

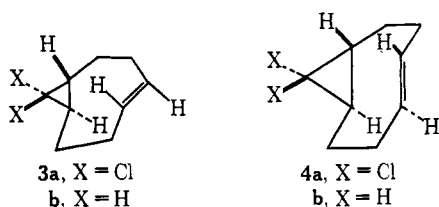
Parallel and Perpendicular
trans,trans-Bicyclo[6.1.0]non-4-ene¹

Sir:

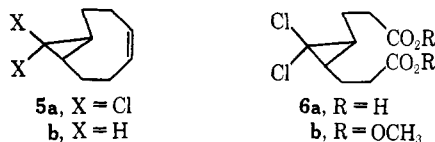
In 1967 Whitesides and Cope reported isolation of *trans,trans*-1,5-cyclooctadiene. These authors pointed out this compound could exist with its bonds oriented in a perpendicular (1) or parallel (2) sense.² Although



they recognized the potential interest in the relative physical and chemical properties of 1 and 2, only one isomer was obtained and they were unable to assign its structure. We would like to report the successful synthesis, separation, and structural assignment of both conformational isomers 3 and 4 of the cyclopropyl analogs of 1 and 2.



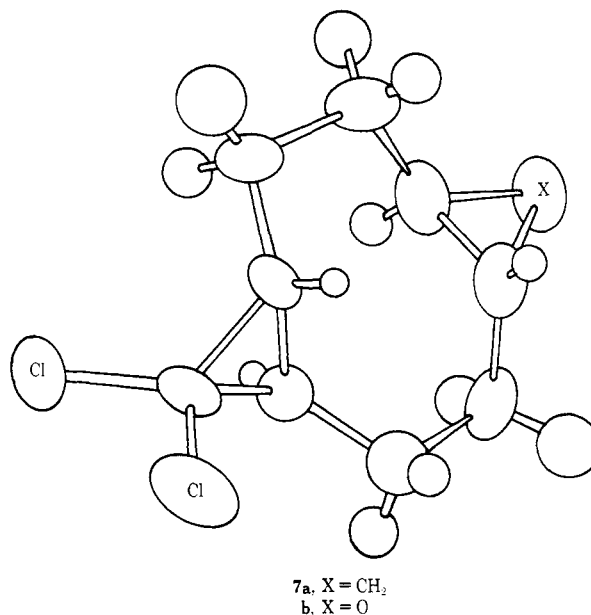
Selective addition of dichlorocarbene to the *trans*-alkene of *cis,trans*-1,5-cyclooctadiene² gave 5a in 30% yield. Irradiation of equal weights of 5a and cuprous chloride at 2537 Å in hexane for 27 hr produced a mixture of 5a (57%), 3a (35%), and 4a (8%).³ The latter two components could be extracted into 20% aqueous silver nitrate.⁴ Liberation of the complexed isomers with aqueous ammonia was followed by preparative gas chromatographic separation to give pure 3a and 4a.⁶ In an analogous fashion, 5b⁷ was converted to a separable 7:1 mixture of 3b and 4b.⁸



Confirmation of the stereochemistry of the cyclopropane ring and the location of the double bond was

obtained by ozonolysis of 5a and the 5:1 mixture of 3a and 4a. Both ozonolyses yielded 6a⁹ in over 92% yield. Correlation of stereochemistry between 3a and 3b was achieved by converting them both to 7a via stereospecific addition of the appropriate one-carbon fragment.¹²

In order to obtain a detailed picture of the molecular shape of these compounds and to distinguish between 3 and 4, we undertook a single-crystal X-ray diffraction analysis. Reaction of 3a with *m*-chloroperbenzoic acid yielded 7b (mp 114–116°). This compound crystallized from pentane in the monoclinic space group *P*2₁/*n* with cell dimensions *a* = 8.968 ± 0.004, *b* = 8.835 ± 0.004, and *c* = 12.121 ± 0.004 Å; β = 93.92 ± 0.02°. There are four molecules per unit cell. Intensity data were collected on a Syntex P1 automatic diffractometer (Mo Kα radiation: λ 0.71069 Å). The structure was refined by full-matrix least-squares methods, assuming anisotropic thermal parameters for C, Cl, and O. All hydrogens were located by difference Fourier synthesis and refined isotropically. The final *R* (the usual residual) for 1189 observed independent reflections was 0.040.



In this manner, the epoxide of 3a was assigned the perpendicular structure 7b. The transannular distance in 7b between the two rings is 2.63 Å. The dihedral angle between the least-squares planes containing the epoxide and cyclopropane rings is 70.26°. Models imply that deviation from a strict perpendicular orientation probably results from transannular nonbonded interactions (H₁–H₅ and H₂–H₆). Similar considerations suggest that the dihedral angle between the cyclo-

(1) We gratefully acknowledge the support of the National Science Foundation (Grant No. GP-17642 JAD) and the University of Florida Computing Center (G. J. P.).

(2) G. M. Whitesides, G. L. Goe, and A. C. Cope, *J. Amer. Chem. Soc.*, **89**, 7136 (1967); **91**, 2608 (1969).

(3) The photoisomerization of cycloalkenes which do not form stable Cu(I) complexes by this method appears to be a general and useful procedure.

(4) The similar solubility of 3a and 4a in silver nitrate is strong evidence for the presence of trans double bonds.⁵

(5) Cf. A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Amer. Chem. Soc.*, **75**, 3212 (1953).

(6) Satisfactory analytical data have been obtained for all new compounds.

(7) K. R. Wiberg and A. de Meijere, *Tetrahedron Lett.*, 59 (1969).

(8) Gas chromatographic separations were achieved on QF-1 (3a and 4a) and XF-1150 (3b and 4b). Both 4a and 4b had longer retention times than 3 (a and b) and 5. A single preparative run and multiple injection separation yielded pure 3 and 4 in approximately 500- and 100-mg quantities, respectively. The ir and nmr spectra of 3, 4, and 5 are distinctly different. These spectral properties will be discussed in the full paper.

(9) This compound has been independently synthesized, compared, and found identical with 6a. All samples of 6a were clearly different from an independently synthesized sample of the *cis* isomer of 6a.^{10,11}

(10) M. Betkouski, unpublished results.

(11) Cf. P. G. Gassman, J. Seter, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 1673 (1971). These authors have explored some of the dynamic aspects of transannular interactions of trans-fused cyclopropane.

(12) In this instance, Zn–Cu plus CH₂I₂ and sodium methoxide–ethyl trichloroacetate.

propane ring and the olefinic bond should be close to 0° for **4**, the minor isomer.

The availability of **3** and **4** offers a unique opportunity to probe small ring-olefin and small ring-small ring interactions through space as a function of two distinct and specified geometries. The potential magnitude of this effect may already be apparent in the vacuum ultraviolet spectrum of **4b**. This spectrum reveals a maximum at 202 nm ($\epsilon \sim 1670$). In contrast, **3b**, **5b**, and *trans*-cyclooctene show maxima of comparable intensity at 196, 193, and 192 nm, respectively. Further work on the physical and chemical properties of these novel systems is in progress.

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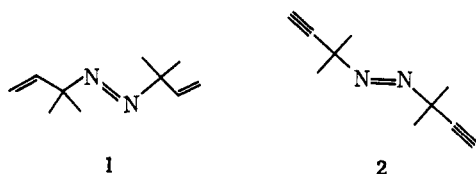
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Recombination of Unsymmetrical Allylic and Propargylic Radicals Produced from Azo Compounds

Sir:

Thermal and photochemical decomposition of acyclic azo compounds constitutes a clean and flexible method of producing free radicals.¹ Until very recently,² however, the cases in the literature were confined to the aliphatic series in which the initial products were alkyl radicals. We report here the preparation and thermolysis of a tertiary allylic azo compound **1** and the first propargylic azo compound **2**. These substances are the cornerstone of a new approach to the study of competing processes in caged radical pairs.³



Reaction⁴ of 3-amino-3-methyl-1-butyne⁵ with sulfonyl chloride produced the corresponding sulfamide: mp 122.8–123.5°; ν 1144, 1349 cm^{-1} . Oxidation with sodium hypochlorite⁴ led to **2**: mp 24.5–26°; ν 355 nm (ϵ 28.3). **1** (ν , λ_{max} 366 nm (ϵ 29.6)) was prepared similarly from the allylic amine derived from partial hydrogenation of 3-amino-3-methyl-1-butyne. The sulfamide in this series had mp 82.5–83.5° and ν 1132 and 1320 cm^{-1} . The nmr spectra of all compounds clearly showed the presence of a dimethylallyl or dimethylpropargyl moiety.

Nitrogen evolution from the thermal decomposition of **1** and **2** in xylene was followed in an automated con-

Table I. Activation Parameters for Thermolysis of Acyclic Azo Compounds

R in $\text{RN}=\text{NR}$	ΔH^\ddagger , kcal M^{-1}	ΔS^\ddagger , eu (298°)	Ref
$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2$	29.0	11.0	<i>a</i>
$\text{NCC}(\text{CH}_3)_2$	30.7	10.5	<i>b</i>
$\text{CH}_2=\text{CHCH}_2$	35.5	10.6	<i>c</i>
$\text{CH}_2=\text{CHC}(\text{CH}_3)_2$	26.3 ± 1.0	5.5 ± 2.9	This work
$\text{HC}\equiv\text{CC}(\text{CH}_3)_2$	27.2 ± 0.4	8.2 ± 1.3	This work

^a S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 137 (1966). ^b F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949).

^c Reference 2a.

stant-volume, variable-pressure kinetic apparatus and proved to be cleanly first order. Activation parameters listed in Table I were computed from a least-squares fit of the data. Activation enthalpies for azo decomposition in general reflect the stability of the incipient radicals.^{6,7} Thus the values determined in this work indicate that dimethylallyl and dimethylpropargyl are of essentially equal stability and that both are more stable than two closely related radicals, cumyl and 2-cyanopropyl. Martin and Sanders⁸ reported that an allylic perester decomposed with an activation enthalpy 4.0 kcal M^{-1} less than that of the analogous propargyl perester. Despite the difficulties associated with correlating structural variation with small differences in activation parameters, we suggest that since azo compounds are in general more sensitive to product stability than are peresters, double and triple bonds differ relatively little in their ability to stabilize an adjacent radical site.

Several reports have appeared concerning the relative reactivity of the ends of delocalized radicals.⁹ However these studies involved chain reactions which are capable of producing undesired side products and they only measured the reactivity of the delocalized radical with a polar molecule. Compounds **1** and **2** provide an opportunity to determine the reactivity of delocalized radicals with themselves. If the head (h) end of the radicals is defined as the one bearing the two methyl groups, the recombination products can be designated hh, ht, and tt. The relative amounts of these hydrocarbons are shown in Table II. All products except 2,7-dimethyl-2,3,5,6-octatetraene were collected by pre-

Table II. Products from Thermolysis of **1** and **2**^a

Compd	%		
	hh	ht	tt
1 ^b	16	30	54
2 ^c	33	57	10

^a Expressed as per cent of total C_{10} hydrocarbons. ^b In *o*-dichlorobenzene at 49°; determined by vpc. ^c Approximately 10% solution in CCl_4 at 42°; determined by nmr.

parative vpc and their structures determined by nmr and ir spectroscopy. Since the octatetraene was unstable

(1) See P. S. Engel and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 5883 (1970), and references cited therein.

(2) (a) B. H. Al-Sader and R. J. Crawford, *Can. J. Chem.*, **48**, 2745 (1970); (b) R. J. Crawford, J. Hamelin, and B. Strehlke, *J. Amer. Chem. Soc.*, **93**, 3810 (1971); (c) N. A. Porter and P. M. Iloff, *J. Chem. Soc. D*, 1575 (1971).

(3) Other approaches to this problem have used azo compounds with asymmetric carbon atoms: see P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967); K. Kopecky and T. Gillan, *Can. J. Chem.*, **47**, 2371 (1969); F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970).

(4) J. C. Stowell, *J. Org. Chem.*, **32**, 2360 (1967).

(5) G. F. Hennion and E. G. Teach, *J. Amer. Chem. Soc.*, **75**, 1653 (1953).

(6) See Table I, footnote *a*.

(7) C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

(8) M. M. Martin and E. B. Sanders, *J. Amer. Chem. Soc.*, **89**, 3777 (1967).

(9) (a) C. Walling in "Molecular Rearrangements," Vol. 1, P. DeMayo, Ed., Wiley, New York, N. Y., 1963, p 433; (b) R. Fantazier and M. Poutsma, *J. Amer. Chem. Soc.*, **90**, 5490 (1968); (c) L. Byrd and M. Caserio, *ibid.*, **92**, 5422 (1970).