

30 hr) leads to the formation of three new photoisomers, shown to be **7** (60%), **8** (15%), and **9** (25%) (eq 2).

The structure of the major product (**7**), analogous to the major dihydropyran produced photochemically from **1**, is apparent from its infrared and nmr spectral characteristics.^{2,3} The second component showed saturated carbonyl absorption in its infrared spectrum at 5.83 μ ; its nmr spectrum showed a single olefinic proton absorption (τ 5.00) and four methyl groups (τ 9.22, 9.00, 8.38, and 7.95), in accord with structure **8**. This product has a prominent peak at m/e 108 in its mass spectrum,⁷ corresponding to loss of acetone in a McLafferty rearrangement. This becomes the base peak at an ionizing voltage of 10 eV. The final component showed upfield absorption in its nmr spectrum at τ 10.00–9.77 (1 H) and 9.44–8.75 (2 H), in addition to other characteristic absorptions compatible with structure **9**.⁸

In benzene, **7** and **8** remain the major products, but **9** is not formed to a significant extent. Using di-*t*-butylnitroxide as a quencher⁹ in a benzene solution of **5**, the dihydropyran **7** continues to form normally, but the cyclopentene **8** almost completely disappears. In methanol, where the formation of **9** assumes major importance, the rate of formation of **9** is not appreciably changed by addition of di-*t*-butylnitroxide. Attempts to sensitize these reactions with benzophenone and acetophenone were frustrated by rapid reactions involving the sensitizers.

The formation of **7** from **6** is analogous to the previously described cyclization of **2** to **3** (which is largely insensitive to quenching by di-*t*-butylnitroxide and piperylene, as well as to sensitization by benzophenone or acetophenone); both reactions appear on this basis to utilize singlet pathways. Both **8** and **9** clearly result from hydrogen-abstraction reactions. The formation of **9** finds close analogy in the work of Jorgenson and Yang on *t*-butyl-substituted α,β -unsaturated ketones.⁸

Two rationalizations may be offered to explain the production of **8**. One involves abstraction of an allylic hydrogen atom from a terminal methyl group by the carbonyl oxygen atom, *via* a nine-membered-ring transition state, followed by radical coupling and ketonization of the resultant enol (eq 3). Alternatively, one can envisage a hydrogen atom abstraction by the α -carbon atom of the enone system, *via* a seven-membered ring, followed by radical coupling to give **8** directly, without intervention of an enol. Evidence in favor of process 3 was provided by irradiation of a solution of **5** in D₂O-dioxane. The **8** thus produced acquires one deuterium atom in the α -methylene group, as determined by nmr and mass spectral evidence.

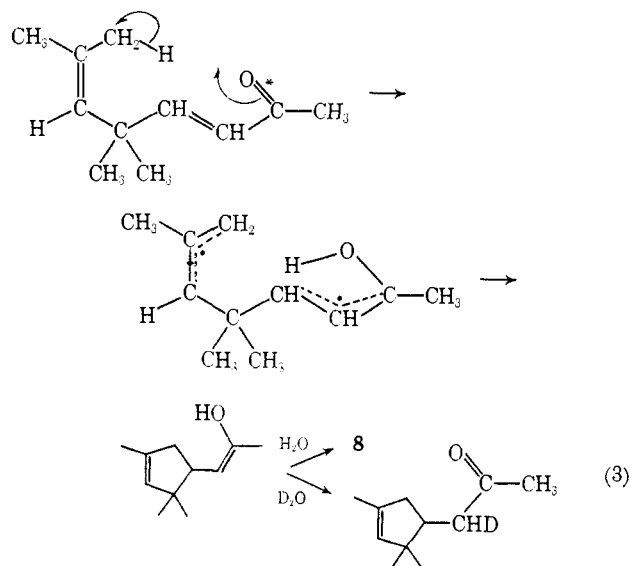
Intramolecular hydrogen-abstraction reactions have generally been considered to occur only when six- or seven-membered-ring transition states were available. Very recently, however, Breslow and Winnik have described intramolecular hydrogen atom abstractions by triplet benzophenones proceeding *via* a large ring.¹⁰ The present results provide the first example of an ex-

(7) Mass spectra were obtained through the good offices of the Cornell High Resolution Mass Spectrometer Facility, sponsored by National Institutes of Health Grant FR-00355.

(8) See, for a leading reference, N. C. Yang in "Reactivity of the Photoexcited Molecule" (Solvay Institute 13th Chemistry Conference), Interscience Publishers, London, 1967, p 145.

(9) See, for example, O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *J. Amer. Chem. Soc.*, **90**, 1657 (1968).

(10) R. Breslow and M. A. Winnik, *ibid.*, **91**, 3083 (1969).



cited acyclic carbonyl compound following a similar pathway *via* a medium-sized-ring transition state. Since this reaction is competitive with two other facile intramolecular processes, it appears that similar reactions may have general importance in favorable cases.

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Alkoxide-Induced Transformations of Epoxy-N-nitrosocarbamates

Sir:

As a continuation of our investigations on small-membered heterocyclic rings, we sought to define the reactivity of a carbenoid center adjacent to a three-membered oxirane ring.¹ We felt that this would be a particularly interesting species since its chemical properties would probably be different from the related carbocyclic system^{2,3} by virtue of the interaction of the carbenoid center with the electron pair on the adjacent heteroatom. Of the variety of methods that have been developed to generate carbenes,⁴ the thermal decomposition of a α -diazo epoxide seemed most appropriate. In this communication we wish to report the synthesis of two potential epoxycarbene progenitors and the novel reactions they undergo upon treatment with base.

Methyl *trans*-N-(1,3-diphenyl-2,3-epoxypropyl)carbamate was synthesized from *trans*-2,4-diphenyl-3-butenic acid⁵ *via* the acid chloride, the acid azide, the isocyanate, and peracid epoxidation of the N-alkenylcarbamate. The N-nitrosocarbamate I, mp 95–96°, was prepared by nitrosation of the corresponding carbamate with dinitrogen tetroxide by established procedures.^{6,7} Methyl *trans*-N-nitroso-N-(3-phenyl-2,3-

(1) For an alternate approach to the preparation of an epoxycarbene, see A. Padwa, *J. Org. Chem.*, **30**, 1274 (1965).

(2) K. B. Wiberg and J. M. Lavanish, *J. Amer. Chem. Soc.*, **88**, 365 (1966).

(3) F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, **88**, 3870 (1966).

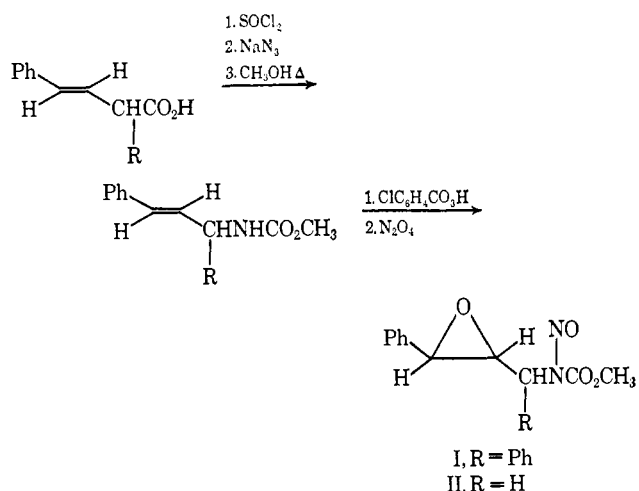
(4) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

(5) T. L. Jacobs and M. H. Goodrow, *J. Org. Chem.*, **23**, 1653 (1958).

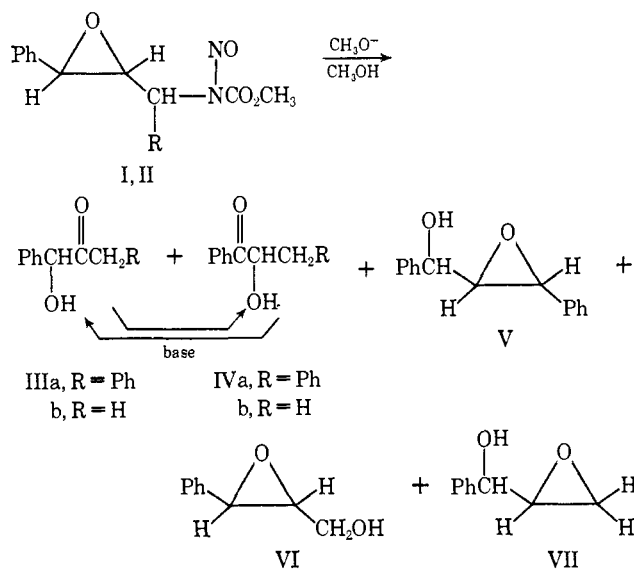
(6) E. H. White, *J. Amer. Chem. Soc.*, **77**, 6008 (1955).

(7) All new compounds were properly characterized, and acceptable chemical analyses were obtained.

epoxypropyl)carbamate (II), mp 61–62°, was prepared in an analogous fashion from *trans*-4-phenyl-3-butenic acid.⁸



Treatment of an anhydrous methanolic solution of epoxy-*N*-nitrosocarbamate I with sodium methoxide resulted in the rapid and near-quantitative evolution of nitrogen. Conventional isolation procedures afforded 1,3-diphenyl-1-hydroxypropan-2-one (IIIa), 1,3-diphenyl-2-hydroxypropan-1-one (IVa) (combined yield IIIa + IVa 40%), and 1,3-diphenyl-1-hydroxy-2,3-epoxypropane (V) (30%). These products were identified by comparison of infrared and mixture melting points with those of authentic samples.^{9–11} Dimethyl carbonate (isolated in over 90% yield) was produced by attack of methoxide ion on the carbonyl carbon of the *N*-nitrosocarbamate and is a coproduct of the reaction.¹² Similar treatment of carbamate II gave com-



(8) R. P. Linstead and L. T. D. Williams, *J. Chem. Soc.*, 2735 (1926).

(9) E. P. Kohler and R. H. Kimball, *J. Amer. Chem. Soc.*, **56**, 729 (1934).

(10) H. Burton and C. W. Shoppee, *J. Chem. Soc.*, 546 (1937).

(11) S. W. Chaikin and W. G. Brown, *J. Amer. Chem. Soc.*, **71**, 122 (1949).

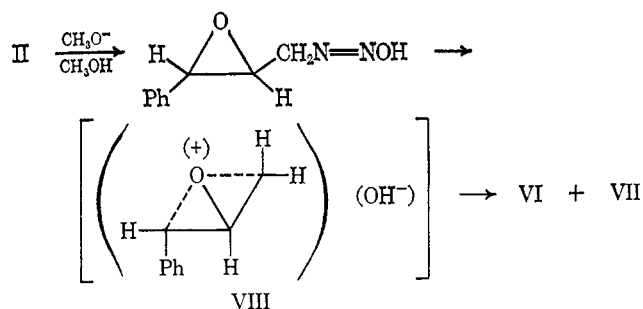
(12) Whether the base attacks at the acyl C or nitroso N depends on the type of substrate, base, and solvent used. Our system is optimal in all factors which favor acyl attack.¹³

(13) W. M. Jones and D. L. Muck, *J. Amer. Chem. Soc.*, **88**, 3798 (1966).

parable results; except for this case a mixture of epoxy alcohols was formed.¹⁴

The relative amounts of III and IV seemed to vary as a function of the experimental conditions and the work-up procedure employed. This variation could be attributed to the facile interconversion of the two ketones under the basic reaction conditions.¹⁰ When the reaction was effected in absolute ethanol using sodium carbonate as the base, only negligible quantities of IV were detected. This result implies that IV is a secondary reaction product derived from enolization of III.

Alkyl nitrosocarbamates are known to react with base in protic solvents to give diazoalkanes as well as solvolysis products that may be attributed to carbonium ion like intermediates.¹⁵ The observations of a number of investigators indicate that the reaction occurs by attack of base on the carbonyl carbon with the formation of an alkyl diazotate.¹⁶ In protic solvents the diazotate accepts a proton to form a diazotic acid which reacts further to form diazo compounds and/or solvolysis products. The observation that nitrogen evolution occurred during the basic cleavage of the nitrosocarbamates suggests that products III–VII were formed before the hydrolysis step. This suggestion is supported by the high yield of alcohols (III–VII) obtained from the reaction mixture prior to the addition of water. One possible explanation to account for part of these results would be that the epoxydiazotic acid decomposes with hydroxide return *via* an intimate diazonium ion–hydroxide ion pair. The rearranged epoxide VII would then arise from an ion-pair intermediate such as VIII.



This result is reasonable in view of the observation by Moss and coworkers that the *N*-nitroso-2-octylurethan system gives considerable net inversion,¹⁷ as well as the results from Hart's group wherein grossly different isomeric mixtures of ethers were obtained from isomeric allyl nitrosocarbamates.¹⁸

The formation of hydroxy ketones III and IV from the reaction of the epoxy-*N*-nitrosocarbamates in methanol may be rationalized on the basis of a nucleo-

(14) H. O. House, D. J. Reif, and R. L. Wasson, *ibid.*, **79**, 2490 (1957).

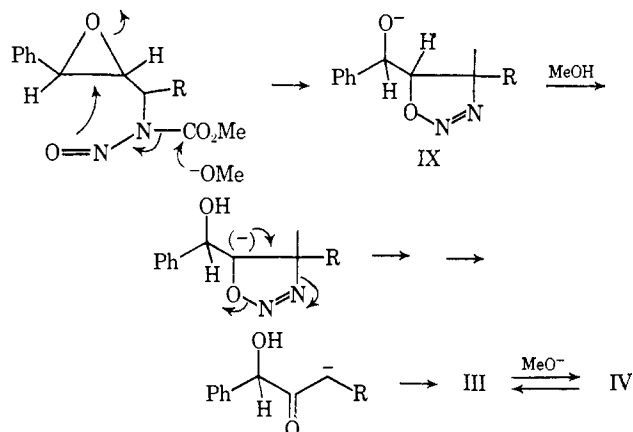
(15) (a) H. V. Pechmann, *Ber.*, **28**, 855 (1895); (b) R. Huisgen and J. Reinsertshofer, *Ann.*, **575**, 174 (1952); (c) C. D. Gutsche and H. E. Johnson, *J. Amer. Chem. Soc.*, **77**, 109 (1955); (d) D. E. Applequist and D. E. McGreer, *ibid.*, **82**, 1965 (1960); (e) R. A. Moss, *J. Org. Chem.*, **31**, 1082 (1966); (f) R. A. Moss and G. H. Temme, *Tetrahedron Lett.*, 3219 (1968).

(16) (a) A. Hantzsch and M. Lehman, *Ber.*, **35**, 897 (1902); (b) E. Muller, H. Haiss, and W. Rundel, *ibid.*, **93**, 1541 (1960); (c) E. K. Tandy and W. M. Jones, *J. Org. Chem.*, **30**, 4257 (1965); (d) R. A. Moss and F. C. Shulman, *Tetrahedron*, **24**, 2881 (1968); (e) R. A. Moss, F. C. Shulman, and E. Emery, *J. Amer. Chem. Soc.*, **90**, 2731 (1968); (f) W. M. Jones and D. L. Muck, *ibid.*, **88**, 68 (1966).

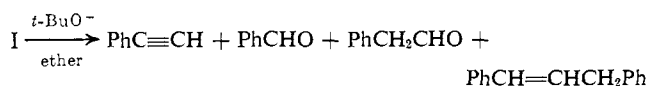
(17) R. A. Moss and S. M. Lane, *ibid.*, **89**, 5655 (1967).

(18) H. Hart and J. L. Brewbaker, *ibid.*, **91**, 716 (1969).

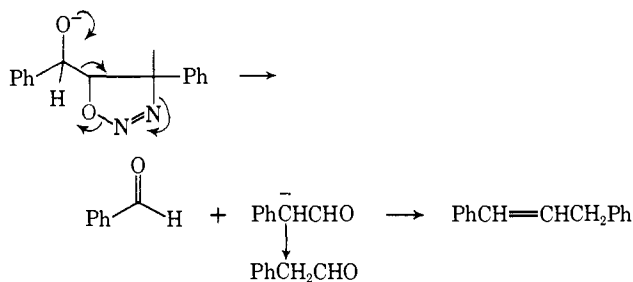
philic attack of the diazotate ion on the epoxide ring. Alternatively, the opening of the three-membered ring may be synchronous with attack of the base on the carbonyl carbon. Proton exchange of intermediate IX followed by collapse of the resultant anion and loss of nitrogen could give the enolate anion of ketone III.



Ketone III could then rearrange to give IV. This conversion would depend on the reaction conditions and the manner in which the products were separated from the reaction mixture. Although we have not been successful in obtaining direct evidence for this mechanism,¹⁹ it appears attractive for several reasons. First, it readily accounts for the presence of the hydroxy ketones in an anhydrous methanolic solution. Secondly, it accounts for the negligible quantities of IV when sodium carbonate was used as the base. This is readily attributed to the low rate of enolization of III with a weak base. A third factor that makes this mechanism intuitively attractive is our finding that the reaction follows a different course in an aprotic medium. Thus, treatment of I with potassium *t*-butoxide in ether resulted in the formation of phenylacetylene, benzaldehyde, phenylacetaldehyde, 1,3-diphenyl-1-propene, and 80% of a carbonate mixture consisting mainly of di-*t*-



butyl carbonate and methyl *t*-butyl carbonate. In this case, intermediate IX cannot undergo proton exchange readily and instead fragments to benzaldehyde and phenylacetaldehyde. The latter undergoes self-condensation to give 1,3-diphenyl-1-propene.²⁰



(19) The mechanisms we have presented here prove useful in explaining the products observed and in pointing the way toward new experiments. In no case do we consider these mechanisms as firmly established.

(20) E. K. Raunio and W. A. Bonner, *J. Org. Chem.*, **31**, 396 (1966).

Further work on the mechanism of the base- and thermal-induced transformations of epoxy-*N*-nitroso-carbamates is currently under way and will be the subject of future reports.

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(21) Alfred P. Sloan Fellow, 1968–1970.

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Quantum Yields for the Sensitized Photoisomerization of *cis*- and *trans*-Stilbene

Sir:

In continuing our study¹ of photosensitization by polymeric sensitizers, we obtained quantum yields for the sensitized isomerization of *cis*- and *trans*-stilbene that were different from those reported by Malkin and Fischer² and by Hammond, *et al.*³ In his thesis,⁴ Valentine has also reported values different from those of the above authors. These numbers are pertinent to the discussion of the mechanism for photoisomerization of the stilbenes in particular and therefore of olefins in general.^{2–5} Further, the sensitized isomerization of *trans*-stilbene has been used as an actinometer for other photochemical studies.^{4,6}

Malkin and Fischer² reported that at 25° the *trans* to *cis* quantum yield, ϕ_i , and the *cis* to *trans* quantum yield, ϕ_c , for 10⁻⁴ *M* methylcyclohexane solutions of stilbene were 0.50 and 0.30, respectively. According to Hammond,³ ϕ_i and ϕ_c for 0.05 *M* stilbene sensitized by a high-energy sensitizer, such as benzophenone or 4-methylbenzophenone, were 0.44 ± 0.01 and 0.39 ± 0.01, respectively. The fact that the sum, $\phi_i + \phi_c$, was less than unity was interpreted as an inefficiency in the stilbene photoisomerization. Furthermore, it was reported that as the concentration of *trans*-stilbene was decreased, ϕ_i increased, becoming about 0.5 at 10⁻⁴ *M*. This was taken as evidence that self-quenching by *trans*-stilbene was the source of some of this inefficiency. On the other hand Valentine⁴ reported a quantum yield of 0.55 for the benzophenone-sensitized isomerization of a 0.05 *M* solution of *trans*-stilbene. We therefore undertook to measure carefully the quantum yields ϕ_i and ϕ_c for several sensitizers over a wide range of stilbene concentrations, and we report here data that verify the value of ϕ_i obtained by Valentine. Our data also demonstrate the lack of self-quenching by *trans*-stilbene.

Solutions for irradiation were made by adding 6 ml of Eastman Spectro Grade benzene to weighed amounts of a sensitizer and either Eastman Scintillation Grade *trans*-stilbene or Aldrich Research Grade *cis*-stilbene (puri-

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(2) S. Malkin and E. Fischer, *J. Phys. Chem.*, **68**, 1153 (1964).

(3) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

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(6) C. DeBoer, *J. Am. Chem. Soc.*, **91**, 1855 (1969).