Transformation: The Higher Series ⇄ the Lower.—Saponification by alcoholic potassium or sodium hydroxide of the esters of either series leads to the corresponding acid, mixed, however, with a certain amount of the isomer. The action appears to explain why in some previous investigations an acid melting at 239–240° was obtained.

Summary

The points of analogy between the corresponding δ-ketonic and δ-carboxylic acids are considered.

α,β-Diphenyl-γ-trimethylacetylbutyric acid has been synthesized and possible isomeric forms are discussed.

The work of previous investigators on α,β-diphenyl-γ-benzoylbutyric acid is reviewed. Discrepancies in the literature are found to have resulted mainly from the hydrolysis of pure esters by sodium or potassium hydroxide, thus forming isomeric mixtures. Through the preparation of new compounds, both series of the isomeric benzoyl derivatives are now fairly complete. Resolution of both isomeric acids into optical isomers may be anticipated.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NORTH DAKOTA]

ACTION OF METALLIC SODIUM ON DIPHENYL- AND DITOLYLTRICHLORO-ETHANES[1]

BY ELWIN E. HARRIS

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In a former report[2] the author stated that when diphenetyltrichloroethane was treated wuth sodium in benzene a good yield of *p,p'*-diethoxystilbene was obtained. He was unable at the time to account for the mechanism of the reaction although similar products had been reported from the reaction of the same compound with zinc.[3] This investigation was undertaken to determine the course of the reaction and the nature of the products formed.

It was found that the presence of moisture is essential to the reaction in benzene, as in its absence no *p,p'*-diethoxystilbene could be isolated and most of the starting product was recovered unchanged. The reaction apparently takes the course

$$(C_2H_5OC_6H_4)_2CHCCl_3 + 4Na + H_2O \longrightarrow C_2H_5OC_6H_4CH{=}CHC_6H_4OC_2H_5 + 3NaCl + NaOH$$

Fritsch[4] found that heating the compound with sodium alcoholate in a

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[1] The author was assisted in this work by Irma Magnusson, graduate assistant in chemistry at the University of North Dakota.

[2] Harris and Frankforter, THIS JOURNAL, **48**, 3144 (1926).

[3] Goldschmidt, *Ber.*, **6**, 990 (1874); Elbs and Foster, *J. prakt. Chem.*, **39**, 298 (1882).

[4] Fritsch and Feldmann, *Ann.*, **306**, 72 (1899).

sealed tube for six hours gave a good yield of the stilbene. To keep the sodium melted and to raise the temperature, toluene was substituted for the benzene. Precautions were taken to prevent moisture from entering the apparatus and all the chemicals were carefully dried. A very violent reaction took place which in a few cases was uncontrollable and a fire resulted. The mixture became deep greenish-brown in color. The reaction was so complex and so many products were formed that further work was postponed on diphenetyltrichloro-ethane and ditolyltrichloro-ethane was substituted in the study. The same kind of reaction resulted except that it was much less violent. About 50% of the starting product could be accounted for as *p,p*-dimethylstilbene and about 45% as *p,p*-dimethyltolane. The equation is

$$2(CH_3C_6H_4)_2CHCCl_3 + 3Na \longrightarrow CH_3C_6H_4CH{=}CHC_6H_4CH_3 + CH_3C_6H_4C{\equiv}CC_6H_4CH_3 + 3NaCl$$

It is obvious that rearrangement and intramolecular oxidation have taken place. Other studies on this interesting reaction are now in progress.

Experimental Part

Apparatus and Materials.—The apparatus used was a round-bottomed flask fitted with a dropping funnel, a mercury-sealed stirrer and a reflux condenser. To give plenty of room for possible frothing, the flask had a capacity ten times the volume of the contents. The dropping funnel and the condenser were fitted with drying tubes.

The toluene was treated first with a small amount of sulfuric acid, washed with water and 10% sodium hydroxide, then dried over calcium chloride and finally allowed to stand over sodium powder for a week or more. It was then distilled from fresh sodium with a distilling tube. Only that portion boiling from 110 to 112° was used, and this was caught in the flask to be used for the experiment. The sodium was the commercial purified form. The crust was removed under toluene and the sodium transferred quickly to the reaction flask. The diphenyl- and the ditolyltrichloro-ethanes were prepared according to the method formerly described by the author.[2] These were recrystallized from toluene just before the experiment.

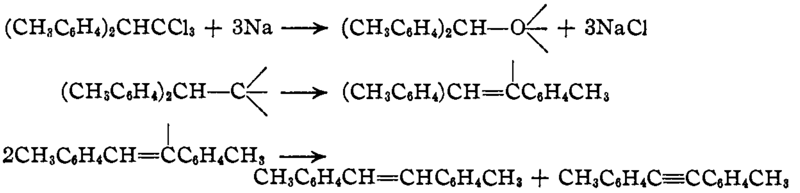
Observations

The Action of Sodium on β,β,-Ditolyl-α,α,α-trichloro-ethane in Boiling Toluene.—Thirty-one grams of ditolyltrichloro-ethane was dissolved in 150 cc. of the purified toluene and placed in the dropping funnel, which was kept warm with a hot cloth, and allowed to drop onto 14 g. of melted sodium in boiling toluene. It was stirred with an electric stirrer to keep the sodium whipped to a very fine powder. A violent reaction began almost immediately and lasted for about twenty minutes. The mixture turned green. It was then heated for an hour with continuous stirring. The sodium was allowed to settle and the toluene solution was decanted off. The sodium was extracted several times with more hot toluene and finally treated with alcohol. No organic product was found in the alcoholic solution from the sodium. The toluene solution was concentrated and cooled. *p,p'*-Dimethylstilbene crystallized out in large plates. These were filtered off and recrystallized from benzene, melting point 177°; dibromide, melting point 214°. The filtrate was again concentrated and another crop of the substituted stilbene separated. The combined portions represented over 45% yield from the starting product. Alcohol was then added to the filtrate from the stilbene and there separated *p,p'*-dimethyltolane and a yellow compound which did not melt sharply; m. p. 85 to 90°. It was very soluble in benzene, and more soluble in alcohol than the stilbene or the tolane. Each crystallization of this yellow compound gave a small amount of *p,p'*-dimethyltolane melting at 135°; dibromide, 204°. The addition of a small amount of hydrochloric acid to the alcohol from which it was crystallized caused all of the yellow compound to change to the tolane. One sample of the yellow compound stood in a tube for four years and was found to have changed over to the tolane, melting at 135°. These combined portions of the tolane brought the yield to about 45%, accounting for 90 to 95% of the starting material.

The Action of Sodium on β,β-Diphenyl-α,α,α-trichloro-ethane.—The reaction described above was performed with diphenyltrichloro-ethane. In all respects it seemed to be much the same as that above, but it has been very difficult to isolate the products formed. Some of each of the following were found, and converted into their dibromide for identification: normal stilbene melting at 124° (dibromide, 236°); isostilbene, an oil (dibromide, 109°) and tolane, melting point 60° (tolane dibromide, 208°). Although it was impossible to obtain very large portions of the above compounds from the reaction, no other products were found; therefore one would be led to believe that the mechanism of the reaction was the same as in the first case.

Attempts to Isolate Intermediate Sodium Compounds.—The above reactions were also run in an atmosphere of nitrogen to eliminate the effect of air on the reaction, which may decompose any sodium organic complex. Carbon dioxide was then passed into the mixture but there was no indication of a reaction to form the acid derivative of tolane or stilbene.

Mechanism of the Reaction.—The formation of an intermediate sodium compound would be a simpler method of accounting for the reaction, but since none could be found, it should not be used in interpreting the reaction. The mechanism given below is similar to one given by Wooster.[5]



$$(CH_3C_6H_4)_2CHCCl_3 + 3Na \longrightarrow (CH_3C_6H_4)_2CH{-}C\begin{smallmatrix}/\\-\\\backslash\end{smallmatrix} + 3NaCl \qquad (1)$$

$$(CH_3C_6H_4)_2CH{-}C\begin{smallmatrix}/\\-\\\backslash\end{smallmatrix} \longrightarrow (CH_3C_6H_4)CH{=}\overset{|}{C}C_6H_4CH_3 \qquad (2)$$

$$2CH_3C_6H_4CH{=}\overset{|}{C}C_6H_4CH_3 \longrightarrow CH_3C_6H_4CH{=}CHC_6H_4CH_3 + CH_3C_6H_4C{\equiv}CC_6H_4CH_3 \qquad (3)$$

The second equation should easily torm a dimolecular compound. If such a dimolecular compound was formed, it must have split immediately, with rearrangement to form stilbene and tolanes. This wandering of groups is similar to that shown by Lachman,[6] also by Stieglitz[7] and Tiffeneau.[8] This reaction is not preceded by the elimination of hydrogen chloride, as was suggested in the reaction by Wooster,[5] for this would give rise to compounds in which the ethane hydrogen is absent. A study of a reaction in which the hydrogen chloride is first removed is to be the subject of another report.

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[5] Wooster, THIS JOURNAL, **52**, 1045 (1930).

[6] Lachman, *ibid.*, **44**, 330 (1922); **45**, 1509 (1923).

[7] Stieglitz, *ibid.*, **36**, 272 (1914).

[8] Tiffeneau, *Rev. Gen. Sci. pur et appl.*, 583 (1907).

Summary

1. The action of sodium on ditolyltrichloro-ethane in boiling toluene results in the formation of p,p'-dimethylstilbene and p,p'-dimethyltolane.

2. A similar reaction takes place when sodium acts on diphenyltrichloroethane.

3. A possible interpretation of the reaction is given, involving the formation of monovalent carbon followed by the rearrangement of the phenyl groups within the molecule and the redistribution of the hydrogens between the molecules.

GRAND FORKS, NORTH DAKOTA

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

THE POLYHYDRIC ALCOHOL–POLYBASIC ACID REACTION. II. ETHYLENE GLYCOL–PHTHALIC ANHYDRIDE

BY R. H. KIENLE AND A. G. HOVEY

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Introduction

In the first paper of this series[1] the reaction between glycerol and phthalic anhydride was described. The changes in properties were shown to be gradual and continuous. The conclusion was drawn that although the reaction proceeded by esterification, it did not necessarily take place with the formation of definite mono-, di- or triglycerides, but that a heterogeneous complexity of esters resulted.

It is interesting to compare the reaction of ethylene glycol and phthalic anhydride with the reaction of glycerol and the same acid, for ethylene glycol is a smaller and simpler molecule than glycerol. Any differences in properties of the resinous products of the reactions should therefore be due to the difference in size and structure of the alcohols.

Historical.—The reaction of ethylene glycol with phthalic anhydride was known to M. J. Callahan[2] in 1914, but the resin did not receive commercial application as soon as that formed from the glycerol–phthalic anhydride reaction, because ethylene glycol has not been available in considerable quantities until within the last five or six years. Much additional work was done by J. G. E. Wright and co-workers, the authors, and others, with the result that certain modifications of the reaction have been effected and several novel resins of commercial value have been produced. Recently, R. H. Kienle and C. S. Ferguson[3] described the product of the ethylene glycol–phthalic anhydride reaction as belonging to a "heat-

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[1] R. H. Kienle and A. G. Hovey, THIS JOURNAL, 51, 509 (1929).

[2] M. J. Callahan, unpublished data and such patents as U. S. Patents 1,091,627, 1,091,628 and 1,091,732.

[3] R. H. Kienle and C. S. Ferguson, *Ind. Eng. Chem.*, 21, 399 (1929).