References and Notes

(1) In this paper, the ground state ($X^3\Sigma_g^-$) of oxygen will be designated as $^3O_2$ and the excited state ($a^1\Delta_g$) as $^1O_2$.
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(6) Bohme and Young have reported the reactions of $C_3H_5^-$, $C_4H_7^-$, and $C_3H_3^-$ with molecular oxygen: Bohme, D. K.; Young, L. B. *J. Am. Chem. Soc.* **1970**, *92*, 3301–3309.
(7) Hunt, D. F.; Sethi, S. K.; Shabanowitz, J. Presented at the Twenty-Sixth Annual Conference on Mass Spectrometry and Allied Topics, St. Louis, Mo., May 28–June 2, 1978.
(8) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395–427.
(9) The absence of oxygen atoms and ozone molecules in our system has been confirmed by ion chemistry.
(10) Ferguson, E. E. "Interactions between Ions and Molecules", Ausloos, P., Ed.; Plenum Press: New York, 1975; p 318.
(11) O_2^- is observed as a product whenever electron transfer is exothermic.

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Photoreaction of Valence-Bond Isomers of Hexakis(trifluoromethyl)oxepin. Synthesis of a Stable Oxetene Derivative

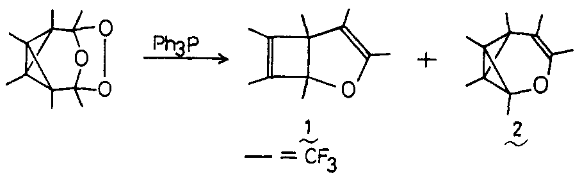
Sir:

The photoreaction of perfluoroalkylated compounds is especially interesting because of the possible isolation of strained compounds by the "perfluoroalkyl effect".[1] Previously we reported the reduction of hexakis(trifluoromethyl)benzvalene ozonide with triphenylphosphine, affording two valence-bond isomers of hexakis(trifluoromethyl)oxepin,[2] hexakis(trifluoromethyl)-2-oxabicyclo[3.2.0]hepta-3,6-diene (**1**) and hexakis(trifluoromethyl)-3-oxatricyclo[4.1.0.0^{2,7}]heptene (**2**) (Scheme I).

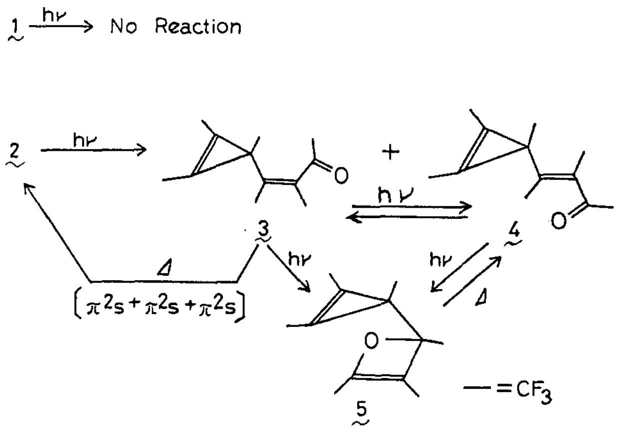
We now report the photoreaction of **1** and **2** including formation of a new stable oxetene derivative. Irradiation[3] of a perfluoropentane solution of **1** in a silica tube at room temperature gave no isomeric product. Irradiation of **2** under the same condition gave a mixture of *Z* and *E* forms (**3** and **4**) of 1,2,3-tris(trifluoromethyl)-3-[1,2,3-tris(trifluoromethyl)cyclopropenyl]propenone in a quantitative yield (Scheme II). These isomers (**3** and **4**) could not be separated even by VPC. The molar ratio of **3** and **4** was 1:1. The structural assignment of **3** and **4** was based on the results of the following reactions and on their spectral data. When a mixture of **3** and **4** in pentane was heated at 140 °C and the reaction was followed by ^{19}F NMR spectra, only the *Z* isomer **3** regenerated **2** and the *E* isomer **4** remained unchanged. On the other hand, irradiation of a mixture of **3** and **4** in perfluoropentane filtered with Pyrex gave only one product (**5**) in a quantitative yield. The ^{19}F NMR spectrum[4] of **5** in a pentane solution showed five multiplets centered at −3.5, −2.9, 1.4, 7.4, and 11.8 ppm (the intensity ratio of signals was 2:1:1:1:1[5]).

The IR spectrum of **5** in pentane revealed absorption bands at 1900 and 1735 cm^{-1}, ascribable to the cyclopropene double bond[6] and the oxetene ring double bond,[7] respectively, and the mass spectrum of **5** showed *m/e* 502 (M$^+$) (calcd for $C_{12}F_{18}O$, mol wt 502). The UV spectrum of **5** showed only one absorption maximum at 207 nm (ϵ 2.80 × 10^3, in *n*-hexane), while that of the mixture of **3** and **4** showed three absorptions at 198 (ϵ 3.72 × 10^3), 250 (sh, 146), and 305 nm (31). These data show that **5** has no carbonyl group, while **3** and **4** have.

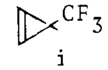
Scheme I



Scheme II



From these data we concluded that **5** is a perfluoromethylated cyclopropenyloxetene,[8] which is a colorless and stable liquid at room temperature and is exclusively converted into the *E* isomer **4** of the enone on being heated at 80 °C (T = 5.7 h in pentane). This result of thermal reaction of **5** is consistent with the results of the thermal reaction of transiently formed oxetene derivatives, which has been reported previously.[9] From the thermal reaction of **5**, pure *E* isomer **4** was isolated in a quantitative yield: colorless liquid; ^{19}F NMR (pentane) −3.6, −2.1, 3.2 (group i), 12.4 ppm ($COCF_3$) (each signal is broad, intensity ratio 3:1:1:1); IR spectrum (pentane) ν(C=O) 1890 (cyclopropene double bond), 1770 cm^{-1}; mass spectrum *m/e* 502 (M$^+$) (calcd for $C_{12}F_{18}O$, mol wt 502). The ^{19}F NMR of *Z* isomer **3** is deduced from those of the mixture of **3** and **4**: −7.4, −4.2, 3.2 (group i), 13.3 ppm ($COCF_3$) (relative ratio 1:3:1:1).



i

A very rapid equilibrium between **3** and **4** was observed on the irradiation of the isolated isomer (**4**). This result shows that **3** and **4** are *Z*/*E* isomers. Moreover, regeneration of **2** from **3** (*Z* form) and not from **4** (*E* form) by thermal reaction supports each of the assigned structures, since regeneration of **2** from **3** is considered to be a thermally allowed (${}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s$) concerted process and, in the case of **4** (*E* form), the thermally allowed concerted process cannot regenerate **2** because of the trans double bond.

References and Notes

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(4) The benzotrifluoride signal is used as an internal standard; upfield shifts are quoted as positive.
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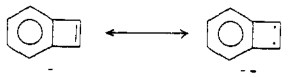
He(I) Photoelectron Spectrum of Benzocyclobutadiene

Sir:

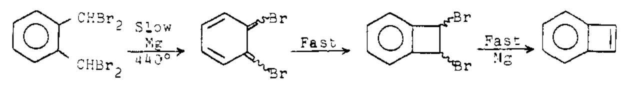
Benzocyclobutadiene[1-3] is a member of the class of hydrocarbon which could be expected to be biradicaloid[4] as qualitatively depicted by structure II. In favorable cases, like the



p-quinodimethanes,[5] photoelectron spectra (PES) can give indications of the importance of this biradical character. We presently report a one-step method of generating I from commercially available $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene (**1**), our observation of the PES of benzocyclobutadiene, and the results of the structure representation (SR), HAM/3, and HAM/3-CI methods for assignments of the observed bands.

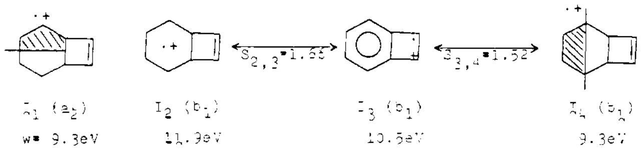
The generation method was pyrolysis of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene (**1**) at 440–470 °C over sublimed magnesium (Scheme I). This route was suggested to us by our inability to observe *o*-xylylene from pyrolysis of the Cava[6] sulfone. All such attempts gave cleanly the spectrum of benzocyclobutene indicating that ring closure of **2** should be fast. The second dehalogenation for the dibromo derivative (**3**), as a fast final step in the overall process, could therefore be expected.

Scheme I



The pyrolysis was first monitored by mass spectrometry. At 470 °C the peaks due to the tetrabromide are negligible and the base peak is *m/e* 102. The only other appreciable peaks (nominal ionizing voltage, 15 eV) are *m/e* 76, the expected fragment of benzocyclobutadiene, and small HBr peaks. The PES from such a pyrolysis stream is shown as Figure 1.

The π part of the PES of benzocyclobutadiene can be simply analyzed by the structure representation (SR) method[7] with the ionic basis structures derived from ground-state structure I (I_1, I_2, I_3, I_4). By inspection, the SR method suggests a $^2A_2$ state at 9.3 eV since symmetry excludes the interaction of this benzenoid ionic species I_1 (a_2) with the olefinic unit (I_3 (b_1)). The second band in the observed spectrum is centered at 9.32 eV.



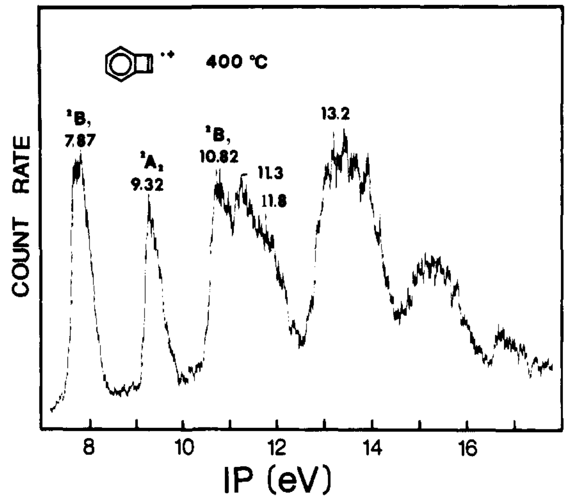


Figure 1. PES of benzocyclobutadiene.

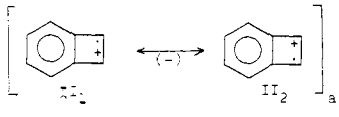
Table I

band	assign-ment	obsd	SR (π only)	HAM/3[a]	HAM/3-CI
1	$^2B_1$	7.87 ± .02	8.0	8.19	8.26
2	$^2A_2$	9.32 ± .02	9.3	9.74	10.04
3	$^2B_1$	10.82 ± .02	10.5	10.78	10.74
4	$^2A_1$	~11.3		11.96	
5	$^2B_2$	~11.8		12.02	
6	$^2B_1$	~13.2	13.2	12.81	

[a] Notes 8 and 9.

The interaction constants among the remaining b_1 ionic basis structures (I_2, I_3, I_4) can be derived from the spectra of 1,3-butadiene and 1,4-cyclohexadiene if contributions from atoms in 1,4 arrangements are neglected throughout. The predictions and assignments of the π-SR scheme are shown in Table I along with those of HAM/3. The first two band assignments seem securely attributable to the formation of the lowest $^2B_1$ and $^2A_2$ ionic states, respectively.

The lowest ionic structure derivable from II would be the negative combination of the two (II_1, II_2) where a localized electron has been lost (II_1-II_2). Appreciable contributions from the diradical structure II would be expected to affect the position and intensity of the second PE band ($^2A_2$) most strongly. The position of the second band is exactly where the SR procedure predicts it[10] and the absence of any other weak band in its vicinity seems to indicate that there is little mixing of I_1 and (II_1-II_2).



In MO language such biradicaloid effects are described by configuration interaction. We have investigated the corrections to the HAM/3 procedure by calculation of (limited) CI corrections to the ground-state wave function from configurations where π electron *pairs* have been promoted from one orbital to another. For the radical cation, CI corrections were calculated from the π configurations with one singly occupied orbital. These calculations showed that, in spite of the small HOMO-LUMO gap (2.45 eV), CI mixing of both the neutral compound and the lowest two radical cation π states is negligible. The calculated character of these $^1A_1$, $^2B_1$, and $^2A_2$ states was 97% in the zero-order configuration. For $^1A_1$ and $^2A_2$ the small mixing was due to the very small CI interaction constants. Both CI results and the SR procedure support the conclusion that little biradical effect is present in benzocyclobutadiene and its electronic structure is most closely related to that depicted by structure I.

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