(14) For a review, see D. N. Kursanov, Z. N. Parnes, and N. M. Loim, *Synthesis*, 633 (1974).

(15) A sample of **5** was obtained by preparative GLC and characterized by ^{1}H NMR, IR, and mass spectral data.

(16) The mixture of diastereoisomers **6** was obtained in high purity by column chromatography and characterized by ^{1}H NMR, IR, and mass spectral data.

(17) A. Streitwelser, Jr., and D. W. Boerth, *J. Am. Chem. Soc.*, **100**, 755 (1978).

(18) Complex **9** was prepared by reaction of *o*-(2-butenyl)anisole with chromium hexacarbonyl in dioxane at reflux in 90% yield, with no evidence of double-bond isomerization (^{1}H NMR) in either position or geometry.

(19) M. F. Semmelhack, G. Clark, R. Farina, and M. Saeman, unpublished work.

(20) For acid-promoted removal of trimethylsilyl groups from arenes, see C. Eaborn, *J. Organomet. Chem.*, **100**, 43 (1975).

(21) We gratefully acknowledge support of this work by the National Science Foundation (CHE 76-01112). We also thank Dr. Robert Farina and Dr. Glenn Clark for preliminary experiments which contributed to the development of the project.

(22) National Science Foundation Graduate Fellow, 1976–1979.

M. F. Semmelhack,* J. Bisaha,[22] and M. Czarny
Department of Chemistry, Cornell University
Ithaca, New York 14853
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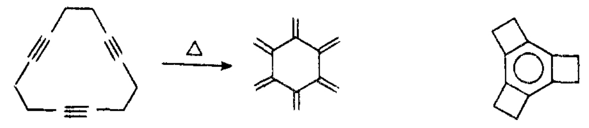
Tricyclobutabenzene

Sir:

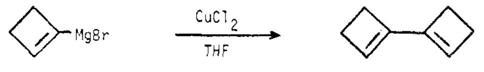
Recently there have been several reports on the preparation of 6-radialene (**2**) utilizing high-temperature reaction conditions.[1] In one instance, pyrolysis of 1,5,9-cyclododecatriyne (**1**) at 650 °C has led to the isolation of 6-radialene and it has been suggested that this isomerization may occur via the intermediacy of tricyclobutabenzene (**3**).[2] Thus far, however, all attempts to isolate **3** have been unsuccessful. The perfluoro analogue of **3** has been prepared by a cyclotrimerization reaction and it is a stable, crystalline material (mp 135–136 °C) which shows no evidence for any bond alternation in the central ring.[3]



1 2 3

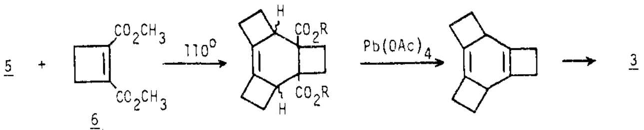
Several years ago we developed a Diels–Alder route to benzocyclobutene and annelated derivatives[4] which has proved to be extremely useful for the preparation of bis- and trisannelated benzenes[5] as well as annelated naphthalenes and anthracenes.[6] In this approach substantial ring strain may be built into the reacting partners of an initial [2 + 4] cycloaddition which is then accompanied by some relief of strain while establishing the cyclic framework of the molecule in a single step. The final aromatization profits from the resonance energy gained by the system and, most importantly, this final step can be carried out under relatively mild conditions (<40 °C).

Lüttke and Heinrich have worked out an elegant preparation of α,α′-dicyclobutenyl (**5**) by the copper chloride promoted coupling of 1-cyclobutenylmagnesium bromide (**4**).[7] This diene is extremely sensitive to acid and oxygen so that appropriate precautions must be taken to prevent its decomposition. After adding 1 equiv of anhydrous copper(II) chloride to a freshly prepared THF solution of the Grignard reagent **4** at 30 °C, the mixture is stirred at room temperature for 1 h and hydrolyzed, and the diene **5** steam distilled along with THF. After dilution of the distillate with pentane, drying over MgSO$_4$, and evaporation of the solvent, the nearly pure diene (mp ~5 °C) is obtained in 41% overall yield from 1-bromocyclobutene.[8]



4 5

The diene **5** is immediately combined with 1 equiv of dimethyl cyclobutene-1,2-dicarboxylate (**6**),[9] sealed in a glass tube, and heated to 110 °C for 12 h. Analysis of the crude Diels–Alder adduct by VPC[10] showed two peaks at 7.0- (19%) and 9.2- (81%) min retention time. Each peak was isolated by preparative VPC and mass spectral analysis showed both to have a parent ion at *m/e* 276 and almost identical fragmentation patterns. The 100-MHz NMR spectra of these two components were very similar with a sharp downfield singlet (6 H) appearing at δ 3.68 for the minor component and 3.64 for the major one. In the upfield region both spectra showed a number of poorly resolved multiplets (14 H). It is presumed that these two peaks represent the endo and exo Diels–Alder adducts, as similar epimers have been observed in other cycloaddition reactions of **6**.[5a,11] After chromatography on silica gel there was obtained 0.61 g (47%) of this mixture of epimers which was then hydrolyzed by treatment with potassium hydroxide in refluxing aqueous methanol. Acidification afforded a nearly quantitative yield of diacid **8**, mp 163–168 °C.



6

7 R = CH$_3$

8 R = H

9

Treatment of the diacid **8** with 2 equiv of lead tetraacetate in dimethyl sulfoxide, with pyridine added to scavenge the acetic acid generated, led to a mildly exothermic reaction accompanied by copious gas evolution. The temperature was maintained at 25–40 °C and, after the gas evolution had ceased (~15 min), the reaction mixture was poured into water and extracted with ether. The ether extracts were dried over MgSO$_4$ and evaporated and the crude product chromatographed on silica gel, eluting with hexane, to provide 2.2 mg (0.5%)[12] of a white solid, mp 141–142 °C. The ^{1}H NMR of this material showed one sharp singlet at δ 3.12. This peak position compares very well with the observed values of δ 3.08 for benzo[1,2:3,4]dicyclobutene[5a] and 3.12 for the cyclobutyl protons of [1,2:3,4]dicyclobuta[5,6]cyclopentabenzene.[13] No peaks were found at either δ 2.30 or 5.31 where the singlets for **1** and **2**, respectively have been reported. The ^{13}C NMR spectrum of **3** showed singlets at δ 138.5 and 29.6 and in the proton-coupled spectrum the upfield singlet splits into a triplet with J = 138.0 Hz. Once again these values correlate very well with the related bisannelated systems.[14]

Analysis of **3** by VPC[15] showed a major peak (96%) at 5.25-min retention time as well as a minor one (4%) at 3.1-min retention time. GC–mass spectrometry of the major peak gave *m/e* (rel intensity) 158 (1.0, M + 2), 157 (13.5, M + 1), 156 (100.0, parent ion), 141 (37.6, M − 15), 128 (19.0, M − 28), and 115 (25.9, M − 41). A high resolution mass spectrum showed the parent ion at *m/e* 156.0932 (calcd for $C_{12}H_{12}$, 156.0939). Whereas Boekelheide does report peaks at *m/e* 141 and 128 for 6-radialene, he also observes only a low intensity parent ion[1c] where this peak is the most intense for compound **3**. As he further points out and as we have also observed, peaks at M − 15 and M − 28 are quite characteristic of benzocyclobutene fragmentation. GC–mass spectrometry of the minor peak showed a parent ion at *m/e* 158 which we take to be good evidence for the dihydro precursor **9**.

The UV spectrum of **3** (isooctane) shows λ_{max} 269 nm (ε 170), 265 (sh, 190), 262 (210), 258 (195), 254 (195), 251 (sh, 170), 247 (sh, 150), 222 (5600), and 201 (25 500). The three

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characteristic benzene bands of weak, medium, and high intensity are all clearly present. Vibrational structure in the longest wavelength band is not very pronounced and exhibits a slight shift toward shorter wavelength and lower intensity when compared with higher homologues. The IR spectrum of **3** ($CHCl_3$) shows bands at 2940, 2870, 1615, 1470, 1384, 1270, and 1100 cm^{-1}.

Unlike 6-radialene, tricyclobutabenzene appears to be a quite stable molecule. It can be remelted with decomposition, will survive VPC temperatures of 250 °C, and remains unchanged after room temperature storage for several days. We are continuing to investigate the chemistry of this intriguing molecule.

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References and Notes

(1) (a) A. J. Barkovich, E. S. Strauss, and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **99**, 8321 (1977); (b) P. Schiess and M. Heitzmann, *Helv. Chim. Acta*, **61**, 844 (1978); (c) L. G. Haruff, M. Brown, and V. Boekelheide, *J. Am. Chem. Soc.*, **100**, 2893 (1978).
(2) A. J. Barkovich and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **98**, 2667 (1976).
(3) (a) R. L. Soulen, S. K. Choi, and J. D. Park, *J. Fluorine Chem.*, **3**, 141 (1973/74); (b) R. P. Thummel, J. D. Korp, I. Bernal, R. L. Harlow, and R. L. Soulen, *J. Am. Chem. Soc.*, **99**, 6916 (1977); (c) R. E. Cobbledick and F. W. B. Einstein, *Acta Crystallogr., Sect. B*, *32*, 1908 (1976).
(4) R. P. Thummel, *J. Chem. Soc., Chem. Commun.*, 899 (1974).
(5) (a) R. P. Thummel, *J. Am. Chem. Soc.*, **98**, 628 (1976); (b) R. P. Thummel and W. Nutakul, *J. Org. Chem.*, **42**, 300 (1977); (c) R. P. Thummel, J. D. Korp, and I. Bernal, *Tetrahedron*, **33**, 3069 (1977).
(6) (a) R. P. Thummel, W. E. Cravey, and W. Nutakul, *J. Org. Chem.*, **43**, 2473 (1978); (b) R. P. Thummel and W. Nutakul, *J. Am. Chem. Soc.*, **100**, 6171 (1978).
(7) F. Heinrich, Ph.D. Thesis, University of Göttingen, 1972.
(8) H. Normant and P. Maitte, *Bull. Soc. Chim. Fr.*, 1424 (1960).
(9) R. N. McDonald and R. R. Reitz, *J. Org. Chem.*, **37**, 2418 (1972).
(10) The VPC column was 5 ft × 1/8 in. 1.5% OV-101 on Chromsorb G 100/120 mesh at 180 °C and 30 mL/min.
(11) D. Belluš, H.-C. Mez, and G. Rihs, *J. Chem. Soc., Perkin Trans. 2*, 884 (1974).
(12) It was found that this yield could be increased to 3.6% (10.8 mg) when only 1 equiv of lead tetraacetate was employed. After chromatography, the material thus obtained appeared to be mostly **9** by NMR but could be smoothly converted to **3** by treatment with DDQ. The fate of the remaining organic material in this decarboxylation is a question which is now receiving our serious attention in an effort to further increase the yield of this reaction.
(13) Although nonequivalent, these cyclobutyl protons show a coincidental singlet. The preparation and properties of this molecule will be described in a full paper regarding this work.
(14) R. P. Thummel and W. Nutakul, *J. Org. Chem.*, **43**, 3170 (1978).
(15) The VPC column was 6 ft × 1/8 in. 3% SP-2100 on Supelcoport 100/120 mesh at 120 °C (programmed at 4°/min) and 30 mL/min.

Wutichai Nutakul, Randolph P. Thummel*
Austin D. Taggart
Department of Chemistry, University of Houston
Houston, Texas 77004

Received September 27, 1978

Intramolecular Excimer-Forming Probes of Aqueous Micelles

Sir:

We describe here the use of intramolecular excimer-forming compounds of type I as microviscometric probes of the interior of aqueous micelles. Since the conformation of I required for excimer formation would be sparsely populated in the ground state, a conformational transition is required during the lifetime of the excited state.[1-3] For a given Ar and X, the rate constant for excimer formation (k_a) is inversely dependent on the viscosity of the medium.[1,2] At sufficiently low temperatures where the dissociation of the excimer (k_d) may be neglected, the ratio of the intensities of excimer and normal fluoresence (I_d/I_m) is characteristic of k_a.[1,4]

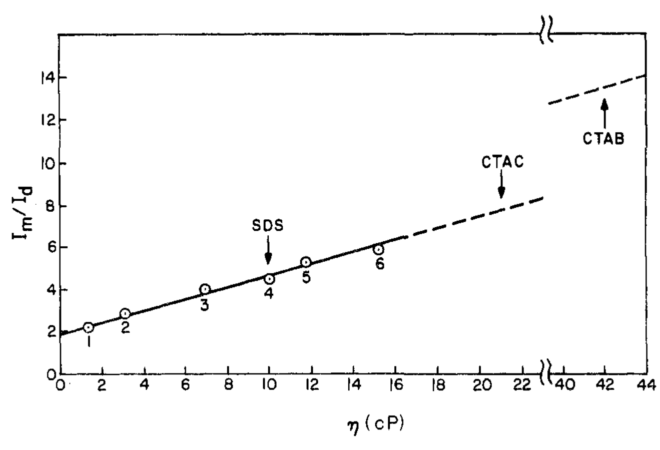
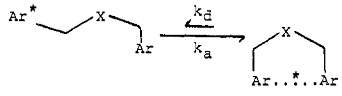


Figure 1. I_m/I_d vs. viscosity for probe Ia at 20 °C: (1) ethanol; (2) 1-butanol; (3) triethylcarbinol; (4) 19:10 (v/v) ethanol-glycerol; (5) tributyrin; (6) 40:60 (v/v) ethanol-glycerol. EG (viscosity of 19.9 cP) exhibited an I_m/I_d ratio of >15. Dotted line represents extrapolation of the experimentally determined plot. Arrows indicate I_m/I_d ratios of Ia solubilized in micellar solutions and their corresponding microviscosities in centipoises.



I

Ia: X=O; Ar=4-biphenyl
Ib: X=$NH_2^+Cl^-$; Ar=1-naphthyl

Since compounds of type I are solubilized in solutions of aqueous micelles, miceller microviscosities may be estimated from a comparison of the I_d/I_m ratios of the solubilized probes with appropriate references. This method has a distinct advantage over the *inter*molecular excimer fluorescence technique[5] because multiply occupied micelles are not required.

Ia[6] was chosen for our initial investigations because of its high quantum yield of emission and because the temperature at which k_d becomes significant is well above room temperature. Conditions were maintained so that >94% of the occupied micelles were singly occupied ([Ia] < 10^{-4} M; [surfactant] = 0.05-0.06 M).[7] Thus, the contribution from intermolecular excimer emission is negligible.

The micelles were labeled either by warming the aqueous micellar solutions containing the probe to 90 °C for 50 min and then cooling rapidly or by injecting an ethanol solution of the probe into the micellar solution (ETOH concentration <1%). Identical spectra resulted from the two labeling techniques. All solutions were prepared under nitrogen using deoxygenated solvents.

In Figure 1, I_m/I_d values for probe Ia dissolved in various solvents at 20 °C are plotted against viscosity. Except for ethylene glycol, a remarkably good correlation was obtained even though a wide spectrum of solvents and solvent mixtures were employed.[8] Using this plot as a reference, micellar microviscosities were estimated from the I_m/I_d ratios exhibited by the solubilized probe. These are shown on the plot for sodium dodecylsulfate (SDS), cetyltrimethylammonium chloride (CTAC), and cetyltrimethylammonium bromide (CTAB) micelles.[12] While previous workers[14] reported significant changes in the fluorescence depolarization of solubilized probes as the micelles aged, we observed little change in I_m/I_d with time.

Figure 2 shows the temperature dependent behavior of I_d/I_m for probe Ia in aquoues SDS, CTAC and CTAB micelles and in ethanol and ethylene glycol (EG) solvents. From the low temperature portion of the logarithmic plot, activation energies