

8. Interconversion of the epimeric starting materials **3** and **4** does not occur.

Both products **7** and **8** show strong infrared absorption bands typical of enol ethers in the 6.0–6.1- μ range. The nuclear magnetic resonance (nmr) spectrum of each shows a methoxyl singlet in addition to a high-field (δ 3.9–4.3 ppm) vinylic absorption typical of a proton in the environment ROC=CH. Hydrolysis of the enol ethers leads to the respective ketones **9'** and **10**.

The composition of the product mixture is virtually unaffected by the duration of the pyrolysis, by the initial pressure, or by large increases in surface-to-volume ratio. It is also insensitive to a 30° temperature variation, which precludes an estimate of the difference in activation energies for the two processes but ensures that it is small.

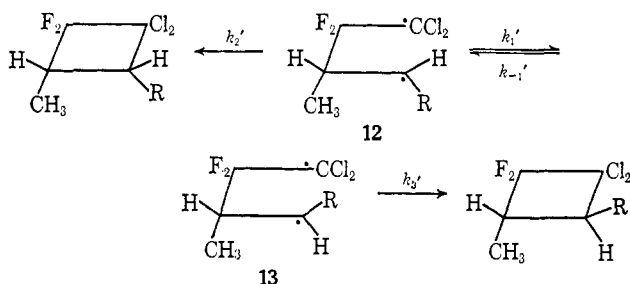
Competition experiments show that the *syn*- and *anti*-vinyl compounds differ but slightly in pyrolysis rate. The reactivity ratio **3**:**4** is only 2.0 ± 0.2 over a 25° temperature range. The appearance of single-inversion product **8** and the absence of any significant rate enhancement for the *syn*-vinyl compound **3** strongly suggest that the rearrangements proceed through diradical intermediates analogous to those proposed for the alcohol series **1** and **2**.²

Although depicted as the diradicals initially formed from **3** and **4** by homolysis of the C-1-C-7 bond, **3a** and **4a** in the kinetic scheme represent more generally the aggregates of conformationally related species that give **7** and **8**, respectively. The steady-state assumption for the concentrations of **3a** and **4a** permits the derivation⁹ of the relationships of eq 1 and 2 between the rate constants of the scheme and the experimental product ratios from *anti* reactant **4**, $(\mathbf{8}/\mathbf{7})_{anti}$, and from *syn* reactant **3**, $(\mathbf{7}/\mathbf{8})_{syn}$.

$$\left(\frac{\mathbf{8}}{\mathbf{7}}\right)_{anti} = \frac{k_3(k_1 + k_2)}{k_{-1}k_2} \quad (1)$$

$$\left(\frac{\mathbf{7}}{\mathbf{8}}\right)_{syn} = \frac{k_2(k_{-1} + k_3)}{k_1k_3} \quad (2)$$

From eq 1 and 2 and the experimental data already given, the ratios of rates of ring closure and rotation in the two diradicals **3a** and **4a** can be calculated as $k_2/k_1 = 1.57$ and $k_3/k_{-1} = 11.6$. The corresponding ratios (k_2'/k_1' and k_3'/k_{-1}') for the 1,4-butadiyl radicals which are intermediates in the additions of 1,1-dichloro-2,2-difluoroethylene to 2,4-hexadienes (**12** and **13**, R =



(7) Supplementing the previous bases for assignments of structure to these ketones² is the observation that the substance **9** is readily distinguishable from an authentic sample of *cis*-bicyclo[4.3.0]non-3-en-7-one.⁸

(8) H. O. House and G. H. Rasmussen, *J. Org. Chem.*, **28**, 31 (1963). We thank Professor House for copies of the ir and nmr spectra of this ketone.

(9) See L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964), for a completely analogous treatment.

propenyl) are 0.082 and 0.38 at 100° (essentially temperature invariant).⁹ Cyclization thus competes with internal rotation 19 and 31 times as effectively in diradicals **3a** and **4a** as in their mechanistic counterparts **12** and **13**. If the rotational barriers in **3a** and **4a** are comparable to those in **12** and **13**,^{9,10} the apparently low rates of ring closure of **12** and **13** may result from the onset of cyclobutane ring strain in the transition state and from the birth of some fraction of these diradicals in conformations unfavorable to cyclization.

The assumptions of a sixfold rotational barrier of at most 3–5 kcal/mol¹⁰ and a preexponential term¹¹ of $10^{11.5}$ lead to a rate of rotation (k_{-1}) between 0.3 and 1.2×10^{10} sec⁻¹ at 250° for diradical **4a**. For cyclization (k_3), a small requirement for steric alignment would result in a preexponential term of about 10^{12} sec⁻¹, so that the computed k_3 ($11.6k_{-1}$) would be associated with a barrier to cyclization of not more than 2–4 kcal/mol.¹²

The total stabilization energy of an allyl and an α -methoxyallyl radical is about 30 kcal/mol. Nevertheless, although some of this must be sacrificed to pay for bond length changes, rehybridization, nonbonded repulsion, and other energy costs in reaching the transition state for combination, the present observations suggest that the loss is either very small or is closely balanced by the onset of bonding.¹³ In either case, the net result is that the approach to the transition state from the direction of separated radicals is along a rather flat plateau of the energy surface. The height of this plateau, the activation energy for thermolysis of the biallylic bond, is then a good approximation of the bond dissociation energy.

(10) E. B. Wilson, Jr., *Proc. Natl. Acad. Sci. U. S.*, **43**, 816 (1957).

(11) Estimated according to H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968). We are indebted to these authors for advance information.

(12) The ratios of rates of ring closure to rotation (k_2/k_1 and k_3/k_{-1}) would be even greater if some crossover (direct **3a** \rightarrow **8** and **4a** \rightarrow **7**) occurred.

(13) Similarly, the relative rates of coupling and diffusion apart of solvent-caged radical pairs are remarkably insensitive to radical stability [P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967)]. The coupling of methyl and allyl radicals is estimated to have $E_a < 2$ kcal/mol [J. W. Simons, B. S. Rabinovitch, and F. H. Dorer, *J. Phys. Chem.*, **70**, 1076 (1966)].

(14) National Institutes of Health Predoctoral Fellow, 1964–1966.

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A Novel Allene Synthesis¹

Sir:

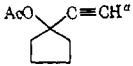
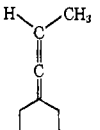
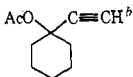
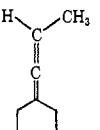
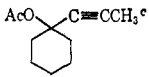
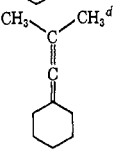
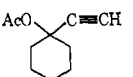
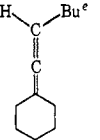
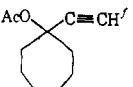
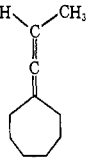
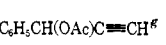
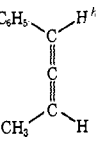
We wish to report a novel synthesis of alkylallenes by the reaction of lithium dialkylcopper reagents² with ethynylcarbinol acetates. The following transformations (Table I) are typical for the reaction studied.

The lithium dimethylcopper reagent was prepared according to the published procedure,² and the lithium di-*n*-butylcopper reagent was prepared in a similar manner.³

(1) Publication No. 343 from the Syntex Institute of Steroid Chemistry. For Publication No. 342, see K. Hiller, B. Linzer, S. Pfeifer, L. Tökes, and J. Murphy, *Tetrahedron Letters*, in press.

(2) H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, **17**, 1330 (1952).

Table I

Starting material	Reagent	Product	Bp, °C (mm)	<i>n</i> _D (°C)	Yield, %
	Li(CH ₃) ₂ Cu		47 (26)	1.4903 (25)	81
	Li(CH ₃) ₂ Cu		55 (26)	1.4941 (20)	85
	Li(CH ₃) ₂ Cu		65 (12)	1.4870 (25)	71
	Li(<i>n</i> -Bu) ₂ Cu		70 (1.5)	1.4770 (27)	65
	Li(CH ₃) ₂ Cu		91 (40)	1.4944 (22)	82
	Li(CH ₃) ₂ Cu		84 (12)	1.5664 (26)	38

^a Bp 47° (4 mm); A. M. Islam and R. A. Raphael, *J. Chem. Soc.*, 2247 (1953), report 68° (15 mm). ^b Bp 53° (1.5 mm); H. Rupe, W. Messner, and E. Kambli, *Helv. Chim. Acta*, **11**, 449 (1928), report 87° (10 mm). ^c Bp 67° (1.5 mm), *n*_D²⁵ 1.4727. ^d 4 mole equiv excess reagent was used. ^e 1 mole equiv excess reagent was used. ^f Bp 65° (1.5 mm); G. Voigt and H. Pfanz, East German Patent 14,182 (Dec 1957); *Chem. Abstr.*, **53**, 1308f (1959), report 88° (5.5 mm). ^g Bp 81° (1.5 mm); E. R. H Jones and J. T. Mc Combie, *J. Chem. Soc.*, 733 (1942), report 124° (18 mm). ^h F. Acree, Jr., and F. B. La Forge, *J. Org. Chem.*, **4**, 569 (1939), report bp 44–47° (0.5–1.0 mm). The low yield is probably due to the known tendency of this compound to polymerize.

In a typical experiment a 5% (w/v) ether solution of the starting material was added to a stirred solution of 20% excess (except as stated in Table I) reagent at –5 to –10°, under nitrogen, and the reaction mixture was allowed to come to room temperature. After 5 hr saturated ammonium chloride solution was added, and the product was isolated after removal of the solvent.⁴

The transformation is neither affected by methyl-lithium alone nor are simple acetylenes transformed by Li(CH₃)₂Cu to allenes. The reaction appears to be related to an S_N2' type displacement of an acetate group by an alkyl anion; however, preliminary results with optically active ethynylcarbinol acetates indicate that the reaction is not stereospecific. Formation of the allene system seems to be facilitated by a synergistic

(3) In the preparation of the LiMe₂Cu reagent an excess of methyl-lithium can be avoided by titrating a suspension of cuprous iodide in ether with methyl-lithium solution to the point where all the yellow precipitate of (CuCH₃)_n is dissolved. When the Li(*n*-C₄H₉)₂Cu reagent was prepared from *n*-butyllithium in hexane and cuprous iodide in ether, it was found that the species formed by the addition of 1 mole equiv of *n*-butyllithium to the cuprous iodide and the one formed by the addition of 2 equiv are both black. Consequently, care must be taken to avoid any excess of *n*-butyllithium.

(4) The products were identified on the basis of their nmr, infrared, and mass spectra. Satisfactory elemental analyses were obtained for all new compounds.

effect brought about by the reagent, acting on the triple bond and the acetoxy group.⁵

Further investigation about the scope, mechanism, and stereochemistry of this transformation is in progress.

(5) Cf. J. J. Eisch and G. R. Husk, *J. Am. Chem. Soc.*, **87**, 4194 (1965).

(6) Syntex Postdoctoral Fellow, 1967–1968.

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Interception of Carbonium Ions in the Deamination of 1-Norbornylamine

Sir:

We wish to report that the deamination of 1-norbornylamine by means of the N-nitro carbamate^{1,2} and N-nitro amide³ decompositions yields reactive car-

- (1) E. H. White and L. A. Dolak, *J. Am. Chem. Soc.*, **88**, 3790 (1960).
(2) E. H. White, M. C. Chen, and L. A. Dolak, *J. Org. Chem.*, **31**, 3038 (1966).
(3) E. H. White and D. W. Grisley, Jr., *J. Am. Chem. Soc.*, **83**, 1191 (1961).