BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3249—3254 (1969)

One-Electron Reduction of Carbonium Ions. II. Reduction of the Tropylium Ion and the Triphenylmethyl Cation with Metallic Powders and Metallic Ions[*1]

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(Received April 28, 1969)

The reaction of tropylium fluoroborate in an aqueous solution has been carried out at room temperature with powders of various metals (Mg, Al, Mn, Zn, Cr, Fe, Cd, Co, Ni, Sn, Pb, Sb, Cu, Hg, and Ag) under heterogeneous conditions and with several metallic ions (Cr(II), Ti(III), Sn(II), Cu(I), Fe(II), Fe(III), Hg(I), Hg(II), and Ag(I)) in a homogeneous solution. All these reagents, except Ag, Fe(III), Hg(I), Hg(II), and Ag(I), reduce with ease the tropylium ion to give the tropyl radical, which then rapidly couples to bitropyl; their reducing powers, estimated by comparing the yields of bitropyl under the same reaction conditions, correlate with their oxidation electrode potentials and oxidation-reduction potentials. The ferric ion, the mercurous ion, the mercuric ion, and the silver ion afforded no bitropyl, but only an oxidation product of the tropylium ion, *i.e.*, benzaldehyde. Silver powder gives neither a reduction nor an oxidation product under these reaction conditions. The reduction has also been carried out in an acetonitrile solution, and the reducibility of tropylium fluoroborate with powders of Zn, Fe, Ni, Sb, Cu, and Ag has been compared with that of triphenylmethyl fluoroborate under heterogeneous conditions. Both the tropylium ion and the triphenylmethyl cation are smoothly reduced by Zn, Fe, Ni, Sb, and Cu in this solvent. The tropylium ion, however, is not reduced by silver powder, while the triphenylmethyl cation is reduced to the triphenylmethyl radical. This greater reducibility of the triphenylmethyl cation is consistent with what could be anticipated from the data of half-wave potentials, ionization potentials, and H.M.O. calculation reported with respect to these two carbonium ions.

Although the reactivity scale of carbonium ions in a one-electron reduction in the gaseous phase has araised much theoretical interest in association with the ionization potential of organic radicals to carbonium ions,[1] relatively little attention has been devoted to the reducibility scale in solutions, and the range of carbonium-ion structures investigated is quite small. Heretofore, the tropylium ion[2] and the triarylcyclopropenyl[3] and polyarylmethyl cations[2c-4] have been reported to be carbonium ions whose reducibilities in the liquid phase have been determined by a polarographical method[2,3] and by the measurement of the reversible-electrode reduction potentials of the solutions of carbonium ions and the corresponding redicals.[4] Thus, a systematic investigation into the reducibility scale in solution for other carbonium ions with a wide range of structures should be of considerable interest. However, preliminary to a systematic scrutiny of the carbonium-ion structure, the exploration of simple reducing agents with a wide range of applicability is needed because of the restricted applicability of the electrochemical measurements.[2-4]

As for the reducing agents of the carbonium ions, Conant and his collaborators[5] first demonstrated that the vanadous ion reduces serveal stable polyarylmethyl cations. There have since been employed such reductants as the chromous ion,[6] zinc,[7]

[*1] Part I: K. Okamoto, Y. Matsui and H. Shingu, This Bulletin, **38**, 153 (1965).

1) For a review, see K. Okamoto, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **69**, 825 (1966).

2) a) M. E. Vol'pin, S. I. Zhdanov and D. N. Kursanov, *Dokl. Acad. Nauk SSSR*, **112**, 264 (1957); *Chem. Abstr.*, **51**, 12057c (1957). b) P. Zuman, J. Chodkowski, H. Potesilova and F. Santavy, *Nature*, **182**, 1535 (1958). c) M. I. James and P. H. Plesch, *Chem. Commun.*, **1967**, 508.

3) R. Breslow, W. Bahary and W. Reinmuth, *J. Am. Chem. Soc.*, **83**, 1763 (1961).

4) E. D. Jenson and R. W. Taft, *ibid.*, **86**, 116 (1964).

5) a) J. B. Conant and A. W. Sloan, *J. Am. Chem. Soc.*, **45**, 2466 (1923). b) J. B. Conant and A. W. Sloan, *ibid.*, **47**, 572 (1925). c) J. B. Conant, L. F. Small and B. S. Tayler, *ibid.*, **47**, 1959 (1925). d) J. B. Conant and L. F. Small, *ibid.*, **47**, 3068 (1925). e) J. B. Conant, L. F. Small and A. W. Sloan, *ibid.*, **48**, 1743 (1926).

6) K. Ziegler, F. A. Fries and F. Sälzer, *Ann.*, **448**, 249 (1926).

7) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).

ferrocene,[8] tetraphenyl-*p*-xylylene,[9] the dinegative ion of cyclooctatetraene,[10] carbazole,[11] phenylenediamine,[11] the triphenylmethyl radical,[12] and others.[13] Among these reducing agents we chose various metals and low-valent metallic ions with the idea that these reducing agents would show various degrees of reducing power, which would correlate with their oxidation electrode potentials and oxidation-reduction potentials, and that a spectrum of the percentage yields of the reduction products would reflect the intrinsic reducibility of the carbonium ion concerned. In this paper we will report on the results of the reduction of the tropylium ion and of the triphenylmethyl cation with these reductants in aqueous and in acetonitrile solutions and will discuss the applicability of the spectrum of the radical yields as a measure for estimating the reducibility of the respective stable carbonium ions.

Reduction of the Tropylium Ion in an Aqueous Solution with Metallic Powders. A 0.1 N solution of tropylium fluoroborate in 0.1 N hydrochloric acid[14] was treated with various metallic powders at room temperature for ten minutes. As Doering and Knox[7] found in zinc-dust reduction, most of the metals examined (see Table 1) were found to reduce the tropylium ion to bitropyl readily. As Table 1 shows, magnesium, aluminum, manganese, zinc, iron, cadmium, cobalt, tin, lead, and antimony afforded bitropyl in fairly good yields, whereas the yield of bitropyl was poor in the cases of chromium (1%), nickel (0.4%), copper (0.2%), and mercury (0.03%). In each reduction only the unchanged tropylium ion was identified as an organic compound other than bitropyl, and a good material balance (>94%) was obtained. Since these reductions were carried out under heterogeneous conditions and with metals of various grain sizes, the percentage yields of bitropyl might not exactly reflect the intrinsic reducing powers of these metals. However, an examination of the standard oxidation electrode potentials of these metals reveals that there exists a correlation between the spectra of the values of the bitropyl yield and of the oxidation electrode potentials of these metals; that is, under these reduction conditions the reducibility of the tropylium ion seems to correspond to the values of the oxidation electrode potential between those of mercury and silver, *i. e.*, −0.789 and −0.799 V.

TABLE 1. THE REDUCTION OF THE TROPYLIUM ION IN THE AQUEOUS SOLUTION WITH METALLIC POWDERS AT 21—31°C[a]

Metal (mesh)	Oxidation potential[b] (V)	Bitropyl Yield (%)	Tropylium ion, unchanged[e] (%)
Mg (200—250)	2.37	92	3.2
Al (200—250)	1.66	99	0.0
Mn (>400)	1.18	98	1.8
Zn (>400)	0.763	100	0.0
Cr (200—250)	0.74	1.0	99
Fe (200—250)	0.440	20	79
Cd (>200)	0.403	26	73
Co (>250)	0.277	94	0.0
Ni (>400)	0.250	0.4[d]	95
Sn (>400)	0.136	100	0.0
Pb (200—250)	0.126	60	41
Sb (200—250)	−0.212	5.4	94
Cu (200—250)	−0.521	0.2[d]	95
Hg (liq.)[c]	−0.789	0.03[d]	99
Ag (≷200)	−0.799	0.0[d]	99

a) Except when otherwise noted, all reactions were conducted with about 15 molar equivalents of metallic powder under an atomosphere of nitrogen for ten minutes, aqueous hydrochloric acid (0.1 N) being used as the solvent. Initial concentration of tropylium fluoroborate was 0.100 N.

b) W. M. Latimer, "Oxidation Potentials," Prentice-Hall (1952).

c) The reaction was carried out for 30 min with 50 molar equivalents of mercury, aqueous nitric acid (0.1 N) being used as the solvent.

d) Estimated by t.l.c. analysis.

e) Determined by UV spectrophotometry.

Reduction of the Tropylium Ion in an Aqueous Solution with Low-Valent Metallic Ions. An aqueous 0.1 N hydrochloric acid solution of tropylium fluoroborate (0.1 N) was treated with about three equivalents of various metallic ions at room temperature under an atmosphere of nitrogen. As is shown in Table 2, bitropyl was readily obtained as the sole product in the reductions with chromous[15] and titanous ions, whereas it was obtained in poor yields in the reduction with stannous, cuprous, and ferrous ions. However, the mercurous ion, which oxidation-reduction potential is the lowest among the ions examined,

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[8] M. F. Hawthorne, *J. Org. Chem.*, **21**, 363 (1956).

[9] a) E. Weitz and F. Schmidt, *Ber.*, **75**, 1921 (1942). b) H. Hart, J. S. F. Flemming and J. L. Dye, *J. Am. Chem. Soc.*, **86**, 2079 (1964).

[10] a) K. Conrow and P. C. Radlick, *J. Org. Chem.*, **26**, 2260 (1961). b) R. W. Murray and M. L. Kaplan, *ibid.*, **31**, 962 (1966).

[11] A. Ledwith and M. Sambhi, *Chem. Commun.*, **1965**, 64.

[12] J. W. Lown, *Proc. Chem. Soc.*, **1963**, 283.

[13] J. E. Leffler, *J. Am. Chem. Soc.*, **75**, 3598 (1953).

[14] The degree of hydrolysis of the tropylium ion in this solution was calculated to be $1.8\times10^{-2}\%$, using the value of the equilibrium constant measured by Doering and Knox (W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954)).

[15] The reduction rate of the tropylium ion by the chromous ion has been measured by a flow method. The details of the experiment will be reported elsewhere.

TABLE 2. THE REACTION OF THE TROPYLIUM ION IN THE AQUEOUS SOLUTION WITH METALLIC IONS AT 18—28°C[a]

Ion	Oxidation potential[b] (V)	Reaction time (hr)	Bitropyl yield (%)	Benzaldehyde yield (%)	Tropylium ion unchanged[e] (%)
Cr(II)[c]	0.41	0.01	100	0.0	0.0
Ti(III)	−0.1	0.17	18	0.0	84
Sn(II)	−0.15	2	0.2[f]	0.0	97
Cu(I)	−0.153	2	0.02[f]	0.0	101
Fe(II)	−0.771	2	0.6[f]	~0.1	102
Hg(I)[d]	−0.920	2	0.0[f]	35	0.0
Fe(III)		2	0.0[f]	9.3	65
Hg(II)		2	0.0[f]	46	0.0
Ag(I)		2	0.0[f]	~1	100

a) Except when otherwise noted, all reactions were conducted with three molar equivalents of metal chloride under an atmosphere of nitrogen, and aqueous hydrochloric acid (0.1 N) was used as the solvent. Initial concentration of tropylium fluoroborate was 0.100 N.

b) W. M. Latimer, "Oxidation Potentials," Prentice-Hall (1952).

c) Chromous sulfate was used.

d) Mercurous nitrate was used, along with 0.02 N nitric acid as the solvent.

e) Determined by UV spectrophotometry.

f) Estimated by t.l.c. analysis.

afforded no detectable amounts of bitropyl, but an oxidation product of the tropylium ion, *i. e.*, benzaldehyde,[16,17] in the 35% yield. Furthermore, in this reaction the mercurous ion was reduced to metallic mercury by the tropylium ion. The formation of benzaldehyde due to the oxidation of the tropylium ion was also observed in the reaction with mercuric, ferric, and silver ions in yields of 46, 9.3, and ~1% respectively (Table 2). Thus, as in the case of metallic powder reduction under heterogeneous conditions, the correlation between the reducing power of low-valent metallic ions, as measured by the use of the yields of bitropyl, and of the oxidation-reduction potential of these metallic ions seems to be fairly good; in Table 2 it is clearly demonstrated that the tropylium ion in an aqueous solution can be reduced by the ions with oxidation-reduction potentials with values higher than that of the ferrous ion, and that under these reaction conditions the oxidation-reduction potential of the tropylium ion seems to be just between those of ferrous and mercurous ions, *i. e.*, −0.771 and −0.920 V.

Reduction of the Tropylium Ion and the Triphenylmethyl Cation in an Acetonitrile Solution with Metallic Powders. Since it has been demonstrated for the tropylium ion that its reducibility can be estimated by the use of a spectrum of bitropyl yields in the reduction with various metallic powders, the reducibility of the other carbonium ion was examined by the use of this method. Among the other carbonium ions the triphenylmethyl cation was chosen as a representative carbonium ion, which is stable in an acetonitrile solution. For purposes of comparison, the tropylium ion was reduced also in an acetonitrile solution. In each reduction the respective carbonium ions were allowed to react with 15 molar equivalents of various metallic powders under exactly the same reaction conditions as those employed in the experiments with the tropylium ion in an aqueous solution.

The spectrum of the yields of the reduction product is shown in Table 3, along with the values for the oxidation-electrode potentials of metals and the half-wave potentials of the respective metallic ions in an acetonitrile solution.

In an acetonitrile solution the triphenylmethyl cation was smoothly reduced by zinc dust to the triphenylmethyl radical, which was identified as triphenylmethyl peroxide and a minor amount of benzophenone after its oxidation by air. Similarly, the tropylium ion in acetonitrile was readily reduced by zinc dust to bitropyl, as was observed in an aqueous solution. Iron powder and copper powder also reduced each carbonium ion with ease. It is of interest to note that the yield of bitropyl in copper reduction increased from 0.2% in an aqueous solution (Table 1) to 100% in acetonitrile (Table 3). This dramatic increase in the yield may be a reflection of an intrinsic increase in the reducing power of copper in acetonitrile, as is shown by the relatively higher values of the oxidation-electrode potential of the metal and the half-wave potential of the ion (Table 3), values which

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16) It is reported that the tropylium ion is oxidized to benzaldehyde by bromine in absolute alcohol,[17] by dilute aqueous permanganate,[17] by chromic acid in acetic acid,[7] and by silver oxide in water.[7]

17) M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, **1956**, 2026.

TABLE 3. THE REDUCTION OF THE TROPYLIUM ION AND THE TRIPHENYLMETHYL CATION IN THE ACETONITRILE SOLUTION WITH METALLIC POWDERS AT 14—24°C[a]

Metal (mesh)	Zn (>400)	Fe (150—250)	Ni (>400)	Sb (200—250)	Cu (>400)	Ag (≳200)
Reduction of tropylium ion:						
Bitropyl, yield (%)	100	48	0.1[c]	2.3	100	0.0[b,c]
Tropylium ion, unchanged (%)[d]	0.0	—	94	—	0.0	82
Reduction of triphenylmethyl cation:						
Triphenylmethyl radical, yield (%)[e]	73	69	0.6	1.7	63	43
Triphenylmethyl cation, unchanged (%)[f]	19	29	98	100	27	51
$-E_{1/2}$ in acetonitrile[g] (Hg electrode) (V)	0.70	1.00	0.33	—	0.36	−0.32
Oxidation electrode pot.[h] in acetonitrile (V)	0.74	—	—	—	0.38	−0.23

a) All reactions were conducted with about 15 molar equivalents of metallic powder under an atmosphere of nitrogen for ten minutes. Initial concentrations of tropylium ion and of triphenylmethyl cation were 0.100 N.

b) Tropone (15% yield), identified by the superimposability of the IR spectrum, was obtained as a reaction product.

c) Estimated by t.l.c. analysis.

d) Determined by UV spectrophotometry.

e) The sum of the yields of triphenylmethyl peroxide and of benzophenone. The yields of benzophenone were *ca.* 1% for Zn, *ca.* 4% for Cu, and *ca.* 2% for Ag. No benzophenone was produced in the reactions with Fe, Ni and Sb powders.

f) Isolated as triphenylcarbinol.

g) The half-wave potentials of the corresponding metallic ions, measured *vs.* aqueous SCE; I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 870, 1852 (1957).

h) W. A. Plaeskow, *Zh. Fiz. Khim.*, **22**, 351 (1948).

are closely related to the stabilization of the cuprous ion caused by the strong solvation by the acetonitrile molecules (see the references cited in Table 3).

As has been shown in an aqueous solution, nickel and antimony, which have relatively lower oxidation-electrode potentials, were found to have low reducing powers in acetonitrile for each carbonium ion, this being shown in the low yields of the reduction product from each carbonium ion (Table 3).

Silver did not show any reducing power to the tropylium ion under these reaction conditions; this is a result similar to that observed in an aqueous solution (Tables 1 and 3). In contrast to this, the triphenylmethyl cation was easily reduced by silver powder, indicating that this cation is more reducible than the tropylium ion (Table 3).

The ready reducibility of the triphenylmethyl cation observed in these experiments is consistent with the following reactivity sequence of these two cations: (a) the half-wave potentials of the tropylium ion and the triphenylmethyl cation, measured in methylene dichloride by direct-current polarography, are estimated to be −0.45 and −0.135 V respectively,[2c] showing the ready reducibility of the latter cation; (b) the ionization potentials of tropyl and triphenylmethyl radicals in the gaseous phase are determined to be 6.60 and 7.25 eV[18] respectively, indicating that the former radical is more easily transformed into the tropylium ion (in other words, the tropylium ion is less reducible). The loss of delocalization energy resulting when the tropylium ion is converted to the tropyl radical is calculated to be $-0.45\,\beta$ (from the simple H.M.O. theory),[19] whereas between the triphenylmethyl cation and radical there exists no difference in delocalization energy. When we assume that the reducibility of the cation is governed by the difference in the electronic stabilization (delocalization) energy between the carbonium ion and the corresponding radical, this reslut of calculation is also consistent with the ready reducibility of the triphenylmethyl cation.

Experimental[20]

Materials. Tropylium fluoroborate was prepared from tropilidene according to the method of Conrow,[21] that is, by hydride abstraction with phosphorus pentachloride and by the subsequent addition of aqueous

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18) Cited in Ref. 2c.

19) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, London (1965).

20) The infrared and the ultraviolet spectra were obtained from Shimadzu models, an IR-27 spectrometer and a UV-50M spectrometer respectively.

fluoroboric acid. Tropilidene was prepared by the reaction of a large excess of benzene with diazomethane in the presence of cuprous bromide as a catalyst, according to the method of Müller and Fricke.[22] Triphenylmethyl fluoroborate was prepared by the reaction of triphenylcarbinol with aqueous fluoroboric acid in propionic anhydride, according to the method of Dauben *et al.*[23] Acetonitrile was refluxed over phosphorus pentoxide and distilled; bp 80.8—81.2°C. For all the inorganic reagents, except silver powder, commercial materials were used as received. Metallic silver was prepared by the reduction of silver nitrate with saccharose, as has been described by Brauer,[24] while metallic copper employed was the electrolytically-prepared material supplied by the E. Merck Co.

The Reduction of the Tropylium Ion in an Aqueous Solution with Metallic Powders. The results are shown in Table 1; the details of the procedure are illustrated in the following description of a representative run with metallic iron.

The Reduction of the Tropylium Ion in an Aqueous Solution with Iron. In a 50-m*l*, round-bottomed flask equipped with a magnetic stirring bar, a thermometer, and a nitrogen inlet and outlet, 0.399 g of tropylium fluoroborate (2.24 mmol) was dissolved in 22.4 m*l* of 0.1 N aqueous hydrochloric acid to give a clear, colorless solution. To the stirred solution of the tropylium ion there was then added a 1.865-g portion of iron powder (200—250 mesh) (33.4 mg atom) under an atmosphere of nitrogen at 30.8°C. The reaction temperature immediately rose by 1.1°C and remained almost constant for 10 min. The reaction mixture was then filtered and washed with three 5-m*l* portions of 0.1 N aqueous hydrochloric acid and with five 10-m*l* portions of ether. The amount of the unchanged tropylium ion in the aqueous layer was estimated from the ultraviolet absorbance of the tropylium ion ($\lambda_{\max}^{0.1\text{N HCl}}$ 219 and 275 mμ); 79.4% of the charged ion. The organic layer was washed once with 40 m*l* of 5% aqueous sodium carbonate and twice with 40 m*l* of 10% aqueous sodium chloride, dried over magnesium sulfate, concentrated by distillation, and evaporated *in vacuo* to give 0.0407 g of bitropyl (0.224 mmol, 20.0% yield), identified by the superimposability of the infrared spectrum on that of the authentic sample.

The Reduction of the Tropylium Ion in an Aqueous Solution with Low-Valent Metallic Ions. The results are shown in Table 2; the details of the procedure are illustrated in the following description of a run which affords a small amount (<1% yield) of the reduction product.

The Reduction of the Tropylium Ion in an Aqueous Solution with Ferrous Chloride. In a 50-m*l*, round-bottomed flask equipped with a magnetic stirring bar, a thermometer, a rubber serum bottle cap, and a nitrogen inlet and outlet, 0.322 g of tropylium fluoroborate (1.81 mmol) was dissolved in 6.0 m*l* of 0.1 N aqueous hydrochloric acid and then kept under an atmosphere of nitrogen. The aqueous solution of ferrous chloride was prepared by dissolving 1.067 g of $FeCl_2 \cdot 4H_2O$ (5.37 mmol) in 12.1 m*l* of 0.1 N aqueous hydrochloric acid. The ferrous chloride solution was added with a syringe through the rubber serum cap to a stirred solution of tropylium fluoroborate. A specific change in neither the color nor reaction temperature was observed. The solution was stirred under nitrogen at 18.0—20.0°C for two hours and then extracted with three 20-m*l* portions of ether. The amount of the unchanged tropylium ion was determined from the ultraviolet absorbance (*vide supra*) of the aqueous layer (102% of the charged tropylium ion). The organic layer was washed with a 40-m*l* portion of 5% aqueous sodium carbonate and with two 50-m*l* portions of 10% aqueous sodium chloride, and was then dried over magnesium sulfate. The dried ethereal solution was concentrated and evaporated *in vacuo* to give 0.0027 g of a colorless oil, which was shown to be a mixture of bitropyl, benzaldehyde, and other minor components by a study of the infrared spectrum. The t.l.c. analysis of the oily product with the authentic bitropyl showed that the bitropyl content was *ca.* 38 wt% of the oil; 0.0055 mmol, 0.6% yield, based on the charged tropylium ion.

The Reduction of the Tropylium Ion and the Triphenylmethyl Cation in an Acetonitrile Solution with Metallic Powders. The results are shown in Table 3; the reaction of the tropylium ion with the metallic powder was carried out at room temperature for 10 min under nitrogen and worked up in a manner similar to that described above. The details of the procedure in the reaction of the triphenylmethyl cation are illustrated in the following description of a representative run with metallic iron.

The Reduction of the Triphenylmethyl Cation in an Acetonitrile Solution with Iron. In a 50-m*l*, round-bottomed flask equipped with a magnetic stirrer, a thermometer, and a nitrogen inlet and outlet there was placed a 0.504-g portion of triphenylmethyl fluoroborate (1.53 mmol). In a stream of nitrogen 15.3 m*l* of acetonitrile was added, and a clear, orange colored solution was obtained by magnetic stirring; the initial concentration of the triphenylmethyl cation was 0.100 N. To the stirred solution there was then added a 1.299-g portion of iron powder (150—250 mesh) (23.3 mg atom) under an atmosphere of nitrogen at 20.5°C. The reaction temperature rose by 4.1°C within two minutes and remained almost constant for the rest of the reaction time. With the increase in the temperature, it was observed that a white precipitate appeared and was dispersed throughout the reaction vessel. After the reaction time of 10 min, 10-m*l* portions of water and ether were added to the reaction mixture with continuous stirring in order to stop the reaction by the hydrolysis of the unchanged cation. The reaction mixture was filtered and washed with three 10-m*l* portions of ether in a stream of nitrogen. Air was then bubbled into the pale yellow organic layer. A white precipitate was formed with the simultaneous disappearance of the yellow color of the solution. This precipitate was filtered, washed with ether, and dried at 60°C under reduced pressure (5 mmHg) to give 0.272 g of white, powdery crystals, identified as triphenylmethyl peroxide by the superimposability of the infrared spectrum; 0.524 mmol, 68.6% yield. The organic layer of the

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21) K. Conrow, "Organic Syntheses," Vol. 43, p. 101 (1963).

22) E. Müller and H. Fricke, *Ann.*, **661**, 38 (1963).

23) H. J. Dauben, Jr., L. R. Honnen and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

24) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart (1954), p. 765.

filtrate was separated, washed with a 80-m*l* portion of 5% aqueous sodium carbonate and with two 80-m*l* portions of 10% aqueous sodium chloride, and dried over magnesium sulfate. The dried ethereal solution was concentrated by distillation and evaporated *in vacuo* to give 0.117 g of white crystals; the crystals were identified as triphenylcarbinol by a study of the infrared spectrum; 0.448 mmol, 29.3% yield.

The authors wish to thank Professor W. von E. Doering of Harvard University for his encouragement and interest.