

out. A similar mechanism is suggested for anodic oxidation of endo alcohol **1c**.

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References and Notes

- P. T. Cottrell and C. K. Mann, *J. Electrochem. Soc.*, **116**, 1499 (1969).
- Thiane (pentamethylene sulfide) was reported¹ to show a peak potential of 0.55 V. However, under our conditions a peak potential of 1.32 V is found.
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- One diastereomer was preferentially produced.
- (a) S. Allenmark and C.-E. Hagberg, *Acta Chem. Scand.*, **22**, 1694 (1968); (b) S. Allenmark and C.-E. Hagberg, *ibid.*, **24**, 2225 (1970); (c) W. A. Pryor and H. T. Bickley, *J. Org. Chem.*, **37**, 2285 (1972); (d) D. Landini, F. Rolla, and G. Torre, *Int. J. Sulfur Chem., Part A*, **2**, 43 (1972); (e) D. Landini and F. Rolla, *J. Chem. Soc., Perkin Trans. 2*, 1317 (1972); (f) O. Bohman and S. Allenmark, *Tetrahedron Lett.*, 405 (1973); (g) T. Varkey, G. F. Whitfield, and D. Swern, *J. Org. Chem.*, **39**, 3365 (1974); (h) T. Numata and S. Oae, *Tetrahedron*, **32**, 2699 (1976).
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- The scan rate dependence of the cyclic voltammetric peak currents suggests an ECE mechanism. Rotating disk electrode data suggest faster chemical rates for **1a,c-e** than for the others. In these cases the currents approach those expected for an overall $2e^-$ process.
- Note that, even though the carboxylate group is the electron source in this mechanism, ultimately the sulfur atom is oxidized.
- For neighboring-group participation by sulfide in O-O bond homolysis, see W. G. Bentrupe and J. C. Martin, *J. Am. Chem. Soc.*, **84**, 1561 (1962); P. Livant and J. C. Martin, *ibid.*, **98**, 7851 (1976).
- No oxidation peak with a peak potential of <1.6 V was observed for the 2,6-di-*tert*-butylpyridine salt of 5-norbornene-2-*endo*-carboxylic acid in acetonitrile and using a $Ag/0.1$ M $AgNO_3$ in acetonitrile reference electrode.

Richard S. Glass,* John R. Duchek
Jacob T. Klug, George S. Wilson

Department of Chemistry, The University of Arizona
Tucson, Arizona 85721

Trifluoromethylated "Dewar" Pyrroles: 5-Azabicyclo[2.1.0]pentene-2 Ring System¹

Sir:

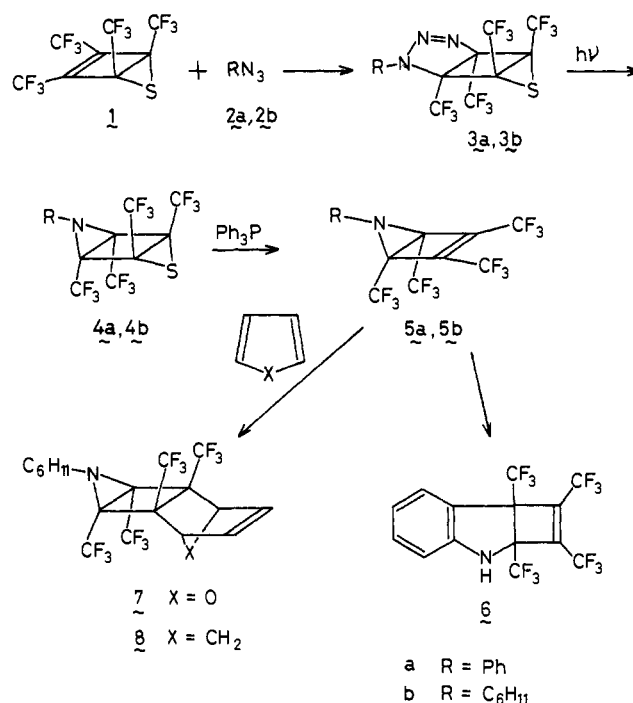
In previous papers,² we reported that 1,2,3,4-tetrakis(trifluoromethyl)-5-thiabicyclo[2.1.0]pentene-2, a "Dewar" thiophene (**1**), reacted as a dienophile with the conjugated dienes. In this report, we discuss the 1,3-dipolar cycloaddition of **1** and transformation of the adducts to "Dewar" pyrroles (Chart I).

Treatment of **1** with phenyl or cyclohexyl azide (**2a** or **2b**) in CH_2Cl_2 at room temperature gave the corresponding adduct (**3a** or **3b**).³ **3a**: 28.1% yield, mp 62–64 °C; IR ($CHCl_3$) 3020, 1600, 1500, 1290, 1185 cm^{-1} (no absorption near 1700 cm^{-1} ascribable to the cyclobutenic double bond²); ¹H NMR ($CDCl_3$) δ 7.43; ¹⁹F NMR ($CDCl_3$) δ -3.6 (3 F, m), -2.6 (3 F, m), -2.0 (3 F, m), 7.4 (3 F, m) ppm; ⁴ m/e 447 ($M - N_2$). **3b**: 81% yield, mp 59–60 °C; IR ($CHCl_3$) 2940, 2860, 1480, 1300, 1180, 1165 cm^{-1} ; ¹H NMR ($CDCl_3$) δ 3.68 (1 H, m, N-CH), 1.2–2.36 [10 H, m, $(CH_2)_5$]; ¹⁹F NMR ($CDCl_3$) δ -4.6 (3 F, m), -2.4 (3 F, m), 1.6 (3 F, m), 6.8 (3 F, m) ppm; m/e 453 ($M - N_2$).

Irradiation of **3a** or **3b** in *n*-pentane with a low-pressure mercury lamp caused elimination of a nitrogen molecule to give the valence-bond isomers of 1,4-thiazine, compounds of a new ring system (**4a** or **4b**). **4a**: 55% yield, colorless oil; IR ($CHCl_3$) 3040, 1600, 1290, 1170 cm^{-1} ; ¹H NMR ($CDCl_3$) δ 7.18; ¹⁹F NMR ($CDCl_3$) δ -5.6 (6 F, s), 2.8 (6 F, s) ppm; m/e 447 (M^+); high resolution, m/e 446.997 (calcd 446.995). **4b**: quantitative yield, colorless oil; ¹⁹F NMR spectrum is quite similar to that of **4a**.

Compounds **4a** and **4b** were desulfurized with triphenyl-

Chart I



phosphine in *n*-pentane at room temperature to yield the corresponding "Dewar" pyrrole (**5a** or **5b**). Compound **5a** was too unstable to be isolated, but its structure could be assumed by transient appearance of a pair of symmetrical peaks in the ¹⁹F NMR spectrum [-0.4 (bridge head CF_3) and 2.8 (olefinic CF_3) ppm] and an absorption near 1715 cm^{-1} ($C=C$) in the IR spectrum. Compound **5a** rapidly isomerized to 1,2,2a,7b-tetrakis(trifluoromethyl)-2a,7b-dihydro-3H-cyclobuta[b]-indole (**6**): 35.6% yield, colorless oil; IR (*n*-pentane) 3430 (N-H), 1715 ($C=C$), 1210 ($C-F$) cm^{-1} ; ¹H NMR (CCl_4) δ 7.2–7.5 (2 H, m), 6.75–7.04 (2 H, m), 4.72 (1 H, b), ¹⁹F NMR ($CDCl_3$) δ -0.8 (3 F, m), 0.0 (3 F, m), 5.2 (3 F, m), 10.8 (3 F, m) ppm; m/e 415 (M^+); high resolution, m/e 415.024 (calcd 415.023). **5b**: 60% yield, colorless oil; IR (CCl_4) 2940, 2860, 1705, 1190, 1160 cm^{-1} ; ¹H NMR (CCl_4) δ 2.6 (1 H, N-CH), 1.15–1.95 [10 H, m, $(CH_2)_5$]; ¹⁹F NMR (CCl_4) 1.52 (6 F, s) (bridgehead CF_3), 2.72 (6 F, s) (olefinic CF_3) ppm; ¹³C NMR ($CDCl_3$) 23.78 (3' and 5'), 25.88 (4'), 31.97 (2' and 6'), 49.95 (1 and 4), 55.11 (1'), 118.08, and 121.24 (CF_3 carbon), and 140.44 (2 and 3) ppm; m/e 421 (M^+); half-life at 100 °C in benzene, about 8.8 h.

Treatment of **5b** with furan and cyclopentadiene gave the Diels-Alder adducts (**7** and **8**).³ **7**: 83% yield, mp 123–125 °C; IR (CCl_4) 2940, 2860, 1210, 1170 cm^{-1} ; ¹H NMR (CCl_4) δ 6.6 (2 H, b, $=CH-$), 5.36 (2 H, s, O-CH<), 3.0 (1 H, b, N-CH<), 1.0–2.0 [10 H, m, $(CH_2)_5$]; ¹⁹F NMR (CCl_4) δ -3.8 (6 F, s), -0.2 (6 F, s) ppm; m/e 421 (**5b**) and 68 (furan). **8**: 73% yield, mp 101–104 °C; IR (CCl_4) 2940, 2860, 1200, 1180 cm^{-1} ; ¹H NMR (CCl_4) δ 6.40 (2 H, b, $=CH-$), 3.44 (2 H, b, $\geq CH$), 3.04 (1 H, b, N-CH<), 1.1–2.3 (12 H, m, methylenes); ¹⁹F NMR (CCl_4) δ -3.5 (6 F, s), -1.8 (6 F, s); m/e 487 (M^+).

In this research, some quite novel compounds of new ring systems, too highly strained to be isolated without the trifluoromethyl groups, were obtained. The formation of these might be due to the stabilization of strained molecules by the perfluoroalkyl effect.

References and Notes

- Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday anniversary.
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2841 (1974); Y. Kobayashi, I. Kumadaki, A. Ohsawa, Y. Sekine, and H. Mochizuki, *Chem. Pharm. Bull.*, **23**, 2773 (1975).

(3) Stereochemistry was assumed on the basis of the structure of the Diels-Alder adduct of 1 (ref 2).

(4) From PhCF_3 as internal standard; positive δ values are upfield.

Yoshiro Kobayashi,* Itsumaro Kumadaki,
Akio Ohsawa, Akira Ando

Tokyo College of Pharmacy
Horinouchi, Hachioji-shi, Tokyo, Japan

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Threshold Photoionization and Dissociation of Toluene and Cycloheptatriene

Sir:

There has been some conjecture as to the threshold structure of the C_7H_7^+ ion formed by ionizing toluene and cycloheptatriene. From investigations using collisional activation mass spectra, McLafferty and Winkler¹ concluded that approximately equal abundances of benzyl and tropylium cations are formed from threshold energy decomposition, following a rapid equilibration between C_7H_8^+ ions with toluene and cycloheptatriene structures. Dunbar² also proposed that such a dynamic equilibrium was consistent with his photodissociation results for the toluene parent ion. However, the fraction of benzyl ion was observed to decrease to zero near the photodissociation threshold. This he interpreted in terms of the activation energy for dissociation being lower for the cycloheptatriene form of C_7H_8^+ than the toluene form. More recently, a MINDO calculation³ has proposed that the easiest route for H loss from C_7H_8^+ for both toluene and cycloheptatriene is via the cycloheptatriene molecular ion to tropylium.

Appearance potentials can be used in conjunction with other thermochemical data as a means of determining possible structures of ions at threshold. However, in the case of C_7H_7^+ formed from toluene and cycloheptatriene there is a large kinetic shift associated with the decompositions which has resulted in previous overestimates of the appearance energies. This energy in excess of threshold, necessary for the ion to react sufficiently fast to be detected, can be minimized by increasing the ion source residence time⁴ and/or increasing the detection sensitivity of the instrument. We wish to report here the use of a photoionization mass spectrometer and associated signal-averaging techniques which has enabled the measurement of $\text{AP}(\text{C}_7\text{H}_7^+)$ from toluene and cycloheptatriene at high sensitivity.

The instrument used in the present experiments consists of a windowless hydrogen discharge lamp and 1-m Seya-Namioka monochromator⁵ attached to a 15-cm single-focusing mass spectrometer. A microprocessor is used for the on-line control and extended signal averaging of experimental data needed to achieve a high sensitivity of detection. A detailed description of the photoionization mass spectrometer will form part of a later publication.⁶

The photoionization efficiency curve for C_7H_7^+ produced from toluene is shown in Figure 1. Using the method of interpretation of photoionization data described by Guyon and Berkowitz,⁷ we obtain an appearance energy of 10.71 ± 0.03 eV. This is in excellent agreement with the results of Gordon and Reid⁴ who obtained a limiting value of 10.70 eV at ion source residence times in excess of 900 μs . The corresponding appearance energy for cycloheptatriene (Figure 2) is found to be 9.36 ± 0.02 eV. Combining the heats of formation for the neutral species⁸ in the reaction $\text{C}_7\text{H}_8 + h\nu \rightarrow \text{C}_7\text{H}_7^+ + \text{H} + \text{e} + (\text{excess energy})$ with the observed appearance energies, and neglecting any excess energy contribution, gives heats of formation for C_7H_7^+ of 206.9 ± 0.7 kcal/mol and 207.6 ± 0.5

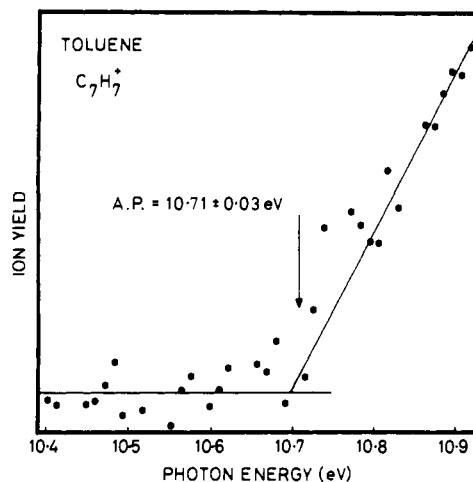


Figure 1. Threshold photoionization efficiency curve for formation of C_7H_7^+ ion from toluene.

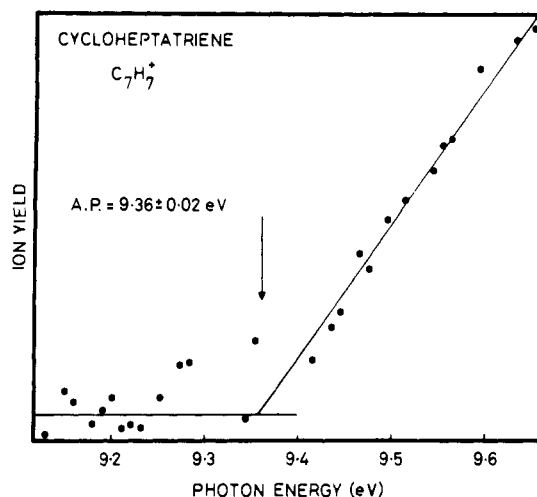


Figure 2. Threshold photoionization efficiency curve for formation of C_7H_7^+ from cycloheptatriene.

kcal/mol from toluene and cycloheptatriene, respectively. The kinetic energy release accompanying both processes has been measured from metastable studies⁹ to be 4.0 kcal/mol which probably represents an upper limit to the reverse activation energy. A recent MINDO calculation³ indicates that the reverse activation energy is indeed small, giving an estimate of only 1.4 kcal/mol.

Lossing¹⁰ has measured the adiabatic ionization energy for the benzyl radical by electron impact to be ≤ 7.27 eV which is in good agreement with a recent corresponding photoelectron spectroscopic value of 7.20 ± 0.03 eV.¹¹ If $\Delta H_f(\text{benzyl})$ is taken as 45 kcal/mol,¹² one obtains $\Delta H_f(\text{benzyl}^+) = 211$ kcal/mol which is lower than either a recent ab initio calculation of 217.1 kcal/mol¹³ or a MINDO calculation of 220.4 kcal/mol.¹⁴ It is also lower than the value of 219 ± 4 kcal/mol obtained by Jackson, Lias, and Ausloos¹⁵ who used ion cyclotron resonance spectroscopy to measure the rate constants for reaction of benzyl ion with a number of alkanes and cycloalkanes. It thus appears that from an energetic viewpoint the C_7H_7^+ ion formed at threshold for toluene and cycloheptatriene cannot have the benzyl structure.

Our value of 207 kcal/mol is in good agreement with the theoretical calculation for tropylium ion by Abboud, Hehr, and Taft¹³ (207.9 kcal/mol) and ionization energy measurements of the tropylium radical^{16,17} (209 kcal/mol), but is at variance with the MINDO value of 195.6 kcal/mol.¹⁴ Dewar and coworkers¹⁴ have suggested that the heat of formation derived from the tropylium radical ionization potential could be due to a large