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

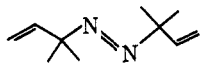
The availability of **3** and **4** offers a unique opportunity to probe small ring–olefin and small ring–small ring interactions through space as a function of two distinct and specified geometries. The potential magnitude of this effect may already be apparent in the vacuum ultraviolet spectrum of **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.

J. A. Deyrup,* M. Betkouski, W. Szabo
M. Mathew, G. J. Palenik
*Department of Chemistry, University of Florida*
*Gainesville, Florida 32601*
*Received December 17, 1971*

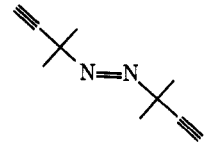
## Recombination of Unsymmetrical Allylic and Propargylic Radicals Produced from Azo Compounds

*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]



1



2

Reaction[4] of 3-amino-3-methyl-1-butyne[5] with sulfuryl chloride produced the corresponding sulfamide: mp 122.8–123.5°; ir 1144, 1349 $cm^{-1}$. Oxidation with sodium hypochlorite[4] led to **2**: mp 24.5–26°; uv $\lambda_{max}$ 355 nm ($\epsilon$ 28.3). **1** (uv, $\lambda_{max}$ 366 nm ($\epsilon$ 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 ir 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 constant-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 Sanders[8] 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.

**Table I.** Activation Parameters for Thermolysis of Acyclic Azo Compounds

| R in RN=NR | $\Delta H^{\ddagger}$, kcal $M^{-1}$ | $\Delta S^{\ddagger}$, eu (298°) | Ref |
|---|---|---|---|
| $C_6H_5C(CH_3)_2$ | 29.0 | 11.0 | *a* |
| $NCC(CH_3)_2$ | 30.7 | 10.5 | *b* |
| $CH_2{=}CHCH_2$ | 35.5 | 10.6 | *c* |
| $CH_2{=}CHC(CH_3)_2$ | 26.3 ± 1.0 | 5.5 ± 2.9 | This work |
| $HC{\equiv}CC(CH_3)_2$ | 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.

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

**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.

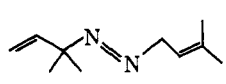
(1) See P. S. Engel and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 5883 (1970), and references cited therein.
(2) (a) B. H. Al-Sader and R. J. Crawford, *Can. J. Chem.*, **48**, 2745 (1970); (b) R. J. Crawford, J. Hamelin, and B. Strehlke, *J. Amer. Chem. Soc.*, **93**, 3810 (1971); (c) N. A. Porter 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. De-Mayo, 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).

to vpc, it was synthesized independently.[10] The decomposition of **1** and **2** was shown by nmr and vpc to be remarkably clean. As in other delocalized radicals,[6] disproportionation is of minor importance; in fact, our value of less than 2% disproportionation relative to recombination appears to be the lowest yet reported.

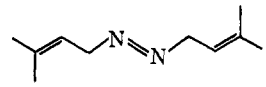
It should be noted that **2** is a potentially dangerous compound. Early in the course of our work a 75-mg neat sample of **2** was sealed into a 30-cm$^3$ evacuated tube. When the tube was lowered into an oil bath at 116°, the sample suddenly decomposed with a flash of yellow light. Although the tube did not break, further work with **2** was confined to solutions, where no such problems were encountered.

Three factors which may affect the distribution of $C_{10}$ products are: (1) relative spin density at the radical termini, (2) steric effects, and (3) product stability. On account of the exothermicity of radical recombination, little importance is attached to the latter. The esr results of Kochi and Krusic[11,12] show negligible dependence of spin density at allylic carbon on alkyl substitution. Thus, the product distribution from **1** reflects only the greater steric hindrance to recombination of a tertiary site compared with a primary site. Propargylic carbon atoms, on the other hand, show substantially greater spin density than allenic ones.[12] In opposition to the steric effect, this favors head-to-head recombination. The optimum occurs in the recombination of an allenyl with a propargyl radical.[13]

The product composition from **1** is approximately the same as that from thermolysis of **3**[14] and **4**.[15] Using 0.00153 *M* Koelsch radical[16] and 0.0344 *M* 2,2,6,6-



**3**



**4**

tetramethylpiperidine-1-oxyl[17] as scavengers, we have found that the cage effect in thermolysis of **1** at 53° in benzene is 0.50 and 0.45, respectively. If the cage effect for **3** and **4** is comparable, rotation of radicals within the solvent cage must be faster than recombination;[3] otherwise, one would expect a different product distribution from each azo compound. The similar behavior of **1**, **3**, and **4** also mitigates against an eight-membered cyclic decomposition mechanism which would produce exclusively the tail-to-tail product. Further evidence that these radicals randomize within the solvent cage before recombining can be adduced from product studies in the presence of excess 2,2,6,6-tetramethylpiperidine-1-oxyl. The $C_{10}$ recombination products, which were isolated by column chromatography of thermally decomposed mixtures in pentane, were shown by vpc to occur in essentially the same ratio as in unscavenged runs.

(10) L. Skattebol and S. Solomon, *J. Amer. Chem. Soc.*, **87**, 4506 (1965).
(11) J. K. Kochi and P. J. Krusic, *ibid.*, **90**, 7157 (1968)
(12) J. K. Kochi and P. J. Krusic, *ibid.*, **92**, 4110 (1970).
(13) Head-to-head and head-to-tail dimers have been isolated previously from the Grignard reagent of 3-bromo-3-methyl-1-butyne; see G. F. Hennion and C. V. DiGiovanna, *J. Org. Chem.*, **31**, 970 (1966).
(14) J. E. Baldwin, J. E. Brown, and G. Höfle, *J. Amer. Chem. Soc.*, **93**, 788 (1971).
(15) Unpublished results of R. J. Crawford.
(16) C. F. Koelsch, *J. Amer. Chem. Soc.*, **79**, 4439 (1957).
(17) R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, **65**, 3273 (1965).

**Acknowledgment**. The authors are grateful to the National Science Foundation, the Research Corporation, and the Petroleum Research Fund administered by the American Chemical Society for support of this work.

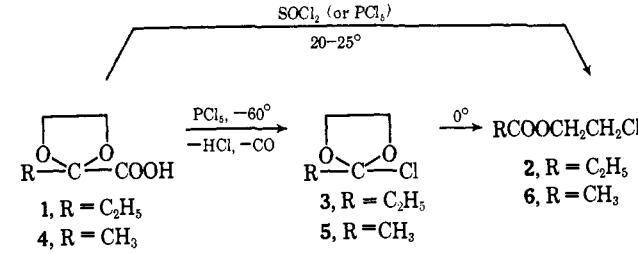
(18) NDEA Graduate Fellow, 1971–present.

**Paul S. Engel,* David J. Bishop**[18]
*Department of Chemistry, Rice University*
*Houston, Texas 77001*
*Received January 8, 1972*

## Stereospecific Formation of Epoxides and Halohydrin Esters from Diols

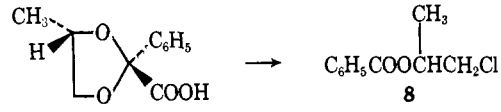
*Sir:*

Treatment of 2-carboxy-2-ethyl-1,3-dioxolane (**1**) with thionyl chloride at room temperature yields 2-chloroethyl propionate (**2**)[1,2] and not 2-chloro-2-ethyl-1,3-dioxolane (**3**)[3] as originally claimed.[4] Actually,




we have shown that treatment of 2-carboxy-2-methyl-1,3-dioxolane (**4**) with phosphorus pentachloride in methylene chloride at −60° yields 2-chloro-2-methyl-1,3-dioxolane (**5**)[5] which rearranges to 2-chloroethyl acetate (**6**) rapidly on warming to 0°.

Although this type of chemistry has been noted by several authors, the synthetic possibilities and advantages have not been explored. In this communication we point out the high regiospecificity and stereospecificity involved in the conversions of ketals of α-keto acids to esters of halohydrins. For example, treatment of 2-carboxy-4-methyl-2-phenyl-1,3-dioxolane (**7**)[6] (trans/cis about 3/2—made from 1,2-propanediol) with phosphorus pentachloride in methylene chloride affords 85–92% yields of 1-chloro-2-propyl benzoate (**8**).[6] No




**7** (trans shown)

trace of isomer was seen in the nmr analysis.

Similar treatment of D(−)-2-carboxy-2,4,5-trimethyl-1,3-dioxolane (**9**),[6] $\alpha^{22}D$ −14° (neat, 1 dm), yields L(+)-*erythro*-3-chloro-2-butyl acetate (**10**),[7] $\alpha^{22}D$ 12.7 (neat, 1 dm), which on treatment with strong base yields D(+)-2,3-epoxybutane (**11**),[8] $[\alpha]^{21}D$ 70° (*c* 0.0149,

(1) S. M. McElvain and A. N. Bolstad, *J. Amer. Chem. Soc.*, **73**, 1988 (1951).
(2) R. P. A. Sneeden, *J. Chem. Soc.*, 477 (1959).
(3) For the formation and reactions of such ortho ester chlorides, see (a) A. Gross, J. Freiberg, and B. Costisella, *Chem. Ber.*, **101**, 1250 (1968), and (b) S. Hünig, *Angew. Chem., Int. Ed. Engl.*, **3**, 548 (1964), for other examples.
(4) E. Vogel and H. Schinz, *Helv. Chim. Acta*, **33**, 116 (1950).
(5) For a similar chlorinated ortho ester chloride see ref 3a.
(6) All new compounds prepared in this work gave analyses, nmr, ir, and mass spectral data consistent with the assigned structures.
(7) For (±)-*erythro*-3-chloro-2-butyl acetate, see R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, **87**, 5172 (1965).