 0.2 mole of benzoyl peroxide. No gas was evolved and quantitative yields of benzoic acid were isolated. B.p. 172°/0.1 mm Hg, $n_D^{20} = 1.5255$. Weight 59.2 g. Yield 80%. (Found: C 68.17; H 5.93. Calc. for $C_{21}H_{22}O_6$: C 68.09; H 5.99).

Diethyl O-benzoyl chloro tartronate. 0.15 mole of diethyl chloromalonate was added slowly at room temp. to 0.15 mole of sodium hydride covered with 200 ml of dry benzene, and the mixture stirred for 5 h. Benzoyl peroxide (0.1 mole) in benzene was added in the usual way. No gas was evolved. Quantitative yields of benzoic acid were isolated. An almost colourless oil of b.p. 140°/0.3 mm Hg, $n_D^{20} = 1.4982$, was obtained. Weight 23.5 g. Yield 75% (Found: C 53.74; H 4.74. Calc for $C_{14}H_{15}O_6Cl$: C 53.43; H 4.80.)

Diethyl O-benzoyl carbethoxy tartronate. 0.2 mole of sodium hydride was covered with 400 ml of benzene to which 0.2 mole of tricarbethoxymethane was added dropwise. After 3 h, the hydride was consumed and 0.1 mole of benzoyl peroxide in 200 ml of benzene was added to the cooled sodium compound. No gas evolution was observed. Quantitative yields of benzoic acid were isolated. White plates (from ethanol) of m.p. 59–60°C were obtained. Weight 32.4 g. Yield 92%. (Found: C 57.95; H 5.75. Calc for $C_{17}H_{20}O_8$: C 57.95; H 5.72). Upon recrystallization, two fractions were obtained, one with m.p. 49–51° and the other with m.p. 59–61°C (from ether and pet. ether). Elementary analyses were identical. After 6 months' storage in closed vials both samples had m.p. 59–60°C.

Preparation of diethyl O-benzoyl tartronate from diethyl O-benzoyl chlorotartronate. a). 24.3 g of diethyl O-benzoyl chloro tartronate was dissolved in 200 ml of dry ether and cooled to 0°C. Ethylmagnesium bromide (from 3 g of magnesium and 8.4 g of ethyl bromide) in 125 ml of ether was added dropwise during one hour. The mixture was stirred overnight then poured into water and extracted with ether. The ether phase was extracted with alkali and dried over sodium sulphate. After the solvent had been distilled off a solid residue was obtained. M.p. 57–59° (from ether and pet. ether). Mixed m.p. with an authentic sample showed no depression. Weight 20.3 g. Yield 95%.

b). Phenylmagnesium bromide (from 15.7 g of bromobenzene and 3 g of magnesium) in 100 ml of dry ether was added dropwise to an ice-cold solution of 32 g of diethyl O-benzoyl chlorotartronate in 200 ml of ether. A yellow precipitate was immediately formed and the mixture stirred for 15 h. Water + hydrochloric acid was added to decompose the magnesium complex. After extracting with ether the combined ether layers were washed with water till neutral and dried over sodium sulphate. The ether was distilled off and a low-boiling fraction of b.p. 130–136°C was obtained. Redistillation gave a product, $n_D^{20} = 1.5254$, which was in all respects identical with chlorobenzene, b.p. 132°C, $n_D^{20} = 1.5247$. When the residue in the distillation flask was cooled a solid precipitated. Recrystallization from ether and pet. ether gave white plates with m.p. 59–60°C. Mixed melting point with authentic diethyl O-benzoyl tartronate gave no depression.

Diethyl benzoyl O-benzoyl tartronate. 2.4 g of sodium hydride was covered with 75 ml of tetrahydrofuran and 23 g of diethyl O-benzoyl tartronate in 150 ml of tetrahydrofuran was added dropwise. A violent evolution of hydrogen was observed and after one hour all hydride was consumed and a clear solution had been formed. 17 g of benzoyl chloride was added all at once (room-temp.) and after stirring for 1–2 min the mixture was neutral and was poured out onto water. The organic layer was separated, the water phase shaken with ether three times and the combined extracts washed once with water and dried over sodium sulphate. After concentration distillation gave a small fraction of benzoyl chloride but attempted distillation of the rest caused decomposition. By adding ligroin a white powder precipitated (16.5 g) and repeated recrystallization from pet. ether + ether

* We wish to express our cordial thanks to Prof Arthur C. Cope of Massachusetts Institute of Technology for providing us with a sample of this compound.

gave white needles, m.p. 80–82°C. Yield 52 %. (Found: C 65.64; H 5.28. Calc for $C_{11}H_{20}O_7$: C 65.61; H 5.24).

Preparation of tartaric acid. Sodium alcoholate, prepared from 2.3 g (0.10 mole) of sodium in 100 ml of absolute ethanol, was added to 12 g of diethyl O-benzoyl tartronate in 50 ml of ethanol. The mixture was stirred for 34 h at room temperature. It was then poured into water, and extracted with ether 3–4 times. The combined extracts were washed neutral with water, dried over sodium sulphate and distilled. Ethyl benzoate, b.p. 86°C/10 mm Hg, $n_D^{20} = 1.5047$, was obtained. Yield 3.9 g (60 %). The aqueous phase was acidified and extracted with ether during 48 h. Concentration of the dried ether phase gave 4.1 g of a solid, which after recrystallization from pet. ether (b.p. 60–71°C) and ether gave white crystals, m.p. 176–178°C. (Lit. 178°C).

n-Propyl tartaric acid. 26.2 g (0.08 mole) of diethyl n-propyl O-benzoyl tartronate was added to a sodium alcoholate solution (from 3.7 g of sodium in 50 ml of ethanol) at room temperature and stirred for 18 h. The mixture was worked up as above, giving 9.2 g (76 %) of ethyl benzoate and 6.9 g (54 %) of n-propyltartaric acid, m.p. 124–124.5° (from ether and pet. ether) (Lit. 122°).

isoButyl tartaric acid. Sodium alcoholate (from 3.2 g of sodium in 75 ml of ethanol) was added dropwise to 23 g (0.07 mole) of diethyl isobutyl O-benzoyl tartronate at room temperature and stirred for 18 h. The usual work up yielded 7.5 g (55 %) of ethyl benzoate and 11.6 g (94 %) of isobutyl tartaric acid, m.p. 126–126.5°C (from pet. ether and ether) (Lit. 107°C). (Found: C 47.55, H 6.92. Calc for $C_7H_{12}O_6$: C 47.72, H 6.87.)

Benzyl tartaric acid. Sodium alcoholate, from 2.6 g (0.12 mole) of sodium in 50 ml of absolute alcohol, was added to 15.7 g (0.06 mole) of diethyl benzoyl tartronate at room temperature. The mixture was stirred for 18 h and worked up as above, yielding 5 g (56 %) of ethylbenzoate and 7.6 g (60 %) benzyltartaric acid, m.p. 156–160°C (from ether and pet. ether).

Ethanolysis and hydrolysis of diethyl phenyl O-benzoyl tartronate. Sodium alcoholate, prepared from 2.3 g (0.1 mole) of sodium in 100 ml of ethyl alcohol, was added dropwise to a solution of 18.4 (0.05 mole) of diethyl phenyl O-benzoyl tartronate in 100 ml of ethyl alcohol; after stirring overnight, the mixture was poured into water, extracted with ether 3 times, washed neutral, dried and distilled: 6 g (80 %) of ethyl benzoate was obtained. The aqueous phase was acidified and extracted continuously during 26 h with ether. 6.3 g (83 %) of mandelic acid was isolated from the ether phase. Recrystallization from formic acid gave pure crystals, m.p. 118–121°; on admixture with authentic mandelic acid, no depression of the melting point was observed.

Ethanolys of diethyl n-butyl O-benzoyl tartronate. Sodium alcoholate, prepared from 3.2 g (0.14 mole) of sodium and 75 ml of water-free ethanol, was added dropwise to 23 g (0.07 mole) of diethyl n-butyl O-benzoyl tartronate and stirred for 24 h at room temperature. The mixture was poured into water and extracted 2 times with ether. 8.7 g (83 %) of ethyl benzoate was isolated from the ether phase. The water phase was neutralized to pH 7 and extracted with ether 10–15 times at low temperature. The combined ether extracts were dried over sodium sulphate, concentrated and distilled; giving 4.5 g (29 %) of diethyl n-butyl tartronate, b.p. 120–123°/10 mm Hg, $n_D^{20} = 1.4292$, identical to a sample prepared as follows:

To 31.3 g (0.18 mole) of diethyl oxomalonate in 100 ml of toluene, cooled to –70°C was added n-butylmagnesium bromide (from 4.3 g of magnesium and 24.6 g of n-butyl bromide) in 150 ml of ether during 90 min. When the temperature of the reaction mixture had risen to about 0°C, the mixture was poured into water and dilute hydrochloric acid. The water phase was extracted 10–15 times with cold ether, the combined organic layers dried over sodium sulphate and finally distilled; giving 22.5 g (54 %) of diethyl n-butyl tartronate, b.p. 117–120°/12 mm Hg, $n_D^{20} = 1.4288$. (Found: C 56.94, H 8.72. Calc. for $C_{11}H_{20}O_4$: C 56.88, H 8.68.)

Ethanolysis of diethyl benzyl O-benzoyl tartronate. 0.1 mole of sodium ethoxide was prepared in the usual way from 2.3 g of sodium in 125 ml of absolute ethanol. The alcoholate was added dropwise with stirring to a cooled (0–5°C) solution of 18.6 g (0.05 mole) of diethyl benzyl O-benzoyl tartronate in 100 ml of ethanol. Stirring was continued for 22 h. The mixture was poured into water and extracted repeatedly with ether. Ethyl benzoate, b.p. 81/10 mm Hg, $n_D^{20} = 1.5068$, was isolated from the ether phase. Yield

6.1 g (81 %). The water phase was neutralized to pH 7 and extracted 10 times with cold ether. The ether was dried, concentrated and distilled, giving 7.4 g (58 %) of diethyl benzyl tartronate, b.p. 102–104°/0.1 mm Hg, $n_D^{20} = 1.4952$. (Found: C 63.37; H 6.98.) Calc for $C_{14}H_{18}O_5$: C 63.14, H 6.81).

Preparation of diethyl benzyl tartronate according to Cope. Benzylmagnesium chloride was prepared from 3 g (0.13 mole) of magnesium and 13 g (0.12 mole) of benzyl chloride in 150 ml of ether. 18.4 g (0.11 mole) of diethyl oxomalonate, in 175 ml of ether was cooled to -70°C and the Grignard reagent added dropwise during 25 min. Stirring was continued for another 45 min, whereupon the mixture was poured into ice-water and hydrochloric acid. After extraction of the water phase with ether six times, the combined extracts were dried, concentrated and distilled giving 10.3 g (35 %) of product, b.p. 101–103°/0.1 mm Hg, $n_D^{20} = 1.4955$.

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