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Isomerization of Gomberg's Trityl by Protonic Acids in Benzene

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Gomberg's trityl (1-diphenylmethylene-4-trityl-2,5-cyclohexadiene) (I) was isomerized by protonic acids such as HCl and phenol in benzene to form *p*-benzhydryltetraphenylmethane (II). *p*-(Benzhydryl-α-*d*)-tetraphenylmethane (III) was formed by the treatment of I with phenol-*d*. Ph_3CH and Ph_3CCl were treated under the same conditions, but II was not obtained. It was not formed either by the reaction of phenylazotriphenylmethane with phenol. This observation indicates that H^+ adds to the terminal methylene of I to form the cyclohexadienyl cation followed by deprotonation to give II. Similarly, treatment of 1-(phenyl-*p*-tolymethylene)-4-(diphenyl-*p*-tolylmethyl)-2,5-cyclohexadiene (IV) with HCl in benzene afforded α,α,α′-triphenyl-α,α′-(di-*p*-tolyl)-*p*-xylene (V). The results support the view that Gomberg's trityl is not hexaphenylethane but 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene as suggested by Lankamp *et al.* (*Tetrahedron Lett.*, **1968**, 249). 1,1,2,2-Tetraphenylethane and 1,1,2,2-tetra-*o*-tolylethane not having the cyclohexadiene structure could not be isomerized by protonic acids (HCl and PhOH) in benzene. Thus, isomerization of this type is characteristic of the cyclohexadiene structure such as that of Gomberg's trityl.

It is believed that the dimerization of the triphenylmethyl radical discovered by Gomberg leads to hexaphenylethane.

However, Lankamp *et al.*[1] reported in 1968 that the monomer-dimer equilibrium of trityl is not the equilibrium, hexaphenylethane ⇄ 2 triphenylmethyl radicals, and should be represented as: 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene ⇄ 2 triphenylmethyl radicals, by the evidence of UV and NMR spectra.

Guthrie and Weisman[2] reported that the dimer structure suggested by Lankamp *et al.* could be supported from the reaction of Gomberg's trityl toward a base.

During our investigation[3] on the reactivity of Gomberg's trityl toward sulphur dioxide, we found that Gomberg's trityl isomerizes into *p*-benzhydryltetraphenylmethane in the presence of protonic acids. This gives a chemical evidence for the 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene structure as the dimer structure of Gomberg's trityl. We wish to report the de-

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[1] H. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Lett.*, **1968**, 249.

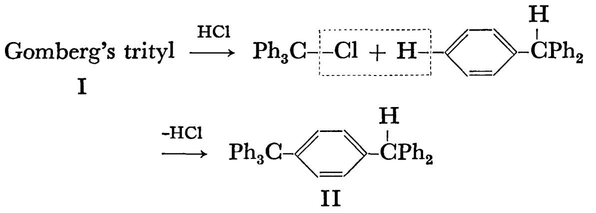
[2] R. D. Guthrie and G. R. Weisman, *Chem. Commun.*, **1969**, 1316.

[3] H. Takeuchi, T. Nagai, and N. Tokura, This Bulletin, **43**, 1747 (1970).

tails of the isomerization of Gomberg's trityl by protonic acids in benzene.

Ullmann and Borsum⁴⁾ reported that the reaction of trityl chloride or triphenylcarbinol with Zn-$SnCl_2$ in acetic acid gave a stable hexaphenylethane (mp 225°C). Gomberg⁵,⁶⁾ also reported the formation of hexaphenylethane (mp 225—227°C) by the treatment of the trityl with HCl or acetic acid.

Tschitschibabin⁷⁾ synthesized *p*-benzhydryltetraphenylmethane (II) (mp 227°C) by the decomposition of the corresponding diazo compound formed from amino-*p*-benzhydryltetraphenylmethane. He argued against the formation of hexaphenylethane. Schlenk *et al.*⁸⁾ postulated the formation mechanism of II (Scheme 1) by the reaction of I with HCl, because II was formed in a 6% yield by the treatment of Ph_3CH with Ph_3CCl.



Scheme 1

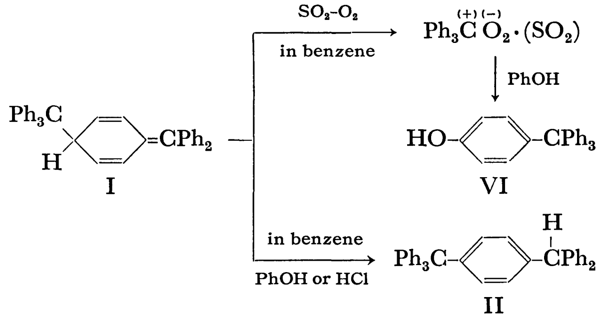
However, Gomberg's trityl (I), which is not hexaphenylethane but 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene as described by Lankamp *et al.*,¹⁾ reacted with HCl to give II in good yield (82%). Hence the sluggish reaction shown in Scheme 1 can be neglected.

The present study was undertaken in order to explain the reaction mechanism of this type. The present paper deals with the reaction of protonic acids such as HCl and phenol with the derivative of I or tetraarylethanes.

Results and Discussion

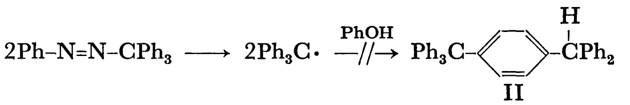
Gomberg's trityl (I) reacted with phenol in the presence of SO_2 and O_2 in benzene at 60°C to give *p*-hydroxytetraphenylmethane (VI) as the product.³⁾ However, in the absence of SO_2 and O_2 in the above system, *p*-benzhydryltetraphenylmethane (II)³⁾ was formed in a 68% yield. When HCl was used in place of phenol, II was formed (82%). Gomberg *et al.*⁴⁻⁶⁾ reported the formation of the compound having the same mp (225—227°C) as that of II by the treatment of I with acetic acid, though they characterized this compound as hexaphenylethane.

Schlenk *et al.*⁸⁾ proposed the mechanism shown in Scheme 1. Ph_3CH and Ph_3CCl were heated at 60°C for 2 hr in benzene in our experiment, but II was not obtained. Thus, the possibility of the pathway in Scheme 1 could be eliminated.



Scheme 2

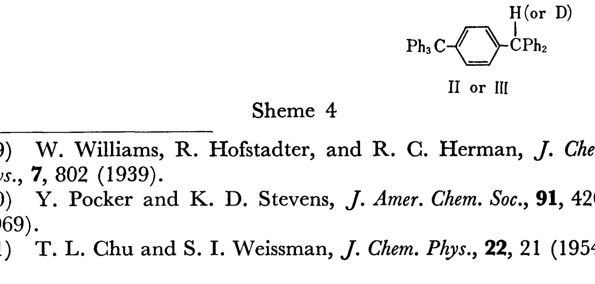
If the formation of II is characteristic of the trityl radical, it should take place by the reaction of phenylazotriphenylmethane with phenol in benzene at 60°C for 2 hr. However, II was not obtained, which indicates that the reaction dose not occur *via* trityl radical as in the Scheme.



Scheme 3

A detailed investigation was carried out by use of 37 mmol of phenol-*d*⁹⁾ (69.5%)—phenol (30.5%) (calculated from mass spectral analysis) and I (4.2 mmol). Formation of *p*-(benzhydryl-α-*d*) tetraphenylmethane (III) was confirmed by IR (ν_{C-D} 2330 cm^{-1}) and mass spectrum (*m*/*e*; 487(M^+), 410(Ph_3C-C_6H_4-$\overset{+}{C}DPh$) and 168 ($Ph_2\overset{+}{C}D$)). The ratio II: III (36.3: 63.7) was calculated by comparison of the mass spectral molecular peaks of this isotope mixture with those of II. Compound II was treated with the labelled phenol, but the mass spectral analysis showed no peak corresponding to III. This indicates that the isotope scramble of II does not occur. Though the first proton donation step is obscure, the value ($k_H/k_D=1.05\pm0.01$) of the isotope effect was obtained on the assumption that this reaction follows first order of I and second order¹⁰⁾ of phenol.

In such solvents as H_3PO_4 and $POCl_3$,¹¹⁾ however, $Ph_3C\cdot$ is transformed into $Ph_3\overset{+}{C}$. Phenylazotriphenylmethane³⁾ or I was also allowed to react with phenol in the presence of SO_2 and O_2 in benzene to give VI by the reaction of PhOH and $Ph_3\overset{+}{C}$ formed in the reaction system such as Scheme 2. Thus, it is plausible that PhOH or HCl in benzene isomerizes I into II more readily than to transform $Ph_3C\cdot$ into $Ph_3\overset{+}{C}$.



Sheme 4

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4) F. Ullmann and W. Borsum, *Ber.*, **35**, 2877 (1902).

5) M. Gomberg, *ibid.*, **35**, 3914 (1902).

6) M. Gomberg, *ibid.*, **36**, 376 (1903).

7) A. E. Tschitschibabin, *ibid.*, **41**, 2427 (1908).

8) W. Schlenk, T. Weickel, and A. Herzenstein, *Ann. Chem.*, **372**, 1 (1910).

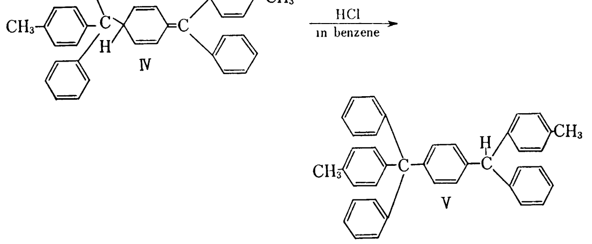
9) W. Williams, R. Hofstadter, and R. C. Herman, *J. Chem. Phys.*, **7**, 802 (1939).

10) Y. Pocker and K. D. Stevens, *J. Amer. Chem. Soc.*, **91**, 4205 (1969).

11) T. L. Chu and S. I. Weissman, *J. Chem. Phys.*, **22**, 21 (1954).

The results may indicate that proton or deuteron adds[10] to the terminal methylene of I to form the cyclohexadienyl cation such as I′, followed by the deprotonation to give II or III (Scheme 4).[12] From the isotope effect, the protonation step in the reaction of I with phenol does not seem to be rate-determining.[10]

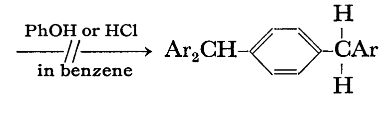
Similarly, the treatment of 1-(phenyl-*p*-tolylmethylene 4-(diphenyl-*p*-tolylmethyl)-2,5-cyclohexadiene (IV) with HCl in benzene afforded α,α,α′-triphenyl-α,α′-(di-*p*-tolyl)-*p*-xylene (V). Confirmation of V was achieved as follows: IR; 810 cm^{-1} (*p*-substituted phenyl). NMR (in CCl_4): τ; 2.5—3.7 (aromatic, multiplet, 27H), 4.6 (methine, singlet, 1H) and 7.7 (methyl, singlet, 6H). Mass: *m*/*e*; 514(M$^+$), 437 ($Ph_2(p\text{-}CH_3\text{-}C_6H_4)C\text{-}C_6H_4\text{-}\overset{+}{C}H\text{-}(p\text{-}CH_3\text{-}C_6H_4)$), 257 ($Ph_2(p\text{-}CH_3\text{-}C_6H_4)\overset{+}{C}$), and 181 ($Ph(p\text{-}CH_3\text{-}C_6H_4)\overset{+}{C}H$).



Sheme 5

On the other hand, 1,1,2,2-tetraphenylethane and 1,1,2,2-tetra-*o*-tolylethane were produced by the reaction of the corresponding diarylchloromethanes with Zn in benzene. However, these ethanes without the cyclohexadiene structure could not be isomerized by protonic acids (HCl or phenol). Thus, isomerization of this type is characteristic of the cyclohexadiene structure such as Gomberg's trityl.

$$2Ar_2CHCl \xrightarrow{Zn} Ar_2CH\text{-}CHAr_2$$



Ar; C_6H_5 and *o*-CH_3-C_6H_4

The results support the idea that Gomberg's trityl is not hexaphenylethane but 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene as described by Lankamp *et al.*[1]

Experimental

Apparatus. IR spectra were obtained on a EPI-S2 type Hitachi IR spectrometer. NMR spectra were obtained with a Japan Electron Optics Lab. spectrometer. UV spectra were taken with a EPS-3 Hitachi recording spectrometer. Mass spectra were recorded on a Hitachi RMU-6E spectrometer.

Materials. Benzene was purified by the ordinary method. Phenol was obtained commercially. The phenol-*d*-phenol mixture was made by the treatment of phenol with D_2O.[9] Gomberg's trityl (1-diphenylmethylene-4-trityl-2,5-cyclohexadine) (I) was prepared by the method of Gomberg and Cone.[13] Phenylazotriphenylmethane was synthesized by the procedure of Cohen and Wang.[14]

Isomerization of I by Phenol. Compound I (4.7 mmol) and phenol (47 mmol) were dissolved in 60 m*l* benzene and the solution was heated at 60°C for 2 hr in Ar atmosphere. The residual after distillation of benzene was chromatographed over silical gel using petroleum ether - benzene mixture as eluents by changing the polarity of the eluting medium. The following compounds were isolated and identified.

p-*Benzhydryltetraphenylmethane (II)*: Mp 225—227°C (recrystallized from benzene - acetic acid), 68%, IR: 2880 (ν_{C-H}), 840 cm^{-1} (*p*-substituted phenyl). $\lambda_{max}^{cyclohexane}$ 263 mμ (log ε 3.11), shoulder; 255 mμ (log ε 3.15), 269 mμ (log ε 2.99) and 272 mμ (log ε 2.67). NMR (in CCl_4): τ; 2.6—3.1 (aromatic, multiplet, 29H) and 4.6 (methine, singlet, 1H). Mass spectrum: *m*/*e*; 486 (M$^+$), 409 ($Ph_3C\text{-}C_6H_4\text{-}\overset{+}{C}HPh$), 243 ($Ph_3\overset{+}{C}$) and 167 ($Ph_2\overset{+}{C}H$).

Found; C, 93.71; H, 6.41%. Calcd for $C_{38}H_{30}$: C, 93.79; H, 6.21%.

Triphenylmethane: Mp 92°C (recrystallized from MeOH) 3%. The compound has same IR spectrum as an authentic specimen and showed no depression of mixed mp.

p-*Hydroxytetraphenylmethane*: Mp 280°C (recrystallized from $CHCl_3$-petroleum ether, 3%. The compound showed no depression of mixed mp and gave an identical IR spectrum with that of an authentic sample.[15]

In order to investigate the isomerization mechanism, I (4.2 mmol) was allowed to react with phenol-*d*[9] (69.5%)-phenol (30.5%) (calculated from mass spectral analysis) in benzene (20 m*l*) at 60°C for 2 hr in Ar. Formation of *p*-(benzhydryl-α-*d*)-tetraphenylmethane (III) was confirmed by IR (ν_{C-D} 2330 cm^{-1}) and mass spectral peaks (*m*/*e*: 487, 410 and 168). The ratio of II: III (36.3: 63.7) was calculated by comparison of the mass spectral molecular peaks of this isotope mixture with those of II. The above phenol-*d*-phenol mixtre was treated with II under the same conditions, but mass spectral analysis showed no peak corresponding to III. Isotope effect (k_H/k_D) was calculated from the results.

Isomerization of I by HCl. Compound I (2.9 mmol) was dissolved in 15 m*l* benzene saturated with HCl gas, and the solution was made to stand at room temperature for 30 min. The residue obtained after evaporation of benzene was crystallized from ether to give II (82%).

*Isomerization of 1-(Phenyl-*p*-tolymethylene)-4-(diphenyl-*p*-tolylmethyl)-2,5-cyclohexadiene (IV) with HCl.* Diphenyl-*p*-tolylcarbinol[16] was prepared by the interaction of PhMgBr in ether and *p*-toluic acid methylester, and yielded diphenyl-*p*-tolylchloromethane (mp 98—99°C) after treatment with dry HCl in ether.[15] The benzene solution of IV was made by the reaction of diphenyl-*p*-tolylchloromethane (8.5 mmol) with Zn (6 g) in benzene (20 m*l*) at room temperature for 1 hr in Ar, and treated with dry HCl after the solid had been removed by filtration. Compound V was separated by column chromatography over silica gel using benzene-petroleum ether as eluents, mp 77—79°C, 42%, identified as follows. IR: 810 cm^{-1} (*p*-substituted phenyl). NMR (in CCl_4): τ; 2.5—3.7 (aromatic, multiplet, 27H), 4.6 (methine, singlet, 1H), and 7.7 (methyl, singlet, 6H). Mass: *m*/*e*: 514, 437, 257, and 181.

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[12] II was not obtained in the experiment using EtOH or Et_3N in place of phenol.

[13] M. Gomberg and L. H. Cone, *Ber.*, **37**, 2034 (1904).

[14] S. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, **75**, 5504 (1953).

[15] M. Busch and R. Knoll, *Ber.*, **60**, 2240 (1927).

[16] A. Bistrzycki and J. Gyr, *ibid.*, **37**, 655 (1904).

Found: C, 93.07; H, 6.53%. Calcd for $C_{40}H_{34}$: C, 93.34; H, 6.66%.

Treatment of Tetraarylethanes with Phenol or HCl. 1,1,2,2-Tetraphenylethane (VII) (39%, mp 210°C[17]) and 1,1,2,2-tetra-*o*-tolylethane (VIII) (15%, mp 250°C) were synthesized by the reaction of the corresponding diarylchloromethanes with Zn in benzene. NMR spectra show that VII and VIII are true ethanes: VII in $CDCl_3$: τ; 2.5—3.2 (aromatic, multiplet, 20H) and 5.25 (methine, singlet, 2H), and VIII in $CDCl_3$: τ; 2.6—3.2 (aromatic, multiplet, 16H), 4.9 (methine, singlet, 2H) and 8.55 (methyl, singlet, 12H). These ethanes were not isomerized by phenol or HCl under the conditions for the isomerization of I.

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17) F. C. Whitmore and E. N. Thurman, *J. Amer. Chem. Soc.*, **51**, 1491 (1929).