Tetrahedron Letters No.25, pp. 2951-2954, 1968. Pergamon Press. Printed in Great Britain.

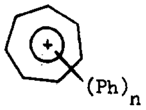
SYNTHESIS AND RELATIVE STABILITIES OF HEXAPHENYL- AND 1,2,3,4-TETRAPHENYLTROPYLIUM CATIONS[1]

Merle A. Battiste[2a] and Thomas J. Barton[2b]
Department of Chemistry, University of Florida
Gainesville, Florida

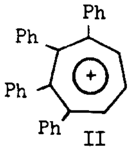
(Received in USA 26 February 1968; received in UK for publication 21 March 1968)

Previous studies of phenyl substituted tropylium[3] and cyclopropenylium[4] cations have indicated relatively little interaction of the phenyl substituent (s) with the central charged ring in the ground state. In a few cases[3a,c,e] phenyl substitution was reported to exert an apparent destabilizing effect particularly when the phenyl group could not achieve coplanarity with the charged ring. In order to further examine this curious "phenyl effect" and to provide more quantitative data on twisted phenyl interactions with stable carbonium ions, we have prepared the interesting hexaphenyl- and tetraphenyltropylium ions I and II and now describe their spectral properties and relative stabilities compared to the previously reported heptaphenyl ion III.[3a]

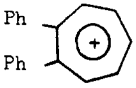
After limited success with other synthetic routes the following method was developed for the synthesis of the hexaphenyltropylium cation (I). Hexaphenylcycloheptatrienecarboxylic acid (IV),[5] m.p. 252.5 - 254°, λ_{max}^{MeCN} 260 mμ (log ε 4.31), prepared from the Diels-Alder reaction of 2,3-diphenylcyclopropenecarboxylic acid and tetraphenylcyclopentadienone, was oxidatively decarboxylated with lead tetraacetate according to Corey's procedure[6] to give high yields (>90%) of hexaphenylcycloheptatrienyl acetate (V),[5] m.p. 185° λ_{max}^{MeCN} 262 mμ (4.19). This acetate was quantitatively converted to the bright yellow hexaphenyltropylium perchlorate (I, ClO_4^-),[5] m.p. 228° λ_{max}^{MeCN} 244 (4.97), 273 (4.28), 322 mμ (4.13), by addition of concentrated perchloric acid to a cold solution of V in 50% acetonitrile-acetic anhydride. The NMR spectrum of I in trifluoroacetic acid showed three phenyl spikes of approximately equal area at τ 2.75, 3.0[illegible], and 3.17 corresponding to the three types of twisted phenyls in I. In comparison the 1,2-diphenyltropylium[3b] and heptaphenyltropylium ions VI and III show singlet phenyl proton absorption at



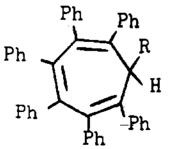
I, n = 6
III, n = 7
IX, n = 1



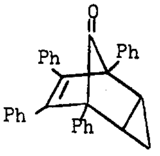
II



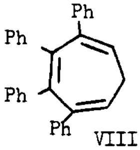
VI



IV, R = CO_2H
V, R = OAc



VII



VIII

τ 2.60 and 3.14 respectively. The higher field aromatic signals for I are thus assigned to the protons of the inner phenyl rings which are internally shielded by the neighboring twisted phenyls. The lone tropylium ring proton of I appeared as a singlet at τ 0.78 as expected. Oxidation of I with hydrogen peroxide[7] afforded hexaphenylbenzene as the only isolable product.

The perchlorate of the 1,2,3,4-tetraphenyltropylium cation (II) was synthesized in high yield by the following three step sequence. Freshly generated cyclopropene[8] was bubbled into a stirred chloroform solution of tetraphenylcyclopentadienone at room temperature until disappearance of the characteristic purple color of the dienone. Workup afforded an 82% yield of a colorless, micro-crystalline ketone (VII),[5] m.p. 168° after gas evolution and resolidification at 155°, $\nu_{C=O}$ 1778 cm^{-1}. Decarbonylation of VII under vacuum at 135 - 140° for 4 hours afforded hydrocarbon VIII,[5] m.p. 168° (no gas evolution at 155°), λ_{max}, 245 mμ (4.40). Hydride abstraction from VIII with trityl perchlorate in acetonitrile[9] gave, after workup and recrystallization from methylene chloride-ether, a 63% yield of bright yellow tetraphenyltropylium perchlorate (II, ClO_4^-),[5] m.p. 157° (dec.) λ_{max}^{MeCN}, 238 (4.8), 275 (4.1), 351 mμ (3.9). The NMR spectrum of II in trifluoroacetic acid revealed two sharp phenyl proton spikes of equal intensity at τ2.76 and 3.07 in accord with the successive arrangement of twisted phenyl groups on the tropylium ring. The protons on the seven-membered ring appeared as a singlet at τ 0.94.

The pK's of cation I - III were determined spectroscopically in sulfuric acid-methanol solutions using the diphenylcyclopropenium cation (pK = 0.32 in water[4b]) as indicator.[10] Examination of the pK values in Table I reveals a marked effect of phenyl substitution on the

TABLE I

pK Data for Some Phenyltropylium Cations

Cation	Solvent	pK	Reference
Tropylium (C_7^+)	H_2O	4.7	a
	50% MeCN-H_2O	4.01	3c
PhC_7^+ (IX)	50% MeCN-H_2O	3.87	3c
$Ph_4C_7^+$ (II)	MeOH-H_2SO_4	0.13[b]	this work
$Ph_6C_7^+$ (I)	MeOH-H_2SO_4	-1.11[b]	this work
$Ph_7C_7^+$ (III)	MeOH-H_2SO_4	-0.54[b]	this work

[a] W. von E. Doering and L. H. Knox, J. Am. Chem. Soc., 76, 3203 (1954).

[b] pK value adjusted to the water scale.

half-neutralization point of the tropylium ion, but unfortunately reveals very little about the relative free energies of the ions in question. In order to assess the effect of a given phenyl substituent one must evaluate its stabilizing effect on the covalent tropilidene system as well as the corresponding cation. Cairncross has recently presented convincing evidence that although the pK of IX is less than that of the tropylium ion by ca. 0.1 - 0.5 pK units, the phenyl group actually stabilizes the ion by 4.4 kcal./mole[3b] compared to 3.7 kcal./mole stabilization provided by a methyl group.[11] The greater acidity of ions I - III cannot then be ascribed entirely to phenyl destabilization by the often invoked phenyl inductive effect.

A further point of interest is the higher pK of the heptaphenyl ion compared to the hexaphenyl ion. Since the seventh phenyl in the heptaphenyl system cannot make a resonance contribution to the covalent compound but only to the cation, this result could be construed as evidence for a stabilization effect provided by a severely twisted phenyl. However, steric crowding in covalent heptaphenyltropyl derivatives is more severe than in the corresponding hexaphenyl compounds, and relief of steric crowding on ionization may well be the important factor in this comparison.

Financial support of this work by the National Science Foundation (Grant Nos. GP-3352 and GP-254) and, in part, the Air Force Office of Scientific Research (Grant No. AF-AFOSR-738-67) is gratefully acknowledged.

REFERENCES

1. (a) Part V in the series Polyaryltropilidenes; (b) Part IV, M. A. Battiste, *J. Am. Chem. Soc.*, **85**, 2175 (1963).
2. (a) Alfred P. Sloan Foundation Fellow, 1967 - 1969; (b) Gulf Oil Corporation Fellow, 1964 - 1965.
3. (a) M. A. Battiste, *J. Am. Chem. Soc.*, **83**, 4101 (1961).
    (b) A. Cairncross, Ph.D. Dissertation, Yale Univ., 1963.
    (c) C. Jutz and F. Voithenleitner, *Ber.*, **97**, 29 (1964).
    (d) M. W. Couch, M. S. Thesis, Univ. of Florida, 1966, and unpublished work.
    (e) G. Berti, *J. Org. Chem.*, **22**, 230 (1957).
4. (a) R. Breslow and H. W. Chang, *ibid.*, **83**, 2367 (1961).
    (b) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961).
    (c) R. Breslow, H. Hover, and H. W. Chang, *ibid.*, **84**, 3168 (1962).
5. Satisfactory carbon and hydrogen analyses were obtained for all new compounds reported.
6. E. J. Corey and J. Casanova, Jr., *J. Am. Chem. Soc.*, **85**, 165 (1963).
7. M. E. Vol'pin, D. N. Kursanov, and V. G. Dulova, *Tetrahedron*, **8**, 33 (1960).
8. G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966).
9. H. J. Dauben, F. A. Gadecki, D. L. Pearson, and K. M. Harmon, *J. Am. Chem. Soc.*, **79**, 4557 (1957).
10. (a) pK determinations in aqueous solvent systems failed due to the extreme insolubility of the covalent alcohols in these solvents. We are aware, of course, of the many hazards associated with pK determinations in non-aqueous media;[10b] however, for the comparisons involved we feel our results are probably as meaningful as most pK values obtained for carbocyclic ions in aqueous media; (b) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).
11. K. Conrow, *J. Am. Chem. Soc.*, **83**, 2343 (1961).