Derivatives of 2-N-Methylaminophenol

2-Acetylmethylaminophenyl Acetate.—A mixture of 10 g. of *o*-methylaminophenol sulfate, 10 g. of fused sodium acetate and 10 cc. of acetic anhydride was heated until liquid, cooled, 50 cc. of water added, and the liquid extracted with ether. The ether was distilled from the dried extract, and the residue that distilled at 195-200° and 30 mm. solidified slowly in the refrigerator. Data for this and other derivatives obtained by standard methods are given in Table V.

2-Methyl-4-bromobenzoxazolone.—When a solution of 2 g. of 2-methylamino-4-bromophenol in 36 cc. of 10% solution of sodium hydroxide was shaken with 2.6 g. of phenyl chlorocarbonate, it gave a pasty solid that was removed by extraction with ether. The extract was shaken with alkali solution, then with water, and the ether evaporated at room temperature. Crystallization of the residue from alcohol gave nearly colorless needles, m. p. 137.5°. The structure of this was proved by preparing it in a different way. A solution of 4.2 g. of 4-bromobenzoxazolone, 1.2 g. of potassium hydroxide and 6.2 g. of methyl iodide in 50 cc. of methyl alcohol was refluxed for three hours and the volatile material distilled off. The residue was extracted with 50 cc. of water, then triturated with potassium hydroxide solution, and the mixture filtered. Crystallization of the solid from alcohol gave colorless needles; m. p. 137.5; yield, 75%. A mixture of these products melted without depression.

Anal. Calcd. for $C_8H_6O_2NBr$: Br, 35.07. Found: Br, 35.18.

2-Methyl-4,6-dibromobenzoxazolone.—This was prepared as indicated above under the monobromo compound. Crystallization from alcohol gave colorless crystalline irregular masses, m. p. 124–125°. The same product was obtained by refluxing for three hours a mixture of 4 g. of the 4,6-dibromobenzoxazolone, previously described, and 5 g. of methyl iodide with 1.2 g. of potassium hydroxide in 50 cc. of methyl alcohol.

Anal. Calcd. for $C_8H_5O_2NBr_2$: Br, 52.10. Found: Br, 51.98.

Summary

1. Several new aromatic chlorocarbonates have been prepared by the action of phosgene on the required phenols. Under the conditions 2,4-dinitrophenol gave di-(2,4-dinitrophenyl) carbonate, while picric acid gave picryl chloride.

2. When the N-carboaryloxy derivatives of *o*-aminophenol and its substitution products are dissolved in alkali they are converted into the corresponding benzoxazolones and a phenol is liberated. The same change occurs when the derivatives of *o*-methylaminophenol are used. The structures of these products were confirmed by synthesis from the required aminophenol and phosgene.

3. 2-Acetylmethylaminophenol was converted into a mono and a dibromo derivative, and their structures were proved. Each of these gave mixed isomeric acetyl-benzoyl derivatives that showed no tendency to rearrange.

4. Under the conditions of these experiments *o*-aminophenol could not be converted into a diacyl derivative containing the radical $\mathrm{Ph{-}O{-}\underset{|}{C}{=}O}$.

5. Further work is in progress.

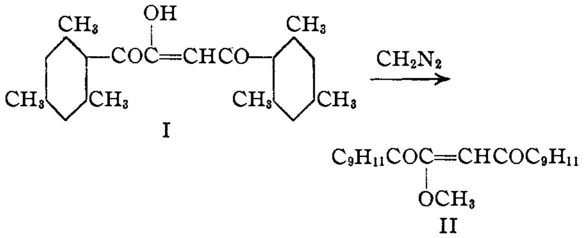
IOWA CITY, IOWA RECEIVED APRIL 16, 1934

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, NO. 133]

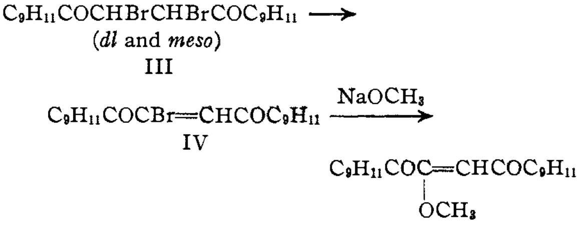
The Alkyl Ethers of 1,2-Di-(trimethylbenzoyl)-ethenol

BY ROBERT E. LUTZ

Two stereomeric methyl ethers of di-(trimethylbenzoyl)-ethenol I are known,[1] one (yellow) II obtained by methylation of the enol with diazomethane, and the other (colorless) prepared by the action of sodium methylate on di-(trimethylbenzoyl)-dibromoethane III.



$$\mathrm{I} \xrightarrow{\mathrm{CH_2N_2}} \mathrm{C_9H_{11}CO\underset{OCH_3}{\underset{|}{C}}{=}CHCOC_9H_{11}} \quad \mathrm{II}$$



$$\underset{\mathrm{III}}{\underset{(dl\ \text{and}\ meso)}{\mathrm{C_9H_{11}COCHBrCHBrCOC_9H_{11}}}} \longrightarrow \underset{\mathrm{IV}}{\mathrm{C_9H_{11}COCBr{=}CHCOC_9H_{11}}} \xrightarrow{\mathrm{NaOCH_3}} \mathrm{C_9H_{11}CO\underset{OCH_3}{\underset{|}{C}}{=}CHCOC_9H_{11}}$$

The latter reaction has been found to give mixtures of both stereomeric ethers (methyl[1a] and ethyl) with the ratio of yields depending on conditions. The colorless isomers are the chief

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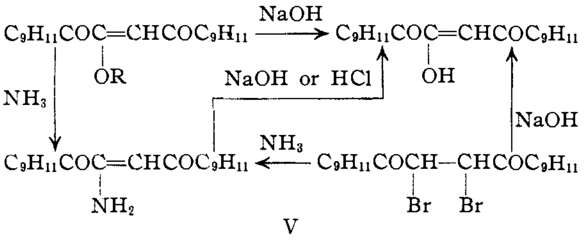
(1) (a) Lutz, THIS JOURNAL, **48**, 2905 (1926); (b) Conant and Lutz, *ibid.*, **47**, 881 (1925).

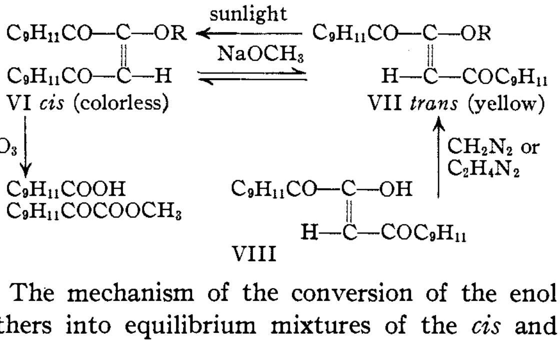
products when the reactions are carried out at room temperature or below with the concentration of alcoholate minimized; but with an excess of alcoholate and at somewhat higher temperatures the yields of the two types are more nearly equal, due to partial rearrangement of the colorless isomers under the influence of sodium alcoholate.

The four alkyl ethers are hydrolyzed by long heating with alcoholic sodium hydroxide, giving the sodium enolate which may either be isolated as such or converted into the free enol I upon acidification. This enol is obtained also by the action of alcoholic sodium hydroxide or sodium acetate[1a] on the di-(trimethylbenzoyl)-dibromoethanes III and by the alkaline or acid hydrolysis of di-(trimethylbenzoyl)-aminoethylene V.[2]



The correspondence in structure of the enol and the methyl and ethyl ethers is established by the following relationships: alkylation of the enol with diazomethane[1a] and diazoethane gives exclusively in good yields the yellow alkyl ethers, which in turn are transformed by the action of sunlight into the colorless isomers. The two types of ethers are therefore stereoisomeric. The direction of enolization and the position of the alkoxyl groups are established by ozonization of the colorless di-(trimethylbenzoyl)-methoxyethylene VI to trimethylbenzoic acid and (trimethylphenyl)-glyoxylic acid methyl ester.[3]

The yellow enol ethers have been assigned the *trans* configuration, and the colorless isomers the *cis*, on the basis of the analogy in color relationship with other similar stereomeric pairs of unsaturated 1,4-dicarbonyl compounds of known configurations, and the characteristic manner and direction of rearrangement of one form into the other. The yellow ethers on exposure to sunlight in ethanol solution are quickly transformed into the colorless isomers (absorption of light energy), and sodium alcoholates acting as catalysts convert either stereomer into an equilibrium mixture of the two with the yellow isomer present in the greater proportion. With acceptance of these configurations, it follows that the enol (which is yellow) is *trans* since it is converted by means of diazoalkanes exclusively into the yellow (*trans*) ethers. The enol is moderately soluble in the alkane solvents; the sodium salt is insoluble in water but is sufficiently soluble in ethanol to permit recrystallizaton. These physical properties are strongly indicative of chelation, which would be expected in a *trans* enol of the structure VIII but not in the hypothetical *cis* isomer.[4]



The mechanism of the conversion of the enol ethers into equilibrium mixtures of the *cis* and *trans* isomers very probably involves the addition and elimination of sodium alcoholate. Evidence for this was found in the transformation of the methyl ethers with sodium ethylate into equilibrium mixtures of the ethyl ethers, wherein replacement of methyl by ethyl is involved as well as inversion of the configuration.

The mechanism of the formation of the enol ethers from di-(trimethylbenzoyl)-dibromoethane III through di-(trimethylbenzoyl)-bromoethylene IV may involve addition to the hypothetical intermediate acetylenic diketone, $C_9H_{11}COC{\equiv}C{-}COC_9H_{11}$,[5] or the addition of alcoholate to IV, followed by loss of sodium bromide; in any case, whatever the mechanism, it is significant that the reaction proceeds in a definite consistent stereochemical sense under controlled conditions to give a *cis* product.

Further studies are in progress in this field.

Experimental Part

The Action of Sodium Methylate on 1,2-Di-(2,4,6-trimethylbenzoyl)-dibromoethane III.—(A) *Meso*-di-(trimethylbenzoyl)-dibromoethane (20 g.) was treated with a solution of 2.9 g. of sodium in 75 cc. of methanol, the

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(2) The structure of the analogous dibenzoylaminoethylene has been determined by ozonization (unpublished results). Further studies on this class of compounds will be reported in later papers.

(3) Ozonization of dibenzoylethylene types under these conditions has been found to give largely benzoic acid instead of the expected phenylglyoxal (unpublished results).

(4) Chelation involving the α-carbonyl is unlikely [*cf.* Kohler and Barnes, THIS JOURNAL, **56**, 211 (1934)].

(5) Attempts to isolate this acetylenic diketone have not been successful as in the dibenzoyl series (Ref. 1).

mixture being heated immediately to boiling. Dilution with water gave an oil which crystallized from ethanol (12 g., yellowish, m. p. 75–85°). Numerous fractional crystallizations from ligroin gave 2.5 g. of nearly pure yellow (*trans*) isomer (of m. p. 105.5°), 4.5 g. of colorless (*cis*) (of m. p. 114–116°), and 3.5 g. of a mixture. The estimated yields of the two were 30% yellow and 55% colorless. The solubilities of the stereomers are very similar and the separation is laborious.

(B) A solution of 1.0 g. of sodium in 50 cc. of methanol was added dropwise with mechanical stirring to a suspension of 10 g. of *meso*-di-(trimethylbenzoyl)-dibromoethane in 100 cc. of methanol, the temperature being kept at 4–5°. The product (8.0 g.) consisted largely of the colorless isomer, containing approximately 1.0 g. of the yellow form.

Yellow (*trans*)1,2-Di-(2,4,6-trimethylbenzoyl)-methoxyethylene VII.—Upon refluxing for seven hours with an excess of sodium acetate in ethanol, a sample of the methyl ether was converted almost completely into the yellow ethyl ether (identified by mixed melting points with a sample prepared from the enol with diazoethane). Methanolic sodium hydroxide (refluxing for five minutes) lowered the melting point of a sample somewhat, the bulk of the material being recovered unchanged.

Colorless (*cis*)-1,2-Di-(2,4,6-trimethylbenzoyl)-methoxyethylene VI, is best prepared by exposing an alcohol solution of the crude products of the above preparations to strong sunlight for one day. A 0.2-g. sample of the yellow (*trans*) isomer in 10 cc. of ethanol was quickly bleached in the sunlight; after seven hours of exposure, 0.18 g. of the *cis* isomer was isolated and identified by a mixed melting point. The colorless isomer was recovered unchanged (a) after seven hours of refluxing with alcoholic sodium acetate and (b) after exposure to sunlight in chloroform with iodine.

Ozonization of 4.0 g. in chloroform for three hours at 0° gave an acidic fraction (extracted with sodium bicarbonate) of 1.8 g. (93%) of trimethylbenzoic acid (m. p. 152°). The alkali-insoluble oil was distilled and gave 1.9 g. (92%) of oil (non-acid), b. p. 275–280° (corr.), which was identified as the methyl ester of (trimethylphenyl)-glyoxylic acid by hydrolysis with alcoholic sodium hydroxide to the free acid (m. p. 115–116°).

The Action of Sodium Ethylate on 1,2-Di-(2,4,6-trimethylbenzoyl)-dibromoethane.—(A) A solution of 1.1 g. of sodium in 100 cc. of absolute ethanol was added quickly to 10 g. of the *meso* dibromoethane. The temperature rose to 42° and the mixture was then heated at 50° for fifteen minutes. On cooling and diluting with water, an oil was obtained which crystallized from alcohol. The product was separated by fractional crystallization from alcohol into 3.15 g. of nearly pure yellow (*trans*) di-(trimethylbenzoyl)-ethoxyethylene (the less soluble isomer), 3.2 g. of the colorless (*cis*) isomer, and 0.65 g. of a mixture. The yields approximated 50% of each isomer.

(B) A solution of 1.0 g. of sodium in 50 cc. of absolute ethanol was added dropwise to a mechanically stirred suspension of 10 g. of the dibromoethane at 4–5° over a period of half an hour, and the mixture allowed then to come to room temperature and filtered free from a little unchanged dibromoethane. The products (isolated as above) were 3.2 g. of pure colorless (*cis*) isomer, 0.15 g. of pure yellow (*trans*) isomer and 3.05 g. of crude colorless isomer which still contained a little of the yellow form.

Colorless (*cis*)-1,2-Di-(2,4,6-trimethylbenzoyl)-ethoxyethylene VI.—This isomer is best prepared by exposing the crude product of reaction B (above) in alcohol to the action of sunlight for one day. A solution of 0.2 g. of the yellow isomer in 10 cc. of ethanol was bleached in the sunlight in seven hours and 0.17 g. of the colorless (*cis*) isomer was isolated and identified by a mixed melting point. It is considerably more soluble than the yellow form, and crystallizes as hexagonal scales or prisms from ethanol, m. p. 106–107° (corr.).

Anal. Calcd. for $C_{24}H_{28}O_3$: C, 79.09; H, 7.74. Found: C, 79.06; H, 7.88.

Hydrolysis of 0.2 g. with 0.03 g. of sodium hydroxide in 5 cc. of ethanol (refluxing five hours) gave 0.18 g. of the enol (identified by a mixed melting point). It is stable in chloroform (with iodine) toward sunlight.

Yellow (*trans*)-1,2-Di-(2,4,6-trimethylbenzoyl)-ethoxyethylene VII.—The yellow isomer is best prepared as above (A), or by ethylation of the enol with diazoethane in ether solution in the usual way. . It crystallized as pale yellow hexagonal prisms or long thin hexagonal scales from ethanol in which it is considerably less soluble than the colorless isomer; m. p. 129° (corr.).

Anal. Calcd. for $C_{24}H_{28}O_3$: C, 79.09; H, 7.74. Found: C, 79.12; H, 7.81.

Upon refluxing 0.2 g. with 5 cc. of ethanol and 0.03 g. of sodium hydroxide for five hours, 0.17 g. of the enol was isolated and identified by a mixed melting point.

Formation of an Equilibrium Mixture of Ethyl Ethers by the Action of Sodium Ethylate.—In a typical experiment, a solution of 1.0 g. of colorless (*cis*) ethyl ether in 10 cc. of absolute ethanol containing 0.07 g. of dissolved sodium, was refluxed for one minute, diluted with water and the product fractionally crystallized from ethanol. This gave 0.43 g. of pure yellow (*trans*) ethyl ether, and 0.36 g. of crude mixture from which a small sample of pure colorless (*cis*) isomer was isolated after several crystallizations.

Similar results were obtained starting with the yellow (*trans*) ethyl ether and the *cis* and *trans* methyl ethers. The action of sodium methylate on the ethyl ethers under these conditions appears to give new products which are now being investigated, but converts the *cis* and *trans* methyl ethers into similar equilibrium mixtures of the two stereomers.

1,2-Di-(2,4,6-trimethylbenzoyl)-aminoethylene V.—A suspension of di-(trimethylbenzoyl)-dibromoethane in methanol saturated with dry ammonia was refluxed for five minutes and the resulting yellow solution was diluted with water and extracted with ether, giving a yellow oil which crystallized from ligroin or alcohol; yellow, m. p. 133° (corr.).

It is prepared also by the action of alcoholic ammonia on the colorless di-(trimethylbenzoyl)-methoxyethylene under similar conditions, probably involving 1,4-addition of ammonia followed by elimination of methanol.

Anal. Calcd. for $C_{22}H_{25}O_2N$: C, 78.80; H, 7.52. Found: C, 78.52; H, 7.50.

Reduction with zinc and acetic acid gave di-(trimethylbenzoyl)-ethane (identified by mixed melting point).

The aminoethylene is stable toward the action of boiling alcoholic sodium acetate and alcoholic hydrogen chloride. It was not easily hydrolyzed with alcoholic alkali; however, 0.85 g., when refluxed with 15 cc. of ethanol and 0.1 g. of sodium hydroxide for five hours, gave 0.8 g. of di-(trimethylbenzoyl)-ethanol. Hydrolysis of 0.5 g. by refluxing with 10 cc. of alcohol, 10 cc. of concd. hydrochloric acid and 10 cc. of water for two and a half hours gave 0.48 g. of the enol (identified by mixed m. p.).

1,2-Di-(2,4,6-trimethylbenzoyl)-ethenol I, is best prepared by the action of boiling 80% methanol containing an excess of sodium hydroxide on di-(trimethylbenzoyl)-dibromoethane; m. p. 112–113° (corr.) (*cf.* Ref. 1a). It is not affected by exposure to sunlight (in ethanol), or when refluxed with alcoholic ammonia. The keto form is readily enolized by the latter reagent, or by refluxing with alcoholic hydrogen chloride. Titration by the K. Meyer method showed the enol to be completely enolized and the keto form not at all.[6] Both keto and enol forms are sublimed easily *in vacuo* at air-bath temperatures of 140–150°.

The sodium salt[6] of I was prepared by heating 2.0 g. of di-(trimethylbenzoyl)-dibromoethane with 25 cc. of 80% methanol until dissolved. On cooling 1.28 g. of the sodium salt crystallized (m. p. 308–310°); recrystallized from alcohol in which it is difficultly soluble; very difficultly soluble in water.

Anal. Calcd. for $C_{22}H_{23}O_3Na$: C, 73.7; H, 6.45. Found: C, 73.6; H, 6.43.

The enol was liberated from the salt upon treating the solid material directly with dilute acid.

Summary

Di-(trimethylbenzoyl)-ethenol and the *cis* and *trans* methyl and ethyl ethers have been studied, and evidence given for their structures and configurations.

UNIVERSITY, VIRGINIA

RECEIVED APRIL 16, 1934

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[6] These experiments were carried out by Dr. C. I. Parrish.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

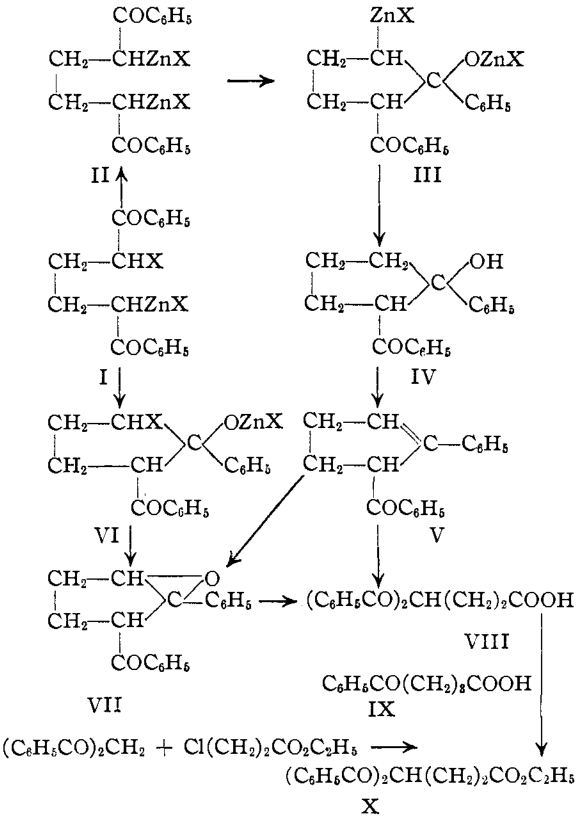
The Action of Zinc on 1,4-Dibromo-1,4-dibenzoylbutane. An Intramolecular Reformatsky Reaction

BY REYNOLD C. FUSON AND MARK W. FARLOW

In a study of the action of zinc on 1,4-dibromo-1,4-dibenzoylbutane it has become apparent that the reaction proceeds in a most unusual and unexpected manner, for no compound containing the cyclobutane ring is produced. Instead, *cyclopentane derivatives* are formed. From a consideration of the structure of the products it appears probable that the reaction involves the intermediate formation of an organo zinc compound which undergoes an intramolecular Reformatsky condensation. These transformations are summarized in the following chart.

The evidence for these reactions derives from the character of the compounds obtained. Three primary reaction products have been isolated and identified.[1] One of these, 1,4-dibenzoylbutane, is apparently a hydrolysis product of an intermediate of the type illustrated by II in which both bromine atoms have been replaced by the metal.

1-Phenyl-5-benzoyl-1-cyclopentene (V).—A second product was an unsaturated compound melting at 99–100°. From the melting point it appeared that the compound might be 1-phenyl-5-benzoyl-1-cyclopentene which has been reported



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[1] A fourth compound proved to be a rearrangement product of one of the others and has not been included in the present report.