m.p. 140–142° (C, 52.22; H, 4.28) was prepared by oxidation of the corresponding dithioacetal, while II–IV were obtained by carbethoxylation of the related methylene disulfones VI–VIII with sodium hydride and ethyl chlorocarbonate: II, m.p. 153–154° (C, 43.49; H, 4.11) from VI, m.p. 166–167° (C, 41.61; H, 3.54); III, m.p. 187–189° (C, 46.88; H, 8.29) from VII, m.p. 110–111° (C, 46.65; H, 8.65); IV, m.p. 90–91° (C, 29.85; H, 4.25) from VIII, m.p. 210–211° (reptd.[4] 204°). The pK_a's[5] of I–IV are listed in Table I. Comparison

TABLE I

Compound	I	II	III	IV
pK_a[5]	4.60	3.35	5.75	4.00

of II and IV shows that no significant effect results from the presence of the unsaturated substituent in II; only a small effect is apparent in the comparison of I and III as well, although here Case I conjugation is not geometrically required.

Furthermore, the comparison of III with IV, and perhaps of I with II, show that there is no large energetic disadvantage to the restriction of the cyclic compounds to Case I conjugation, so if the open-chain compounds utilize the Case II mode at least the preference cannot be large. Finally the pK_a of II shows that no particular effect attends the formation of a cyclic conjugated anion, so that apparently a new aromatic system has not been formed.

I, R = CO₂C₂H₅
V, R = H

II, R = CO₂C₂H₅
VI, R = H

III, R = CO₂C₂H₅
VII, R = H

IV, R = CO₂C₂H₅
VIII, R = H
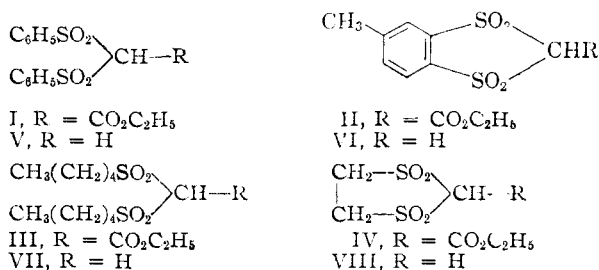
It is interesting that we find the pK_a of V to be 11.5 while that of VI is greater than 13. Thus the order of stability of these systems is reversed when the carbethoxyl group is missing. This may reflect a changed hybridization at carbon when the substituent no longer demands sp²–p hybridization, and we are further investigating systems of this type. However, it is clear from our results that a large extra conjugation effect, such as was predicted from the Koch and Moffitt treatment of Case I interaction between a carbon 2p orbital and the sulfone hybrid orbitals, is not found experimentally.

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(4) E. Baumann and G. Walter, Ber., 26, 1124 (1893).

(5) The pK_a's were determined in a standard fashion. An accurately weighed sample of the compound (0.5 mmole) was dissolved in 13.5 ml. of acetonitrile, 9 ml. of water was added, and the titration was performed at 26° under nitrogen by adding 0.206 N aqueous sodium hydroxide and observing the pH with a Beckmann model G pH meter and E-2 glass electrode. Smooth classical titration curves were obtained. Duplicate runs agreed within 0.05 pH unit, and back titration with hydrochloric acid and recovery of the unchanged starting materials establish the reversibility of the titrations. Of course, these pK's cannot be referred directly to dilute aqueous solution.

SALTS OF THE HEPTAPHENYLTROPYLIUM ION AND THEIR STABILITY

Sir:

In a recently reported study,[1] Breslow and co-workers investigated the effect of phenyl substituents on the stabilities of the triphenyl- and di-phenylcyclopropenyl cations. Unfortunately, in this series a direct comparison with the as yet unknown, unsubstituted cyclopropenyl cation is not possible. In the tropilidene series, however, the stabilities of various aryl or alkyl substituted tropylium ions may be conveniently related to the stable tropylium ion.[2] Consequently, phenyl substituted tropylium ions have immediate interest in connection with the effect of phenyl groups on stable carbonium ions, and in this Communication we wish to report our observations on the synthesis and stability of heptaphenyltropylium bromide (Ia), tribromide (Ib), and fluoroborate (Ic), the first reported persubstituted tropylium salts.

The treatment of a carbon tetrachloride solution of heptaphenyltropilidene (II),[3] obtained from the Diels–Alder reaction of tetraphenylcyclopentadienone and triphenylcyclopropene, with a slight excess of bromine resulted in the slow liberation of hydrogen bromide and the formation of an amor-

Ia, X = Br
Ib, X = Br₃
Ic, X = BF₄

IIIa, R = H
IIIb, R = CH₃
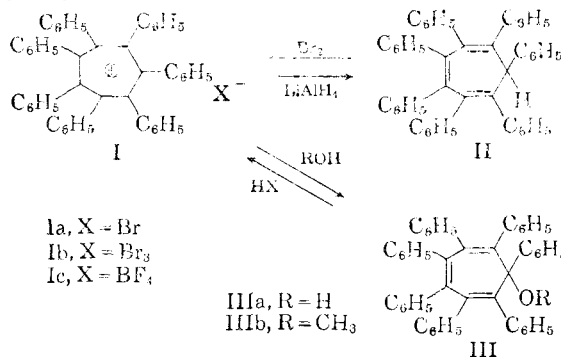
phous yellow solid (mainly the tribromide Ib), m.p. ca. 270° (dec.), λ_{max}^{MeCN} (log ε), 250 (4.96), 268 (4.67) mμ. Digestion of this solid in acetonitrile, containing a few per cent. of acetone to remove positive bromine, converted the amorphous material to bright red needles of the bromide Ia, m.p. 265–270° (dec.), slightly soluble in acetonitrile and chloroform, insoluble in benzene, ether, acetone and water, λ_{max}^{MeCN}, 250 (4.96), 284 (sh.) (4.22) mμ. Anal. Calcd. for C₄₉H₃₅Br: C, 83.63; H, 5.01; Br, 11.36. Found: C, 83.78; H, 4.75; Br, 11.53. When a 5:1 mole excess of bromine was used, with recrystallization of the yellow product from chloroform–acetonitrile, reddish–orange prisms were obtained, m.p. 270–272° (dec.) (λ_{max}^{MeCN}, 250 (4.96), 268 (4.82) mμ. Anal. Calcd. for C₄₉H₃₅Br₃: C, 68.15; H, 4.08; Br, 27.77. Found: C, 68.26; H, 4.29; Br, 27.71), whose analysis and spectral properties[4] confirm its tribromide structure Ib.

(1) R. Breslow, J. Lockhart and H. W. Chang, J. Am. Chem. Soc. 83, 2375 (1961).

(2) W. v. E. Doering and L. H. Knox, ibid., 76, 3203 (1954).

(3) M. A. Battiste, Chemistry and Industry, 550 (1961).

(4) Popov and Swenson (J. Am. Chem. Soc., 77, 3724 (1955)) have found the ultraviolet absorption maximum for the tribromide ion (as tetra-n-butylammonium tribromide) at 269 mμ (log ε 4.74) in acetonitrile solvent.

As expected, acetonitrile solutions of Ia and Ib have instantaneous precipitates of silver bromide on treatment with silver nitrate reagent. More importantly, lithium aluminum hydride reduction of an ether suspension of Ia regenerated hepta-phenyltropilidene in high yield.

The infrared spectra (KBr pellets) of the salts Ia and Ib (and the yellow bromination product before digestion or recrystallization) were closely similar to the spectrum of heptaphenyltropilidene (II) with three important differences: (i) in the C–H stretch region Ia and Ib show a single absorption band at 3040 cm.$^{-1}$, whereas II and other covalent heptaphenyltropyl derivatives have an additional absorption band at 2990–3000 cm.$^{-1}$ of slightly greater intensity; (ii) the major absorption band for the salts Ia and Ib occurs at 1325 and 1315 cm.$^{-1}$, respectively, a region in which II has only weak absorption; (iii) a strong absorption band observed at 760 ± 3 cm.$^{-1}$ for all covalent heptaphenyltropilidenes is totally absent in the spectra of Ia and Ib though the normal aromatic bands at 780, 720 and 695 cm.$^{-1}$ appear undisturbed. These relatively simple spectral changes offer strong support for the symmetrically delocalized ion represented in structure I.[5]

Addition of small amounts of water or methanol to dark red acetonitrile solutions of Ia (or Ib) resulted in rapid decolorization and the formation of, respectively, heptaphenyltropyl alcohol (IIIa), m.p. 233–236° (rapid heating[6]) (λ_{max}^{MeCN}, 258 (4.41), 293 (sh.) (4.16) mμ. Anal. Calcd. for C$_{49}$H$_{36}$O: C, 91.84; H, 5.66. Found: C, 91.96; H, 5.75), and methyl ether (IIIb), m.p. 229–232° (λ_{max}^{MeCN}, 256 (4.42), 293 (sh.) (4.14) mμ. Anal. Calcd. for C$_{50}$H$_{38}$O: C, 91.71; H, 5.85. Found: C, 91.92; H, 6.11), in good yield. Both covalent derivatives are excellent precursors of heptaphenyltropylium salts which they generate on treatment with the corresponding acid. Accordingly, fluoroboric acid in acetonitrile–acetic anhydride solvent quantitatively converted IIIa to the yellow-orange fluoroborate salt Ic, m.p. 267–272° (dec.) (λ_{max}^{MeCN}, 250 (4.98), 285 (sh.) (4.20) mμ. Anal. Calcd. for C$_{49}$H$_{35}$BF$_4$: C, 82.82; H, 4.96. Found: C, 82.77; H, 5.13). The infrared spectrum of Ic was identical in detail to the spectra of the other salts, Ia and Ib, except for the region 1025–1125 cm.$^{-1}$ where the fluoroborate ion absorbs strongly.

Solubility difficulties encountered with the salts of I have thus far prevented determination of a meaningful value of the pK_a of the heptaphenyl-tropylium ion; however, ultraviolet spectral studies have established that the pK_a of the unsubstituted tropylium ion is greater than that of the hepta-phenyltropylium ion in 50% methanolic acetonitrile by at least 3 pK units. Thus, in this solvent, the unsubstituted tropyl methyl ether was ionized completely to tropyl cation by 0.01 N fluoroboric acid, while heptaphenyltropyl methyl ether was less than 10% ionized at 1 N concentrations of

acid. In acetonitrile IIIb was converted entirely to cation I at 10^{-3} N and greater concentrations of fluoroboric acid.

Clearly, the substitution of phenyl groups for the hydrogens of the tropylium ion has decreased the stability of I, probably as a result of the increased importance of the phenyl inductive effect. Normally swamped by a much larger conjugative effect, the inductive effect becomes increasingly important in I as π-conjugation is disrupted by non-co-planarity of the seven phenyl rings with the tropylium ring. This inductive effect is probably the major factor affecting the relative stability of I and III since the extra resonance stabilization of I and the covalent heptaphenyltropyl derivative III due to the phenyls are not likely to be very different.[7]

Helpful discussions with Professor S. Winstein during the course of this work are gratefully acknowledged.

(7) Solvation factors will also affect this equilibrium between ionic and covalent forms; however, only a qualitative assessment of this effect can be made for a given solvent.

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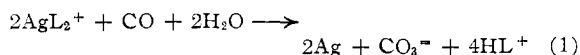LOS ANGELES 24, CALIFORNIA
RECEIVED AUGUST 21, 1961

REDUCTION OF SILVER AMINE COMPLEXES BY CARBON MONOXIDE

Sir:

The reduction of Ag$^+$ by CO in aqueous perchloric acid solution is very slow and attains measurable rates only at elevated temperatures ($>100°$) and pressures. We have found, however, that the addition of ammonia or of organic amines to the solution, to raise the pH and complex the silver ions, enhances the reactivity of the latter to a remarkable degree so that reduction proceeds readily at room temperature and atmospheric pressure. We report here the results of some preliminary kinetic measurements on these systems which suggest an explanation for this effect.

The experimental procedure was essentially similar to that employed in an earlier study[1] of the reduction of silver amines by H$_2$, except that the rates with CO were somewhat higher and, in most cases, the conditions employed correspondingly milder. In a typical experiment, CO at atmospheric pressure was bubbled through a solution, containing initially 0.01 M AgClO$_4$, 0.2 M CH$_3$NH$_2$ and 0.1 M CH$_3$NH$_3$$^+ClO_4$$^-$, at 25°; reduction to metallic silver proceeded smoothly with a half-time of about 40 min. In this and all the other kinetic experiments the concentration of free amine was sufficiently high so that the silver was present in solution predominantly as the diamine complex, AgL$_2$$^+$ (where L denotes amine). The over-all reaction under these conditions is thus represented by

$$2AgL_2^+ + CO + 2H_2O \longrightarrow 2Ag + CO_3^- + 4HL^+ \quad (1)$$

(1) J. Halpern and J. B. Milne, Proc. 2nd Intern. Cong. Catalysis, Paris, 1960, Vol. 1, p. 445.

(5) Preliminary attempts to confirm this conclusion by proton magnetic resonance spectrometry were not successful because of the low solubilities of salts of I in the appropriate solvents.

(6) At moderate heating rates partial melting occurred at 215–220°, but no further change was noted up to 350°. Hexaphenylbenzene has been isolated from this thermal reaction in good yield as will be reported on later.