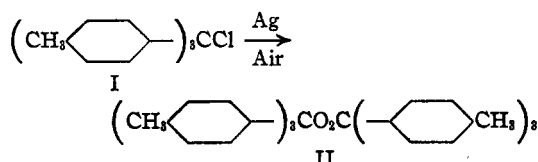


[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Effect of Substitution on the Dissociation of Hexaarylethanes. VIII.¹ The Disproportionation of Tri-*p*-tolylmethyl

BY C. S. MARVEL, WILLIAM H. RIEGER AND MAX B. MUELLER

Gomberg² has found that hexa-*p*-tolylethane does not dissociate reversibly to give a stable triarylmethyl radical as do many hexaarylethanes. The radical is formed when tri-*p*-tolylmethyl chloride (I) is treated with silver as shown by the fact that the expected peroxide (II) is obtained when the reaction is carried out in the presence of air or oxygen. If a benzene solution of the chlo-



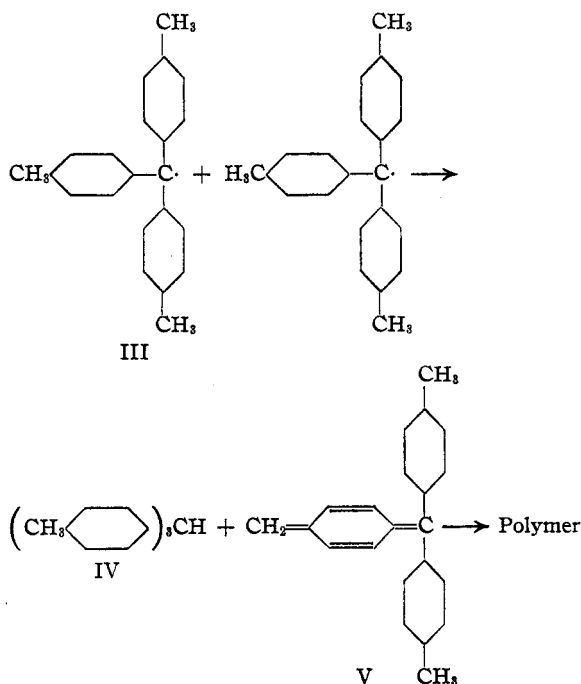
ride is treated with silver in the absence of oxygen a light orange colored solution is produced but the color fades rapidly. Removal of the solvent at this stage leaves a glassy residue which has never been satisfactorily characterized.

A further study of hexa-*p*-tolylethane now has been undertaken in connection with the study of the effect of alkyl groups on the dissociation of hexaarylethanes. When tri-*p*-tolylmethyl chloride (I) was purified carefully to remove all traces of moisture and hydrogen chloride before treating it with silver, it was possible to obtain a benzene solution of hexa-*p*-tolylethane which was light orange in color. Magnetic susceptibility³ measurements showed that this ethane was dissociated to the extent of at least 16%. If the solution was allowed to stand at room temperature (25–30°) for a few hours the color disappeared entirely and magnetic susceptibility measurements showed that no free radical remained.

The solvent was removed from this decolorized solution and the glassy residue described by Gomberg² was obtained. By putting this residue in a molecular still⁴ and warming it to about 85° under a pressure of 10^{−4} mm., a distillate consisting of pure tri-*p*-tolylmethane (IV) was obtained. The material which did not distill consisted of a brownish-yellow powder soluble in hexane and benzene

but almost insoluble in ether. It was obviously polymeric in nature. Attempts to determine a molecular weight by cryoscopic methods gave no satisfactory results.

The identification of tri-*p*-tolylmethane (IV) and a polymeric residue as the products of disproportionation of tri-*p*-tolylmethyl (III) makes



it possible to suggest a mechanism for the reaction. If one free radical strips a hydrogen atom from one of the *p*-methyl groups of another radical to give tri-*p*-tolylmethane (IV), the dehydrogenated radical can stabilize itself by assuming the quinoid structure (V). This molecule is one of the activated vinyl types and it should be expected to polymerize with ease. Since the polymer is not a pure hydrocarbon, some oxidation must occur during its isolation. The color change from an orange to an almost colorless solution shows that the polymerization must have occurred before the tube was opened to the air.

Confirmation of this explanation of the disproportionation reaction has been obtained. Schlenk and Meyer⁵ have found that pyridine will remove

(1) For the seventh communication in this series, see *THIS JOURNAL*, **61**, 2008 (1939).

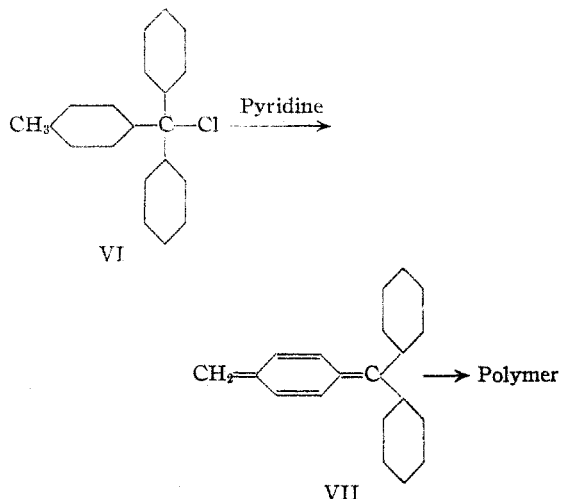
(2) Gomberg, *Ber.*, **37**, 1626 (1904).

(3) (a) Müller, *et al.*, *Ann.*, **520**, 235 (1935); **521**, 89 (1935); (b) Roy and Marvel, *THIS JOURNAL*, **59**, 2622 (1937).

(4) Washburn, *Bur. Standards J. Research*, **2**, 476 (1929).

(5) Schlenk and Meyer, *Ber.*, **52**, 9 (1919).

hydrogen chloride from diphenyl-*p*-tolylmethyl chloride (VI) to give a polymeric product. They postulate a quinoid intermediate (VII) and have actually isolated properly substituted molecules of this type.



Treatment of tri-*p*-tolylmethyl chloride with pyridine in an oxygen-free atmosphere produced a solution which was qualitatively indistinguishable in color from the corresponding free radical solution. When this solution was allowed to stand, the color faded and when the pyridine hydrochloride and excess pyridine were removed a polymeric residue remained. This residue had approximately the same solubilities and carbon and hydrogen content as did the polymer obtained by disproportionation of the free radical. While comparisons of polymers are not completely satisfactory for identification purposes, there seems to be little doubt that these products were the same.

Experimental

Tri-*p*-tolylmethyl Chloride.—The tri-*p*-tolylmethylcarbinol was obtained in 65% yield from *p*-tolylmagnesium

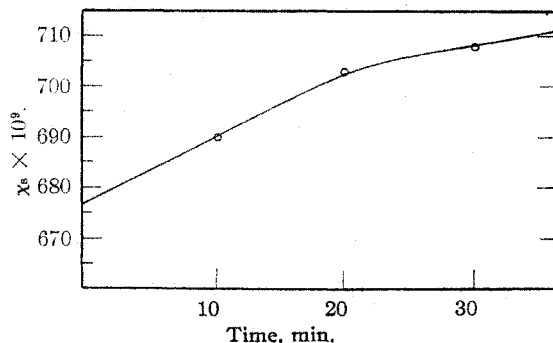


Fig. 1.—Change of magnetic susceptibility (χ_M) of hexa-*p*-tolyethane solution with time.

bromide and diethyl carbonate.⁶ It was converted to the chloride by treating its dry ether solution with dry hydrogen chloride. The chloride was recrystallized from carefully dried ethyl acetate and stored in a desiccator over solid potassium hydroxide under reduced pressure. This product melted at 171–172° (literature² gives m. p. at 173°).

Anal. Calcd. for $C_{22}H_{21}Cl$: Cl, 11.08. Found: Cl, 11.10.

Dissociation of Hexa-*p*-tolyethane.—A benzene solution of 1.032 g. of tri-*p*-tolylchloromethane was shaken with 3 g. of molecular silver for ten minutes in the apparatus described previously.^{3b} The radical solution was filtered immediately from the silver-silver chloride residue and its magnetic susceptibility was determined. Two more determinations were made at ten-minute intervals. Extrapolation to zero time (see graph) indicates that hexa-*p*-tolyethane is 20% dissociated in 0.05 molar benzene solution. Assuming that the dissociation of hexaarylethanes obeys the mass law, this corresponds to a dissociation of 16% in 0.08 molar benzene solution.

These calculations are based upon the assumption that the reaction between tri-*p*-tolylchloromethane and molecular silver is 80% complete at the end of ten minutes. This assumption is supported by the observation that about 80% of the theoretical amount of oxygen is absorbed in ten minutes by a similarly treated bromobenzene solution of the chloromethane. Since the ethane is so unstable no more satisfactory determination was possible; however, it seemed probable that the assumed concentration is accurate within $\pm 10\%$. A variation in concentration within these wide limits would cause a maximum variation of only $\pm 2\%$ in the value of the dissociation.

Disproportionation of Radical.—A solution of 2 g. of tri-*p*-tolylmethyl chloride in 150 cc. of dry benzene was frozen in a dry-ice-acetone bath and 0.8 g. of molecular silver was added. The flask was swept out with dry nitrogen, evacuated and sealed. The solution was allowed to warm to room temperature and it took on the characteristic light orange color. The flask was shaken for twenty-four to thirty hours at which time the color had faded to a very light yellow. The flask was opened, the silver recovered by filtration and the solvent removed under reduced pressure. The residual amber colored oil set to a hard glassy solid on cooling to room temperature.

A sample (1.219 g.) of this glassy solid was placed in a molecular still under a pressure of 10^{-4} mm. The bath temperature was maintained at about 85°. The distillate (0.239 g.) was a white solid which melted at 57°. A mixture of this material with an authentic specimen of tri-*p*-tolylmethane showed no depression in melting point.

The residue which did not distill was a light brown powder. It was fairly soluble in benzene and hexane and almost insoluble in ether. Attempts to determine its molecular weight in freezing benzene gave erratic results typical of polymeric materials.

Anal. Found: C, 89.79; H, 7.48.

This analysis shows the carbon and hydrogen ratio is that expected for a polymer of the quinoid type of molecule shown in formula V but there apparently has been added about one atom of oxygen for each quinoid unit. A poly-

(6) Copenhaver, Roy and Marvel, *THIS JOURNAL*, **57**, 1311 (1935).

merization of the vinyl type would still leave a conjugated system in each unit which might readily add oxygen.⁷

Preparation of Polymer from Tri-*p*-tolylmethyl Chloride and Pyridine.—A solution of 2.72 g. of tri-*p*-tolylmethyl chloride in 15 cc. of pure dry pyridine was heated under a reflux condenser in an atmosphere of dry nitrogen. The solution became yellow almost at once, then light orange and wine red. In about five minutes the color began to fade and heating was stopped. In about thirty minutes the solution was a yellowish brown and white crystals of pyridine hydrochloride had separated in the cold solution. Some dry ether was added and the pyridine hydrochloride was removed by filtration. The ether and excess pyridine were removed by evaporation under reduced pressure. A yellowish oil remained and on cooling in air it set to a hard, glassy solid. This solid was also soluble in benzene and hexane and almost insoluble in ether.

Anal. Found: C, 87.62, 87.93; H, 7.16; 7.45.

(7) Compare Kogerman, *Trans., 2nd World Power Conf., Berlin*, 8, 33 (1930); *C. A.*, 25, 5549 (1931).

Summary

1. Determination of the degree of dissociation of hexa-*p*-tolylethane on a rapidly prepared benzene solution shows it is dissociated to the extent of $16 \pm 2\%$ in 0.08 molar solution in benzene at 30° .

2. Tri-*p*-tolylmethyl rapidly undergoes disproportionation in benzene solution to give tri-*p*-tolylmethane and a polymeric material.

3. Removal of hydrogen chloride from tri-*p*-tolylmethyl chloride by the action of pyridine leads to a polymer apparently identical with that obtained by disproportionation of the radical. These facts are used to explain the course of the disproportionation reaction.

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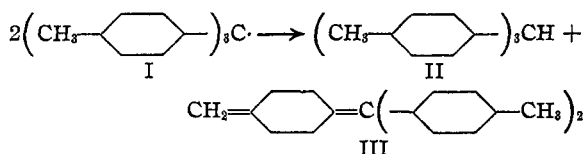
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Disproportionation of Hexa-*p*-alkylphenylethanes and the Effect of ortho-, meta-, and para-Alkyl Groups on Dissociation of Hexaarylethanes¹

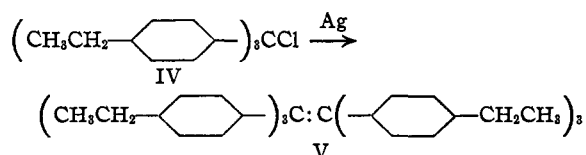
BY C. S. MARVEL, MAX B. MUELLER, CHESTER M. HIMEL AND JULIUS F. KAPLAN

The discovery¹ that tri-*p*-tolylmethyl (I) undergoes rapid disproportionation to yield tri-*p*-tolylmethane and a quinoid residue (III) which rapidly polymerizes, has made it seem probable that groups other than methyl which still have hydrogen on the alpha carbon should likewise cause instability of the radical. Accordingly we



have reinvestigated the series of *p*-alkylphenylethanes which was recently described from this Laboratory.²

When tri-*p*-ethylphenylchloromethane (IV) in benzene solution was shaken with molecular silver



(1) This is the ninth communication on the effect of alkyl groups on the dissociation of hexaarylethanes. For the eighth, see *THIS JOURNAL*, **61**, 2769 (1939).

(2) (a) Copenhaver, Roy and Marvel, *ibid.*, 57, 1311 (1935);
(b) Roy and Marvel, *ibid.*, 59, 2622 (1937).

for only fifteen minutes and the magnetic susceptibility of the resulting solution was examined, it was found that the free radical was present to the extent of 17%. On standing there was little change in the color of the solution but the change in magnetic susceptibility showed that the free radical was disappearing very rapidly. The experiments were carried out at higher temperatures (30°) than had been used previously (20°)^{2b} and in the present series of tests no radical remained in the solution after twenty-four hours, the time used before for the preparation of the solutions to be studied.

The fact that the color of the solution did not fade appreciably during the disproportionation of the free radical (VI) is of interest. It indicates that in the series above methyl the quinoid hydrocarbon (VIII) produced in the disproportionation does not polymerize. This is to be expected

