

responding to the molecular weight of the 1:1 adduct. Drying of this "2:1 adduct" for 5 days at 110° *in vacuo* over P<sub>2</sub>O<sub>5</sub> resulted in complete loss of one molecule of ethanol to give the 1:1 adduct II (R = CH<sub>3</sub>; R' = H); its nmr spectrum (DMSO-*d*<sub>6</sub>) was identical with that of the "2:1 adduct" except for loss of one of the two OH signals and the ethyl signals at δ 0.9 and 4.1. The uv spectra of the 1:1 adduct and its ethanolate were identical ( $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  (m $\mu$  (log  $\epsilon$ )) 239 (4.07), 288 (3.94)) and almost superimposable with the spectrum of the 6,7-dihydro compound III.<sup>3</sup>

Irradiation of I under similar conditions in 2-propanol gave III (6% yield) and the 1:1 adduct II (R = R' = CH<sub>3</sub>) (64% yield, mp 190° dec; ir (KBr) 3380 (sh), 3260 (NH and OH), 1655 cm<sup>-1</sup> (NHCOCH<sub>3</sub>); nmr (DMSO-*d*<sub>6</sub>) δ 1.08, 1.35 (each 3 H, C(CH<sub>3</sub>)<sub>2</sub>),<sup>4</sup> 1.80 (3 H, CH<sub>3</sub>CONH), 5.23 (1 H, OH), 7.55 (3 H, aromatic multiplet), 7.94 (2 H, aromatic multiplet), 8.42 and 8.60 (each 1 H, broad, CH<sub>3</sub>CONH and NH); uv  $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  (m $\mu$  (log  $\epsilon$ )) 239 (4.11), 292 (3.96)). Analogously, the 1:1 adduct II (R = R' = H) was obtained by irradiation of I under similar conditions in methanol (61% yield, mp 224–225° dec; ir (Nujol) 3460, 3350, 3270 (OH, NH), 1665 cm<sup>-1</sup> (CH<sub>3</sub>CONH); nmr (DMSO-*d*<sub>6</sub>) δ 1.75 (3 H, CH<sub>3</sub>CONH), 3.86 (2 H, diffuse doublet, *J* = 7 Hz, CH<sub>2</sub>OH), 5.41 (1 H, OH), 7.58 (3 H, aromatic multiplet), 8.05 (2 H, aromatic multiplet), 8.85 and 9.05 (each 1 H, broad, NH and CH<sub>3</sub>CONH)).

Finally, prolonged (72 hr) irradiation of I in *t*-butyl alcohol surprisingly gave the 1:1 adduct IV (35% yield, mp 192–193.5° dec; ir (KBr) 3525, 3515, 3420 (sh), 3300 (NH and OH), 1660 cm<sup>-1</sup> (CH<sub>3</sub>CONH); uv  $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  (m $\mu$  (log  $\epsilon$ )) 239 (4.12), 290 (3.98); nmr (DMSO-*d*<sub>6</sub>) δ 0.95 (6 H, singlet, C(CH<sub>3</sub>)<sub>2</sub>), 2.35 (2 H, multiplet, CH<sub>2</sub>C(OH)(CH<sub>3</sub>)<sub>2</sub>), 1.70 (3 H, singlet, CH<sub>3</sub>CONH), 4.35 (1 H, broad singlet, OH, deuterium exchangeable), 7.5–7.9 (5 H, aromatic multiplet), 8.6 and 8.9 (each 1 H, broad, CH<sub>3</sub>CONH and NH, deuterium exchangeable), in which a methyl group has added across the 6,7-amidine C=N bond.

Using as input the precise bond lengths found for 7-aminofurazano[3,4-*d*]pyrimidine,<sup>5</sup> MO calculations were carried out on this system.<sup>6</sup> Of particular interest to the present results are the localization indices, *L<sub>r</sub>*, obtained in this way for the carbon atoms at positions 3a, 5, 7, and 7a (see structure I). The calculated values

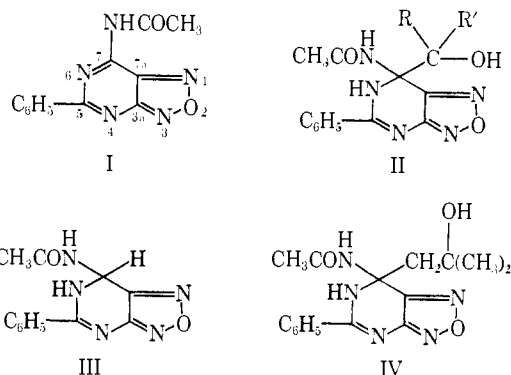
(3) It has previously been reported that alcohols may be added photochemically to an azomethine (C=N) bond in purine (H. Linschitz and J. S. Connolly, *J. Am. Chem. Soc.*, **90**, 2979 (1968)), quinolines and isoquinolines (F. R. Stermitz, C. C. Wei, and W. H. Huang, *Chem. Commun.*, 482 (1968); F. R. Stermitz, R. P. Seiber, and D. E. Nicodem, *J. Org. Chem.*, **33**, 1136 (1968)), pyrimidines and pyrazolo[3,4-*d*]pyrimidines (M. Ochiai and K. Morita, *Tetrahedron Letters*, 2349 (1967); M. Ochiai, E. Mizuta, Y. Asahi, and K. Morita, *Tetrahedron*, **24**, 5861 (1968)), and 9,4a-dialkyl-1,2,3,4-tetrahydrocarbazolenium salts (P. Cerutti and H. Schmid, *Helv. Chim. Acta*, **45**, 1992 (1962)) to give  $\alpha$ -hydroxyalkyl derivatives, which in some cases are isolable and in others dehydrate to the C-alkyl heterocycle. Addition to an amidine C=N bond, however, is unprecedented and unexpected.

(4) Nonequivalence of the two methyl groups is ascribed to restricted rotation about the C<sub>7</sub>-C bond; an analogous nonequivalence has been observed in the photoadduct of 2-propanol to purine (Linschitz and Connolly<sup>3</sup>).

(5) We are indebted to Professor Eli Shefter, Department of Pharmacuetics, School of Pharmacy, State University of New York at Buffalo, for the X-ray analysis, details of which will be the subject of a separate paper.

(6)  $\beta$  proportional to *S* (R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949)), variation of  $\alpha$  (A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, p 135); complete inclusion of overlap (P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950)).

were found to be 4.07, 3.19, 2.17, and 4.36  $\beta$ , respectively (*cf.* benzene (2.5) and anthracene (2.0),<sup>7a</sup> styrene (terminal position) (1.7),<sup>7b</sup> and purine, which undergoes photoaddition of alcohols to the 6-position<sup>3</sup> (2.329)<sup>8</sup>). The *L<sub>r</sub>* difference between positions 7 and 5 (1.02  $\beta$ ) represents a relative reactivity difference<sup>7c</sup> to  $\cdot\text{CCl}_3$  in the neighborhood of 10<sup>12</sup>; while the 5-phenyl and 7-acetamido groups of I would undoubtedly affect these values to some extent, this overwhelming propensity toward radical reaction at the 7 position correlates extremely well with our observed quantitative attack at position 7 both in photoreduction and photoaddition reactions.



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(7) *Cf.* Streitwieser:<sup>6</sup> (a) p 399; (b) p 408; (c) p 399 ff.

(8) B. Pullman, *J. Chem. Soc.*, 1621 (1959).

(9) On leave from the Gifu College of Pharmacy, Gifu, Japan.

(10) National Science Foundation Predoctoral Fellow, 1967–1969.

Edward C. Taylor, Yoshifumi Maki,<sup>9</sup> Ben E. Evans<sup>10</sup>

Department of Chemistry, Princeton University  
Princeton, New Jersey 08540

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## The *pK<sub>a</sub>* of Triphenylcyclopropene. Electrochemical Determination of an Inaccessible Equilibrium Constant

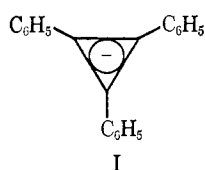
Sir:

We have earlier reported<sup>1</sup> kinetic evidence that triphenylcyclopropene is considerably less acidic than is triphenylmethane; no conditions were found in which triphenylcyclopropenyl anion (I) could be demonstrated to be even a transient intermediate. The situation is related to the low kinetic acidities of other cyclopropene derivatives.<sup>2</sup> However, with electrophilic carbonyl, sulfone, and cyano groups<sup>2</sup> the hybrid structure of the anion leaves less of the charge on the three-membered ring; antiaromatic destabilization of the cyclopropenyl anion system should manifest itself even more strongly with only the three electron-accepting phenyl substituents in I. Thus, the *pK<sub>a</sub>* of triphenyl-

(1) R. Breslow and P. Dowd, *J. Amer. Chem. Soc.*, **85**, 2729 (1963).

(2) R. Breslow, J. Brown, and J. J. Gajewski, *ibid.*, **89**, 4383 (1967); R. Breslow and M. Douek, *ibid.*, **90**, 2698 (1968); R. Breslow, *Angew. Chem. Intern. Ed. Engl.*, **7**, 565 (1968).

cyclopropene is of particular interest. Since direct methods for determining this  $pK_a$  have failed, we have devised a novel indirect method in which electrochemical data are used in a thermodynamic pseudocycle.



The fundamental idea is that the equilibrium constant for conversion of a covalent cyclopropene to the cyclopropenyl anion can be determined from (a) the equilibrium constant for conversion to the cyclopropenyl cation together with (b) the electrochemical potentials for reversible reduction of the cation through the radical to the anion. The virtue of this approach derives from the wide ranges of energy available electrochemically and the fact that modern techniques involving high-frequency scanning permit the determination of thermodynamic reversible potentials even for very reactive species. Linear scan voltammetry, with a hanging mercury drop electrode, and chronopotentiometry were used with a standard three-electrode cell. Solutions were 1 mM in the carbonium ion fluoroborates, in purified hexamethylphosphoramide with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The reference electrode, a silver wire in 0.1 M silver perchlorate in hexamethylphosphoramide, has a potential of +0.32 V vs. the saturated calomel electrode.

Triphenylmethyl fluoroborate shows a one-electron reversible wave at  $-0.08$  V by either rapid method, and in this case even direct current polarography is reversible. This agrees well with our previous finding<sup>3</sup> of  $-0.09$  V in acetonitrile. Triphenylcyclopropenyl fluoroborate gave irreversible waves with direct current polarography, as we have reported,<sup>3</sup> but linear scan voltammetry over the frequency range 30–100 Hz gave well-defined one-electron cathodic and anodic waves, from which  $E_{1/2}$  was  $-1.11 \pm 0.02$  V. Chronopotentiometry affords a reversible  $E_{1/2}$  of  $-1.12$  V. This agrees with our previous report of  $E_{1/2}$  of  $-1.13$  V in acetonitrile for reduction of triphenylcyclopropenyl cation to triphenylcyclopropenyl radical. Controlled potential electrolysis of the cation has been found<sup>4</sup> to yield the dimer of triphenylcyclopropenyl radical. Thus, as we have concluded previously,<sup>3</sup> it is approximately 1 V more difficult to reduce triphenylcyclopropenyl cation to the radical than to reduce triphenylmethyl cation.

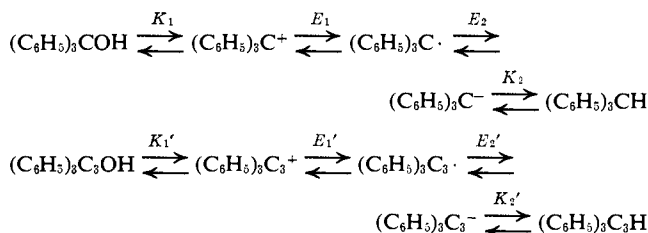
By simple molecular orbital theory this 1.0-V difference between the two systems should also be found for the addition of the next electron to the same orbitals, to form carbanions. In fact, we find a second reversible one-electron wave for the triphenylmethyl system with  $E_{1/2} - 0.83$  V, but for triphenylcyclopropenyl the second wave, again by linear scan voltammetry, has  $E_{1/2} - 1.56 \pm 0.02$  V. Thus it is again more difficult to add an electron to the triphenylcyclopropenyl system, but the difference is only 0.7 V, which must reflect a decreased electron repulsion in the larger cyclopropenyl system.

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

(4) W. Bahary, Ph.D. Thesis, Columbia University, 1961.

These data can be combined with the known  $pK_{R^+}$ 's of triphenylmethyl<sup>5</sup> and triphenylcyclopropenyl<sup>6</sup> cation and the  $pK_a$  of triphenylmethane<sup>7</sup> to calculate a  $pK_a$  for triphenylcyclopropene. The argument is shown in outline form in Scheme I. The essential point is that the

#### Scheme I



equilibrium constants for carbanion formation from the hydrocarbons ( $K_2$  and  $K_2'$ ) can also be calculated if thermodynamic data are available for the sequence:  $R-H \rightleftharpoons R-OH \rightleftharpoons R^+ \rightleftharpoons R\cdot \rightleftharpoons R^-$ . We have data for all except the first step; our pseudocycle involves the approximation that the  $R-H \rightarrow R-OH$  energy change is the same for two different R's. Then the fact that  $(E_1 + E_2) - (E_1' + E_2') = 1.7$  V (39 kcal/mol, 28 pK units at room temperature) means that a  $K_1'/K_1$  ratio of  $10^{9.7}$  (triphenylcarbinol has<sup>5</sup>  $pK_{R^+} = -6.6$  and triphenylcyclopropenol has<sup>6</sup>  $pK_{R^+} = +3.1$ ) translates to a  $K_2'/K_2$  ratio of  $10^{-18.3}$ . Since triphenylmethane has<sup>7</sup>  $pK_a = 33$ , triphenylcyclopropene has  $pK_a = 51$ .

Although this is only an estimate, because of our assumption of constancy in the  $R-H \rightarrow R-OH$  energy change, variations in the relative heat of formation of hydrocarbons and alcohols are small enough<sup>8</sup> that the error is unlikely to exceed 3–4 pK units. Furthermore, the direction of the change is such that the increased electronegativity of a cyclopropene carbon<sup>9</sup> should destabilize the alcohol relative to the hydrocarbon, so the actual  $pK_a$  is somewhat greater than 51.

This  $pK_a$  for triphenylcyclopropene, considerably higher than at least some of the estimates<sup>10</sup> for simple methane, reflects striking instability of triphenylcyclopropenyl anion. Of course, our comparison with triphenylmethane does not remove the factor of angle strain in the cyclopropene, as was done in our earlier kinetic studies.<sup>2</sup> However, of the 20 units by which the  $pK_a$  of triphenylcyclopropene exceeds that of triphenylmethane, a substantial portion is undoubtedly a reflection of the antiaromaticity of cyclopropenyl anions.<sup>11</sup>

(5) N. Deno, J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3044 (1955).

(6) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961).

(7) D. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 19.

(8) Cf. the variations, using data in standard sources such as Y. Yukawa, "Handbook of Organic Structural Analysis," W. A. Benjamin, Inc., New York, N. Y., 1965. Of course, reversible formation of a carbanion from an alcohol is just as theoretically significant as from a hydrocarbon. The difference between a true  $pK_a$  and our pseudo  $pK_a$  would reflect differences in single-bond energies, not the conjugative effects with which we are concerned here.

(9) Cf. H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(10) Cram<sup>7</sup> cites two estimates of  $pK_a = 40$  and one of  $pK_a = 58$  for methane. The latter seems more likely.

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Ronald Breslow, K. Balasubramanian

Department of Chemistry, Columbia University  
New York, New York 10027

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