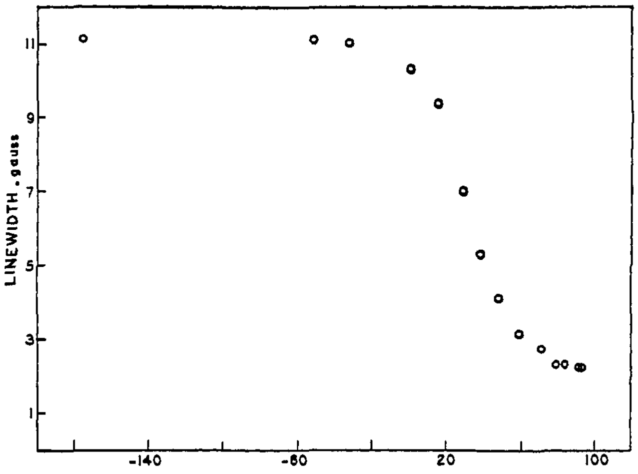

Figure 1. Line width as a function of temperature for bullvalene.

We wish to report an nmr investigation of bullvalene in the solid state. A Varian DP-40 spectrometer equipped with a Varian Fieldial magnetic field regulator was used for this study of a powdered sample. Spectra were recorded as the derivative of the absorption curve, and the line widths quoted herein are the separations between maxima and minima in these derivative curves. It may be seen from Figure 1, where the line width is plotted as a function of temperature, that above 0° the line width begins to decrease as the temperature is raised. This reduction in line width can be ascribed to molecular motion which averages the direct dipole–dipole interaction of the hydrogen nuclei. In bullvalene this motion may be reorientation about a molecular axis or possibly valence isomerization which has been observed in solution.[3,4] The observed second moment of 10 gauss^2 for the spectrum at $-33°$ is a reasonable value for a rigid lattice. At a temperature of 83°, which is above the line-width transition, the second moment is reduced to 5 gauss^2. This is larger than the value which would be expected for general reorientation of the molecules in the crystal lattice.

If it is assumed that the process which narrows the resonance line is an activated one, then it is possible to calculate an activation energy[5] from the line-width data in Figure 1. A value of 9.2 kcal/mole is obtained for the activation energy and 0.2×10^{12} sec^{-1} for the frequency factor which may be compared with the solution results of 11.8 kcal/mole and 0.8×10^{13} sec^{-1}.[4]

In a further attempt to characterize the motion in solid bullvalene, the nmr spectra of the dimer of cyclooctatetraene, which melts at 76° and which is the precurser in the photochemical synthesis of bullvalene,[1] were examined. Because of its shape this dimer would not be expected to undergo reorientation in the solid. It is, however, a derivative of homotropylidene and is thus capable of valence isomerization. Line widths for this material were measured from $-170°$ up to the melting point and were found to be essentially constant in this temperature range with a value of approximately 10.5 gauss. This observation does not preclude the possibility of observing the effect of valence isomerization in the solid because in the case of the dimer only some of the protons would be affected by this process. A better molecule to study in this regard would be homotropylidene.

If the line-width transition shown in Figure 1 is due to reorientation, then it is possible that bullvalene belongs to a special class of solids, the so-called plastic crystals, in which case it should undergo a crystal–crystal transition and the molecules in the high-temperature crystalline form would reorient.

We have also observed that below 0° bullvalene apparently has a long relaxation time since time intervals of several minutes are required before spectra with reproducible intensities can be observed.

Acknowledgment. We are indebted to Union Carbide European Research Associates for the materials studied in this work.

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(5) H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.*, **18**, 162 (1950).

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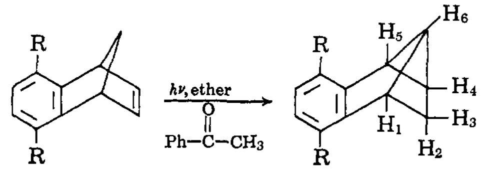
The Photorearrangement of Benzonorbornadienes

Sir:

The photoisomerization of norbornadienes to quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptanes (quadricyclanes) appears quite general.[1] We report at this time the isomerization of benzonorbornadienes when irradiated in the presence of a sensitizer to tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-trienes.



1, R = H
2, R = OAc

3, R = H
4, R = OAc

Irradiation of a 1% solution of benzonorbornadiene[2] (**1**) in ether containing 0.01% acetophenone for 24 hr with a bank of 16 F8T5·BLB bulbs[3] gave 95% conversion[4] to **3**; bp 220° (760); n^{27}D 1.5742. *Anal.* Calcd for $C_{11}H_{10}$: C, 93.04; H, 6.96; mol wt, 142. Found: C, 92.52; H, 7.12; mol wt, 142 (mass spectroscopy). The structure of compound **3** was established by its nmr spectrum and the isomerization **2** → **4**. The nmr spectrum[5] contained a complex aromatic region at δ 7.45–6.78 with an integrated intensity of 4 compared to the aliphatic region. The aliphatic region

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(1) (a) S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **80**, 1950 (1958); (b) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); (c) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961); (d) H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963); (e) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 1270 (1964); (f) P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **86**, 4211 (1964); (g) D. M. Lamal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965); (h) H. Tanida, Y. Hata, Y. Matsui, and I. Tanaka, *J. Org. Chem.*, 30, 2259 (1965).

(2) G. Wittig and E. Knauss, *Ber.*, **91**, 895 (1958).

(3) Rayonet photochemical reactor from the Southern N. E. Ultraviolet Co. F8T5·BLB bulbs peak at 3500 A; G8T5 bulbs have maximum output at 2537 A.

(4) Based on glpc peak areas.

(5) Compound **3** run in CCl_4–TMSi, **4** in $CDCl_3$–TMSi; δ values in parts per million downfield from TMSi at 0.

(Figure 1) gave five distinct areas (a–e) of relative intensities 2:1:1:1:1. By analogy with tricyclo[4.1.0.0^{3,7}]heptene,[6] the signal at δ 0.73 can be assigned to the *endo* methylene proton H_2. Although primary coupling of H_2 with H_3 and H_4 should produce a quartet, secondary coupling of an unknown nature has complicated the pattern. Irradiation of the signal at e caused an effect on the patterns at a and b but not c and d. Since H_1 should give a quartet through primary coupling with H_3 and H_6 ($J_{H_1H_2} = 0$),[6] we can tentatively assign c to H_5, d to H_6, and place H_1 in a. Although the placement of H_3 and H_4 cannot be made at this time,[7] the gross features of the spectrum are consistent with the proposed structure.

Irradiation of a 1% solution of *p,p'*-diacetoxybenzonorbornadiene[8] (**2**) in ether containing 0.01% acetophenone for 24 hr gave an 80% yield of white leaflets melting at 160–160.5° (recrystallized from acetone–ether). *Anal.* Calcd for $C_{15}H_{14}O_4$: C, 69.83; H, 5.86; mol wt, 258. Found: C, 70.19; H, 5.50; mol wt, 258 (mass spectroscopy).

The ultraviolet spectrum of the diacetoxy photoproduct, **4**, $\lambda_{max}^{CH_3CN}$ 266 mμ (log ϵ 2.53), and its carbonyl absorption at 1750 cm^{-1} (Nujol), were similar to those of the starting material **2**, λ_{max}^{EtOH} 260 mμ (log ϵ 2.50),[8] ν 1748 cm^{-1} (Nujol). The nmr spectrum consisted of an AB pattern centered at δ 6.81 (J_{AB} = 9 cps), a complex absorption centered at δ 3.25, a triplet similar to b in Figure 1, a triplet at δ 2.50, a sharp peak at δ 2.30 and 2.20, a multiplet at δ 2.04, and a poorly resolved quartet at δ 0.88. The relative areas were 2:2:1:1:3:3:1:1, corresponding to two *ortho* aromatic protons, two acetoxy methyl groups (δ 2.30 and 2.20), and six aliphatic protons. Except for the two methyl peaks, the absorptions in the aliphatic region were the same as those in compound **3**.

Reduction of the photoproduct, **4**, with hydrogen over Pd–C gave *p,p'*-diacetoxybenzonorbornene,[8] identical with an authentic sample prepared from **2**. Reduction of **4** with deuterium over Pd–C gave a benzonorbornene containing 0.9 mole of deuterium, none of it at the aromatic, acetoxyl methyl, or benzylic positions. The analytical and spectral data and chemical behavior[9] are consistent only with structure **4** and establish it as the photoproduct.

Irradiation for 24 hr of degassed 1% solutions of **2** in ether in sealed quartz tubes with a bank of 16 G8T5 bulbs[3] in the absence of a sensitizer gave no detectable concentration of **4**. Irradiation of **1** under the same conditions gave less than 1% conversion to **3**. These results suggest that the rearrangement proceeds *via* an excited triplet state of the benzonorbornadienes and that the efficiency of intersystem crossing in these compounds must be very poor. Work on the mechanism of the rearrangement is currently underway.

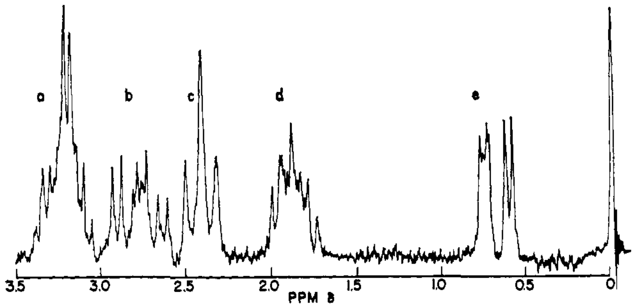

Figure 1.

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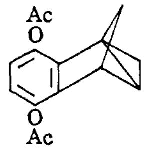
(6) P. R. Story, *J. Am. Chem. Soc.*, **83**, 3348 (1961).

(7) The choice between areas a and b cannot be made on the basis of the decoupling experiment.

(8) J. Meinwald and G. A. Wiley, *J. Am. Chem. Soc.*, **80**, 3667 (1958).

(9) The analytical and spectral data could conceivably fit structure **5**.



5

Reduction of the photoproduct with hydrogen over Pd–C to a benzonorbornene is characteristic of the tricyclo[4.1.0.0^{3,7}]heptane ring: W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961). Barring rearrangements, reduction of 4 with deuterium should not introduce any deuterium in the benzylic positions of the resulting benzonorbornene. This is not true of structure **5**.

Synthetic Peptide Models of Enzyme Active Sites. III. Stereoselective Esterase Models[1]

Sir:

The pentapeptide L-threonyl-L-alanyl-L-seryl-L-histidyl-L-aspartic acid (I) previously has been shown[1] to exhibit catalytic activity more than six times greater than that reported for any other synthetic peptide in the hydrolysis of *p*-nitrophenyl acetate. In addition, we have now found that treatment with diisopropyl fluorophosphate (DFP), a known inhibitor of α-chymotrypsin,[2] leads to a 48% decrease in the catalytic coefficient of I. We now wish to report the preparation of an even more potent esterase model (Table I), as

Table I. Hydrolysis of *p*-Nitrophenyl Acetate[a]

Catalyst	Catalytic coefficient,[b] l./mole/min
Histidine·HCl[3]	6
Gly-His-Ser[3]	15
Copoly His, Ser[b]	9.7
Imidazole[c]	20
Ser-His-Asp	45
His + Ser + Asp	19
I[1]	92
I + DFP	48
II	147
III[3]	7
α-Chymotrypsin[b]	10^4

[a] The experimental conditions of Sheehan and McGregor (ref 3) were employed in all kinetic runs. [b] E. Katchalski, G. D. Fasman, E. Simons, E. R. Blout, F. R. N. Gurd, and W. L. Koltun, *Arch. Biochem. Biophys.*, **88**, 361 (1960). [c] Unfortunately the catalytic coefficient of imidazole was reported in ref 1 as 2 rather than 20 by typographical error.

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