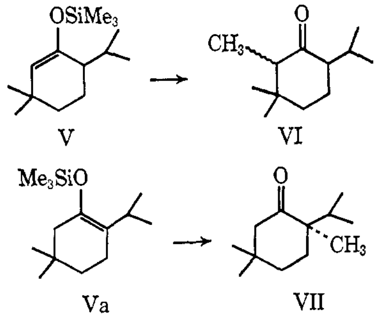
t-alkoxides present when enol acetates[4] are used as precursors) which can promote polyalkylation. The expected structural integrity of enolates from silyl ethers is illustrated by the alkylation[5] of the lithium enolates from the silyl ethers V and Va[1] to the respective methylated substances VI and VII[6] in 80% yield.[7]



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(4) H. O. House and B. M. Trost, *J. Org. Chem.*, **30**, 2502 (1965).

(5) The alkylation of various cyclohexanone enolates is being studied more intensively by Dr. P. Tardella.

(6) VI was separable into two base-interconvertible components (*cis* and *trans*), the major isomer having a retention time of 15.4 min and the minor 14.1 min on 10-ft 20% LAC 2-R-446 columns at 140° (120 ml/min). The major component was characterized as the 3,5-dinitrobenzoate, mp 72–75°, of the corresponding alcohol (LAH). Both isomers of VI showed three methyls as doublets and two as singlets in the nmr, in contrast to VII (retention time 15.1 min) which showed three methyls as singlets and two as doublets. The main difference in the mass spectra of VI and of VII was the much larger peak at *m/e* 140 (loss of propylene) from the latter.

(7) We thank the National Science Foundation for the support of this work.

Gilbert Stork, P. F. Hudrlik
Department of Chemistry, Columbia University
New York, New York 10027

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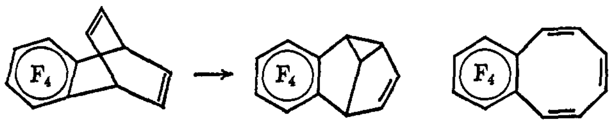
Photoisomerization of Mono- and Dibenzobarrelenes

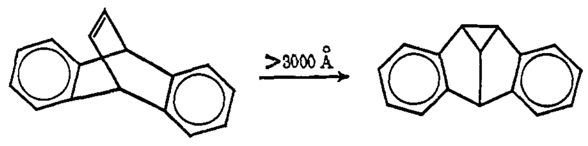
Sir:

It was recently reported[1] that the photosensitized (acetone) rearrangement of barrelene (bicyclo[2.2.2.]-octa-2,5,7-triene) yields semibullvalene (tricyclo[3.-3.0.0.^{2,8}]octa-3,6-diene). Similarly, tetrafluorobenzobarrelene[2] was converted to the corresponding semibullvalene derivative,[3] while direct irradiation reaction gave tetrafluorobenzocyclooctatetraene.



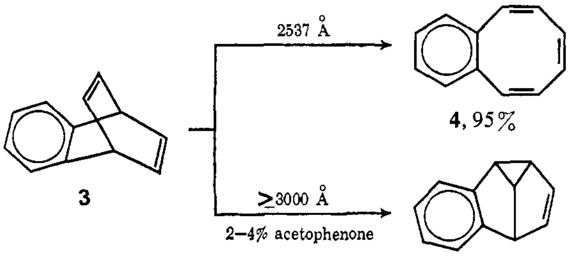
(pentane, quartz) 17% 56%
(4% acetone, quartz) 66% trace

However, the photolysis of dibenzobarrelene[4] (**1**) in acetone or benzene (Pyrex filter) is reported to give only dibenzosemibullvalene (**2**).



1 **2**, 85%

We now wish to report that direct irradiation (2537 Å) of benzobarrelene[5] (**3**) (in cyclohexane) leads to the exclusive formation of benzocyclooctatetraene (**4**) while photosensitization (acetophenone or acetone) produces benzosemibullvalene[6,7] with only a trace of **4**.



3 **4**, 95% **5**, 99%

Contrary to the previous interpretation,[4] the unsensitized[8] photoisomerization of dibenzobarrelene (**1**)[9] leads to the formation of *sym*-dibenzocyclooctatetraene (**6**).[10] From the relative amounts of **6** (or **6a**) and **2** (or **2a**) obtained, it is concluded that photoisomerization of $^{1}\mathbf{1}^{*}$ proceeds more rapidly (10–20 times) than intersystem crossing.

Direct irradiation of **7**[11] in cyclohexane produced only **8**,[4] probably from $^{3}\mathbf{7}^{*}$. On the other hand, compound **9** (mp 105–107°) was smoothly converted to the cyclooctatetraene derivative **10** (mp 105–107°). It fol-

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(1) H. Zimmerman and G. Grunewald, *J. Am. Chem. Soc.*, **88**, 2882 (1966).

(2) J. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967).

(3) A single photoproduct was obtained in the photolysis of bis-(perfluoromethyl)benzobicyclo[2.2.2]octatriene. Unpublished results (H. Zimmerman) for the conversion of benzobarrelene to benzosemibullvalene are cited: R. Liu, *J. Am. Chem. Soc.*, **90**, 215 (1968).

(4) E. Ciganek, *ibid.*, **88**, 2882 (1966).

(5) Prepared in 20% yield from the reaction of benzyne and benzene: L. Friedman and D. F. Lindow, *ibid.*, **90**, 2329 (1968).

(6) (a) All new products have satisfactory spectral data and microanalyses. (b) The nmr spectra of benzosemibullvalene showed multiplets centered at τ 2.92 (4), 4.52 (1), 4.97 (1), 6.28 (1), 7.18 (3).

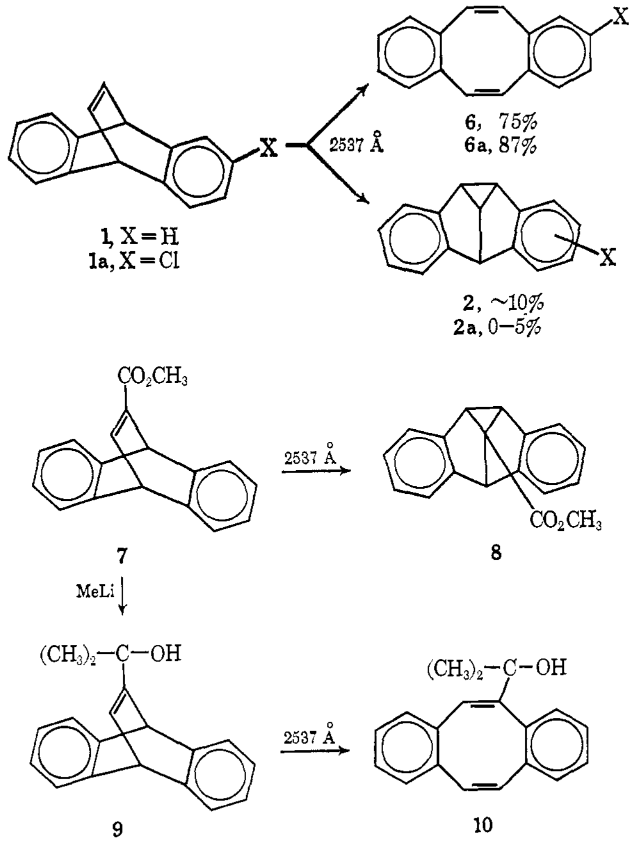
(7) (a) A solution of 2% acetophenone in cyclohexane is five times more effective (20 min, using an immersed 100-W GE medium-pressure Hg lamp (H100A4/T), Pyrex glass filter) than neat acetone as the photosensitizer, and is easily removed from the reaction mixture by chromatography on alumina. Direct irradiation (>3000 Å) gave **5** very slowly (3% conversion, 2 days). (b) Benzosemibullvalene is unstable to continued irradiation at 2537 and >3000 Å with or without photosensitization. The products are benzocyclooctatetraene (~50%) and polymeric residues.

(8) In this study direct irradiation (nonsensitized) was effected in cyclohexane and tetrahydrofuran at 2537 Å (60 hr, Rayonette photochemical reactor) and is different from that described by Ciganek (Pyrex cutoff, in benzene).[4] Tetrahydrofuran is the preferred solvent since polymer formation is surpressed. The material balance is excellent (>90%) and essentially all **1** is consumed. **1a** (mp 123.5–124.5°) is converted to **6a** (mp 71–72°) and a mixture, **2a** (mp 74–82°, not resolved by glpc), more rapidly than **1** is. We find that direct irradiation at longer wavelengths (>3000 Å) slowly gives **2** (~1% conversion, 2–3 days) when conducted in benzene (*i.e.*, benzene photosensitization), while in cyclohexane **6** and **2** are slowly formed.

(9) Dibenzobarrelene can be prepared in 53% yield by the reaction of *cis*-acetylene dichloride and anthracene followed by dehalogenation: S. Cristol and R. Bly, *J. Am. Chem. Soc.*, **82**, 6155 (1960). This material can also be made by the reaction of benzyne and naphthalene: 7% yield, R. Miller and M. Stiles, *ibid.*, **85**, 1798 (1963); 20–30% yield by a modification in procedure, L. Friedman and P. W. Rabideau, unpublished results.

(10) This material is identical with that prepared by Wittig [G. Wittig, G. Koenig, and K. Clauss, *Ann.*, **593**, 127 (1955)] and Griffin [C. Griffin and J. Peters, *J. Org. Chem.*, **28**, 1715 (1963)] but different from that reported by Fieser [L. F. Fieser and M. Pechet, *J. Am. Chem. Soc.*, **68**, 2577 (1946)], Cope [A. Cope and S. Fenton, *ibid.*, **73**, 1668 (1951)], Nenitzescu [M. Avram, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Ber.*, **93**, 1789 (1960)], and Schroeder [G. Schroeder, W. Martin, and J. Oth, *Angew. Chem. Intern. Ed. Engl.*, **6**, 870 (1967)]. This discrepancy is under current investigation.

(11) W. Vaughan and K. Milton, *J. Am. Chem. Soc.*, **74**, 5628 (1952).



lows then that the conjugated double bond is the active chromophore.

These results support the mechanism proposed by Brewer and Heaney,[2] wherein rearrangement to cyclooctatetraenes occurs from the excited singlet, and semibullvalenes from the excited triplet.

Thus, in view of the ready accessibility of benzo-[5] and dibenzobarrelenes,[9] direct irradiation (2537 Å) appears to be the most convenient synthetic route to benzo- and dibenzocyclooctatetraenes. Elucidation of the mechanistic details and the efficiency (Φ) of the direct and sensitized irradiation of **1** and **3** are presently being investigated.

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Peter W. Rabideau, John B. Hamilton, Lester Friedman
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

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The Fate of the Isobutyldiazonium Ion[1]

Sir:

There is lack of agreement on the mechanisms and processes involved in product formation from thermal decomposition of N-alkyl-N-nitrosoacetamides[2] and diazotization of alkylamines[3,4] since product compositions vary widely with changes in reaction conditions.[2–4] In this investigation, the isobutyl system was studied since from product analysis coupled with suitable labeling experiments the product-forming processes can be unravelled.

With the exception of isobutylene all products can be related to a unique structural precursor. For example, 1-butene, *cis*- and *trans*-2-butenes, and the *sec*-butyl substitution products result from the *sec*-butyl cation. However, isobutylene can arise either from the isobutyldiazonium ion (**1d**$^+$) by concerted loss of nitrogen and protium or from the *t*-butyl cation which is formed from **1d**$^+$ by hydride shift. Thus, by means of appropriate labeling experiments[5] it is determined that from either protic or aprotic reactions approximately 70% of the isobutylene is formed *via* the *t*-butyl cation (Table I).[5] With this information it is now possible to ascertain the amounts of isobutyl, *sec*-butyl, and *t*-butyl product-forming precursors. The various reaction pathways are outlined in Scheme I and tabulated in Table II. Thus in the poorly solvating medium, chloroform, hydrocarbon and substitution products

Table I. Extent of Hydride Shift in Isobutylene Produced from Isobutyldiazonium Ion

	Isobutylene			
	Deuterium content % mole[a,b]		% hydride shift	
Amine precursor	d_{n-1}	d_n	Uncor[c]	Cor[d]
$(CH_3)_2CHCD_2NH_2$ (d_2)	13.5	86.5	61	73[e]
$(CH_3)_2CDCH_2NH_2$ (d_1)	46	54	63	60[e]
$(CD_3)_2CDCH_2NH_2$ (d_7)	76	24	108	61

[a] Low-voltage mass spectrometry, corrected for isotopic content of amine precursor. [b] Values are from typical runs in protic and aprotic media. [c] Calculated using statistical factors. [d] Calculated using a k_H/k_D value (multiplicative) of 1.12–1.13/D atom; *i.e.*, this value gives the best fit; *cf.* ref 5. [e] Estimated primary k_H/k_D for hydride shift is 1.2.

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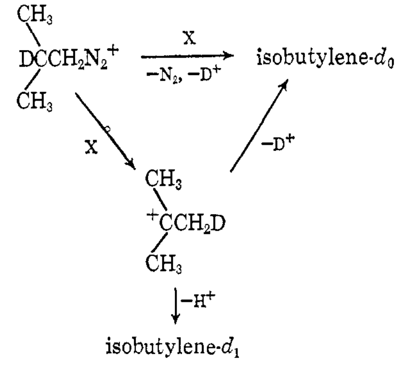
[1] Financial support (Grant No. GP-3976) from the National Science Foundation is gratefully acknowledged.

[2] Previously observed from thermal decomposition of N-isobutyl-N-nitroso amides in various aprotic media. It was suggested that the reaction proceeds predominantly *via* concerted cyclic processes of the covalent diazo ester intermediate and that isomerization is controlled by steric factors: E. H. White, *J. Am. Chem. Soc.*, **77**, 6014 (1955).

[3] (a) J. H. Bayless, F. D. Mendicino, and L. Friedman, *ibid.*, **87**, 8790 (1965), reported that diazotization of isobutylamine in chloroform gives substitution products consisting of 5% *t*-butyl, 9% *sec*-butyl, and 86% isobutyl derivatives. This is not compatible[3] with "proposed" carbonium ion reactions of isobutyl precursors in *protic* media where large amounts of rearrangement occur leading predominately to *t*-butyl substitution products.[4]

[4] L. G. Cannell and R. W. Taft, *ibid.*, **78**, 5812 (1956).

[5] For 2-deuterioisobutylamine the followihg scheme outlines the routes to isobutylene-d_0 and -d_1. *X*, the extent of hydride shift, was



calculated using the equation

$$X = d_n\left[\frac{n}{m(k_H/k_D)^n} + 1\right]$$

where *m* and *n* are the number of H atoms and D atoms in the amine and d_n is the mole fraction of isobutylene that did not lose deuterium. The (k_H/k_D) is an unresolved combination of primary and secondary deuterium isotope effects.