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Thermal and Base-Induced Transformations of Epoxy-*N*-nitrosocarbamates[1]

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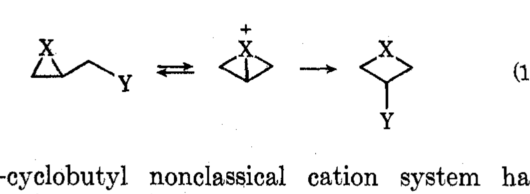
The thermal and base-catalyzed behavior of several *N*-nitrosoepoxycarbamates has been examined in mechanistic detail. Reaction of the *N*-nitrosocarbamates with base gave products resulting from both epoxide ring opening and collapse of intimate diazonium–hydroxide ion pairs. Thermal decomposition of methyl *trans-N*-nitroso(1,3-diaryl-2,3-epoxypropyl)carbamates gave the corresponding carbonates as the major products. Thermolysis of the related monophenyl epoxycarbamate proceeded *via* a different path. The thermal decomposition involves rearrangement of the nitrosocarbamate to a diazo ester which rapidly decomposes. For the diarylnitrosocarbamates, the decomposition involves dissociation into an ion pair, whereas a diazoalkane intermediate is formed with the monophenyl carbamate system.

Considerable attention has been focused in recent years on the conjugative properties of small rings when joined directly to an unsaturated grouping.[3] Among these studies have been many concerned with the conjugative interaction of small rings with adjacent carbonium ions.[4] Cyclopropylcarbinyl derivatives solvolyze with markedly enhanced rates to give rearranged and position-scrambled products of the allylcarbinyl, cyclobutyl, and cyclopropylcarbinyl types. There appears to be extensive charge delocalization from the carbinyl carbon of the cyclopropyl carbonium ion to the cyclopropane ring. Increased emphasis has also been given during the past few years to the solvolytic behavior of three-ring heterocyclic compounds.[5-10] The formal relationship of eq 1 to the cyclopropylcarbinyl–cyclobutyl nonclassical cation system has stimulated investigations with aziridinyl carbinyl derivatives,[5,6] as well as thirane[7-9] and oxirane analogs.[10] Replacement of a methylene group in cyclopropane by a heteroatom has been found to severely dampen the ability of the three ring to delocalize the charge.[5-10]



(1)

As part of a program designed to delineate the interaction of small ring heterocycles with adjacent reaction centers, we sought to define the reactivity of a carbenoid center adjacent to a three-membered heterocyclic ring. We felt that this would be a particularly interesting species, since its chemical properties would probably be different from the related carbocyclic system[11,12] (as was noted for the above carbonium ion system) 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,[13] the thermal decomposition of an α-diazo epoxide seemed most appropriate. A standard method used for generating diazoalkanes and, hence, potential carbenes is the reaction of the appropriate *N*-nitrosocarbamate with base.[14] The purpose of this paper is to report the synthesis of several potential epoxycarbene progenitors and the novel reactions they undergo upon thermolysis or by treatment with base.

Methyl *trans-N*-(1,3-diphenyl-2,3-epoxypropyl)carbamate (**2**) was synthesized from *trans*-2,4-diphenyl-3-butenoic acid *via* the acid chloride, the acid azide, the isocyanate, and peracid epoxidation of the *N*-alkenylcarbamate. The *N*-nitrosocarbamate **4**, mp 95–96°, was prepared by nitrosation of carbamate **2** with dinitrogen tetroxide by established procedures.[15]

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(1) For a preliminary report, see A. Padwa, N. C. Das, and D. Eastman, *J. Amer. Chem. Soc.*, **91**, 5178 (1969).

(2) Alfred P. Sloan Foundation Research Fellow, 1968–1972.

(3) For a review, see M. Y. Lukina, *Russ. Chem. Rev.*, 419 (1962).

(4) For a review, see R. Breslow in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 4.

(5) V. R. Gaertner, *Tetrahedron Lett.*, 5919 (1969); *J. Org. Chem.*, **35**, 3952 (1970).

(6) J. A. Deyrup and C. L. Moyer, *Tetrahedron Lett.*, 6179 (1969).

(7) J. C. Martin and D. J. Anderson, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, p O-31.

(8) M. Sander, *Monatsh. Chem.*, **96**, 896 (1965).

(9) E. P. Adams, K. N. Ayad, F. P. Doyle, D. O. Holland, W. H. Hunter, J. H. C. Nayler, and A. Queen, *J. Chem. Soc.*, 2665 (1960).

(10) H. G. Richey, *Tetrahedron Lett.*, 5919 (1968).

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

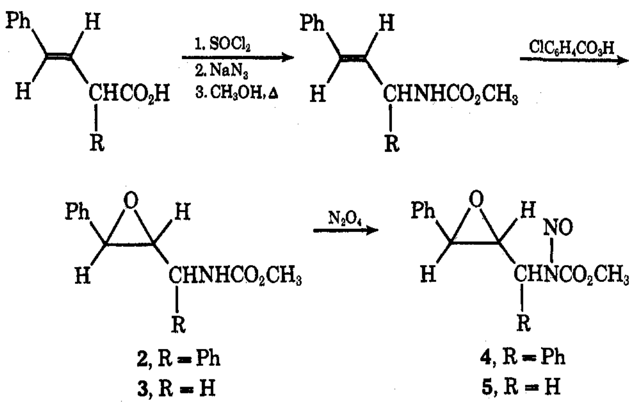
(12) F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, **88**, 3870 (1966).

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

(14) H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1961, pp 21–23.

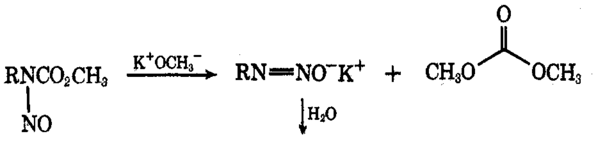
(15) E. H. White, *J. Amer. Chem. Soc.*, **77**, 6008 (1955).

SCHEME I



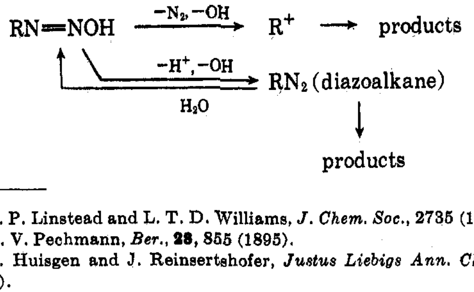
Methyl *trans*-*N*-nitroso-*N*-(3-phenyl-2,3-epoxypropyl)carbamate (**5**), mp 61–62°, was prepared in an analogous fashion from *trans*-4-phenyl-3-butenoic acid[16] (see Scheme I). The spectral data (infrared, ultraviolet, nmr) and elemental analysis of carbamates **2**–**5** were consistent with their assignments and are summarized in the Experimental Section.

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-like intermediates.[17-22] 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 and dialkyl carbonate.[23-28] Attack of the base at the acyl C or nitroso N has been shown to depend on the type of substrate, base, and solvent used.[29] The diazotates can, in the absence of protic solvents, be isolated as salts.[23-28] Addition of water to the diazotate salt involves a rapid proton transfer to produce a diazotic acid.



$$\underset{\text{NO}}{\text{RNCO}_2\text{CH}_3} \xrightarrow{\text{K}^+\text{OCH}_3^-} \underset{\text{RN}{=}\text{NOH} + \text{K}^+\text{OH}^-}{\underset{\downarrow\ \text{H}_2\text{O}}{\text{RN}{=}\text{NO}^-\text{K}^+}} + \text{CH}_3\text{OC(=O)OCH}_3$$

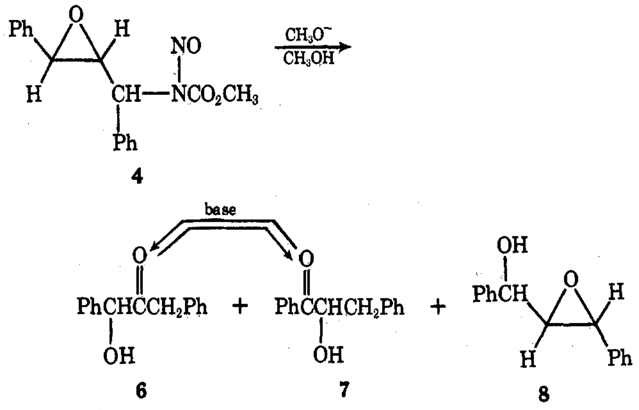
Two modes of decomposition are available to the diazotic acid in basic media.



$$\text{RN}{=}\text{NOH} \xrightarrow{-\text{N}_2,\,-\text{OH}} \text{R}^+ \longrightarrow \text{products}$$
$$\text{RN}{=}\text{NOH} \underset{\text{H}_2\text{O}}{\overset{-\text{H}^+,\,-\text{OH}}{\rightleftharpoons}} \text{RN}_2\ (\text{diazoalkane}) \longrightarrow \text{products}$$

The partition between carbonium ion derived products and products resulting from diazoalkanes is dependent upon the structure of the alkyl groups and the nature of the reaction medium. In general, secondary alkyl diazotates seem to decompose in aqueous solution to give carbonium ion products unless some structural feature is present to stabilize the diazoalkane.[30] Diazo compounds are favored in methanol compared with water. Since carbamate **4** bears a phenyl group in the α position whereas **5** does not, it was reasonable to assume that the epoxy diazotic acids derived from **4** and **5** would partition in different directions.

Treatment of an anhydrous methanolic solution of epoxy-*N*-nitrosocarbamate **4** with sodium methoxide resulted in the rapid and near-quantitative evolution of nitrogen. Conventional isolation procedures afforded 1,3-diphenyl-1-hydroxypropan-2-one (**6**), 1,3-diphenyl-2-hydroxypropan-1-one (**7**) (combined yield of **6** + **7** 40%) and 1,3-diphenyl-1-hydroxy-2,3-epoxypropane (**8**, 30%). These products were identified by comparison of infrared and mixture melting points with those of authentic samples.[31-33] 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. Attack of the base at the carbonyl group was expected, since the reaction was carried out under conditions which favor acyl attack.[29] The relative amounts of **6** and **7** 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.[32] When the reaction was effected in absolute ethanol using sodium carbonate as the base, only negligible quantities of **7** were detected. This result implies that **7** is a secondary reaction product derived from enolization of **6**.



Similar treatment of carbamate **5** gave comparable results, except that in this case small amounts of 1-phenyl-1,2-propanedione (2%) (**11**) and a mixture of epoxy alcohols **12** and **13** were formed. The identity of the products derived from **5** was established by comparison with authentic samples (see Experimental Section). Again the relative amounts of hydroxy ketones **9** and **10** varied as a function of experimental conditions and can be attributed to their facile inter-

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

[17] H. V. Pechmann, *Ber.*, **28**, 855 (1895).

[18] R. Huisgen and J. Reinsertshofer, *Justus Liebigs Ann. Chem.*, **575**, 174 (1952).

[19] C. D. Gutshe and H. E. Johnson, *J. Amer. Chem. Soc.*, **77**, 109 (1955).

[20] D. E. Applequist and D. E. McGreer, *ibid.*, **82**, 1965 (1960).

[21] R. A. Moss, *J. Org. Chem.*, **31**, 1082 (1966).

[22] R. A. Moss and G. H. Temme, *Tetrahedron Lett.*, 3219 (1968).

[23] A. Hantzsch and M. Lehman, *Ber.*, **35**, 897 (1902).

[24] E. Muller, H. Haiss, and W. Rundel, *ibid.*, **93**, 1541 (1960).

[25] E. K. Tandy and W. M. Jones, *J. Org. Chem.*, **30**, 4257 (1965).

[26] R. A. Moss and F. C. Shulman, *Tetrahedron*, **24**, 2881 (1968).

[27] R. A. Moss, F. C. Shulman, and E. Emery, *J. Amer. Chem. Soc.*, **90**, 2731 (1968).

[28] W. M. Jones and D. L. Muck, *ibid.*, **88**, 68 (1966).

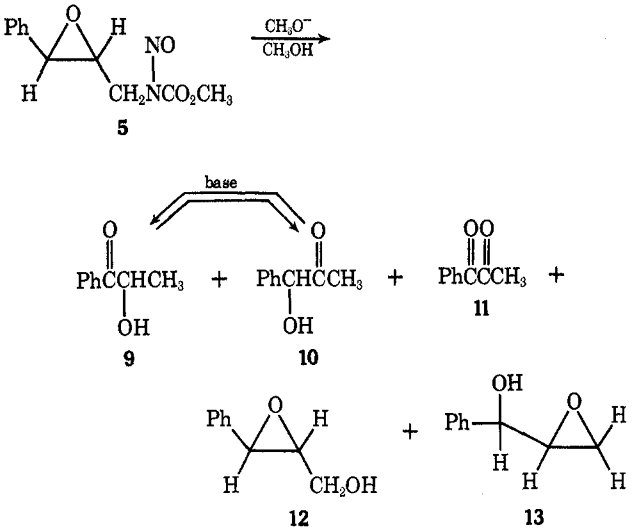
[29] W. M. Jones and D. L. Muck, *ibid.*, **88**, 3798 (1966).

[30] E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, p 462.

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

[32] H. Burton and C. W. Shoppe, *J. Chem. Soc.*, 546 (1937).

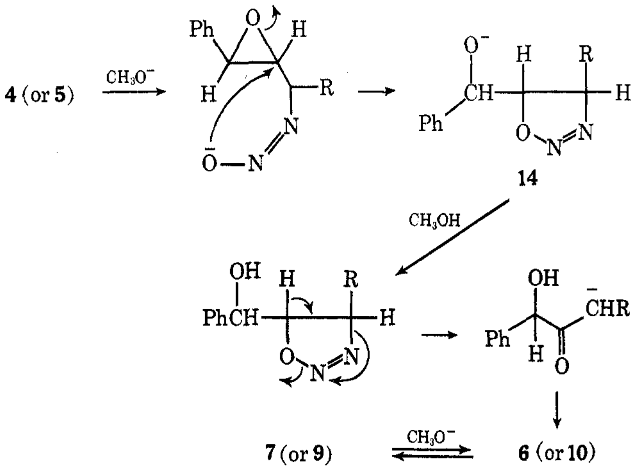
[33] S. W. Chaikin and W. G. Brown, *J. Amer. Chem. Soc.*, **71**, 122 (1949).



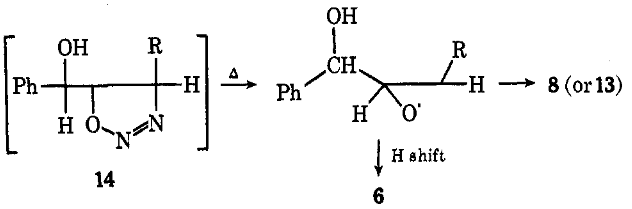
conversion under the reaction conditions.[32] The small amount of **11** formed is presumably due to the air oxidation of **9** or **10**.

These results are surprising, since the base-induced decomposition of nitrosocarbamates in anhydrous methanol should lead to methyl ethers rather than alcohols. The observation that nitrogen evolution occurred during the basic cleavage of nitrosocarbamates **4** and **5** suggests that products **6–13** were formed before the hydrolysis step. This suggestion is supported by the fact that similar yields of alcohols **6–13** were obtained from the reaction mixture prior to the addition of water.

The formation of hydroxy ketones **6** and **7** or **9** and **10** from the reaction of the epoxy-*N*-nitrosocarbamates in methanol may be rationalized by a nucleophilic attack of the diazotate on the epoxide ring to generate intermediate **14**. A related internal ring cyclization of an allenyl diazotate has been reported by Jones and Northington[34] and provides reasonable chemical precedent for the cyclization step.



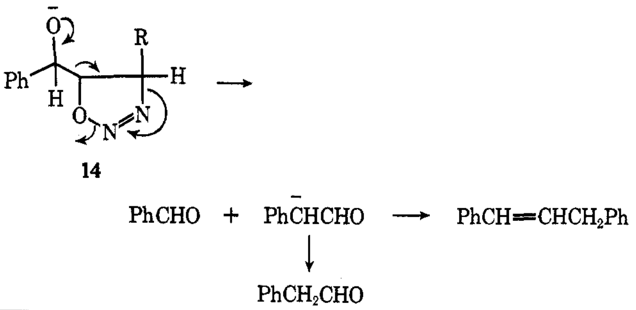
Alternatively, the opening of the three-membered ring may be synchronous with attack of the base on the carbonyl carbon. Protonation of intermediate **14** followed by extrusion of nitrogen and loss of a proton could give the enolate anion of ketone **6** (or **10**). These ketones could then interconvert under the reaction conditions. The conversion (**6** → **7**) would depend on the reaction conditions and the manner in which the products were separated from the reaction mixture. Another possibility would involve thermal loss of nitrogen from protonated **14** and formation of a diradical which could close to give an epoxy alcohol or undergo hydrogen migration to give ketone **6** (or **10**).



This latter sequence is reminiscent of the type of path involved in the photochemistry of α,β-epoxy ketones.[35] Whether hydroxy ketone **6** arises from the reaction of **14** with base or by thermal nitrogen extrusion remains an open question.[36]

Although we have not been successful in obtaining direct evidence for this mechanism, it appears attractive for several reasons. First, it readily accounts for the presence of hydroxy ketones in an anhydrous methanolic solution. Secondly, it accounts for the negligible quantities of **7** (or **9**) when sodium carbonate was used as the base. This is readily attributed to the low rate of enolization of **6** (or **10**) with a weak base. A third factor that makes this mechanism intuitively attractive is our finding that the reaction of epoxycarbamate **4** follows a different course in an aprotic medium. Thus, treatment of **4** with potassium *tert*-butoxide in ether resulted in the formation of benzaldehyde, phenylacetaldehyde, 1,3-diphenyl-1-propene, 80% of a carbonate mixture consisting mainly of di-*tert*-butyl carbonate and some methyl *tert*-butyl carbonate, and small quantities of phenylacetylene. In this case, intermediate **14** is poorly solvated and since it cannot undergo ready proton exchange it fragments to benzaldehyde and phenylacetaldehyde. The latter is known to undergo self-condensation to produce 1,3-diphenyl-1-propene.[37]

$$\mathbf{4} \xrightarrow[\text{ether}]{tert\text{-BuO}^-} \text{PhCHO} + \text{PhCH}_2\text{CHO} + \text{PhCH}{=}\text{CHCH}_2\text{Ph} + \text{PhC}{\equiv}\text{CH}$$



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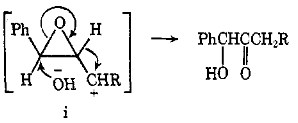
[34] D. J. Northington and W. M. Jones, *Tetrahedron Lett.*, 317 (1971).

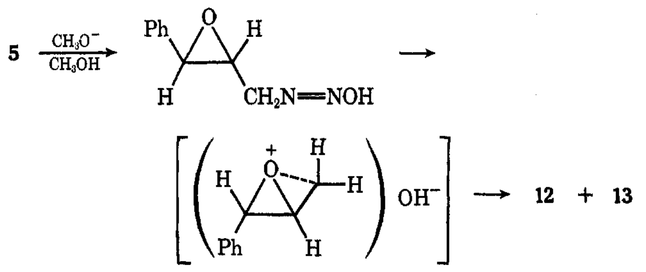
[35] A. Padwa in "Organic Photochemistry," Vol. I. O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 92.

[36] Still another possibility involves collapse of a tight ion pair such as i to keto alcohol **6** (or **10**). This would require a very tight and transient ion pair; otherwise it would be very difficult to explain the absence of methoxy products.


i

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

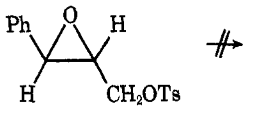
The mechanism of the epoxy alcohol formation is somewhat unclear. One possible explanation to account for the results would be that the epoxy diazotic acid decomposes with hydroxide return *via* an intimate diazonium–hydroxide ion pair. The rearranged epoxy alcohol **13** would then arise from an ion-pair intermediate such as **15**. This result is reasonable in



15

view of the observation by Moss and coworkers that the *N*-nitroso-2-octylurethan system gives considerable net inversion,[38] as well as the results from Hart's group wherein grossly different isomeric mixtures of ethers were obtained from isomeric allyl nitrosocarbamates.[39]

It is noteworthy that 2-phenyl-3-oxetanol was not detected as a by-product in the above reaction. Richey and Kinsman[10] have reported that the solvolysis of esters of several 2,3-epoxy-1-propanols led to the formation of 3-oxetanol derivatives by way of 1-oxabicyclobutonium cations. These workers did not dectect any epoxide rearrangement in the series investigated. It should be pointed out, however, that the epoxides examined in that study were so substituted as to minimize such a rearrangement. In an attempt to determine whether epoxy–carbinyl cations undergo epoxide scrambling, we have investigated the solvolytic behavior of tosylate **16**. After refluxing **16** for 2 days in aqueous dioxane, there was no evidence of reaction and consequently we have not been able to reach a satisfactory conclusion in this regard.



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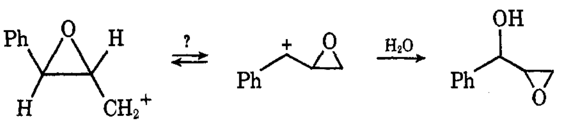
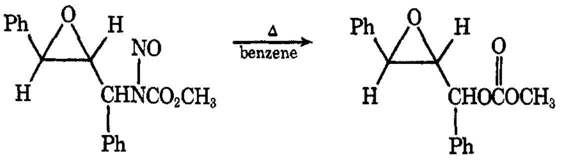


16

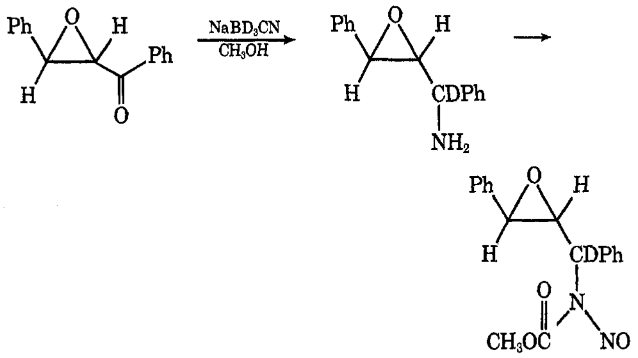
The thermal decomposition of *N*-alkyl-*N*-nitrosoamides and *N*-alkyl-*N*-nitrosocarbamates has been well studied by White[40] and others.[41,42] The first step involves rearrangement of the nitroso compound to a diazo ester, which then rapidly decomposes to esters and olefins; the exact mechanism for this decomposition depends upon solvent polarity and the type of amine. For nitrosocarbamates of secondary amines, the decomposition involves dissociation of the initially formed diazo ester into an ion pair, extrusion of nitrogen to form a second ion pair, and the formation of either esters or olefins from the latter ion pair. In order to obtain additional data on the behavior of epoxy–carbinyl cation ion pairs, we have investigated the thermolysis of several *N*-nitrosocarbamates.

Thermal decomposition of **4** at 80° in benzene gave methyl 1(1,3-diphenyl-2,3-epoxypropyl)carbonate (**17**) as the sole product (90%). The structure of the product was established by its spectral data and by hydrolysis to the corresponding alcohol followed by Sarett oxidation to *trans*-chalcone oxide.



4 **17**

In order to test for possible epoxide scrambling, we investigated the thermolysis of epoxycarbamates **18**, **19**, and **20**. The synthesis of epoxycarbamate **18**, containing 85% deuterium at the 1 position, was carried out by sodium cyanodeuterioborate reduction[43] of *trans*-chalcone oxide, followed by reaction with methyl chloroformate and dinitrogen tetroxide. Thermal rearrangement of **18** at 80° in benzene gave a 93% yield of **21**. Nmr analysis of carbonate **21** indicated that no deuterium scrambling had occurred. Simi-



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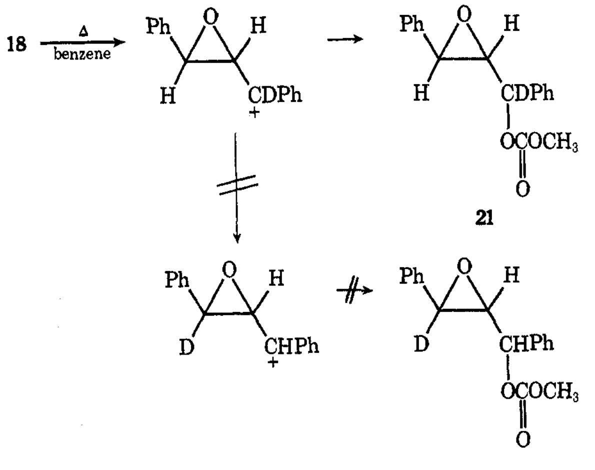

21

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(38) R. A. Moss and S. M. Lane, *J. Amer. Chem. Soc.*, **89**, 5655 (1967).

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

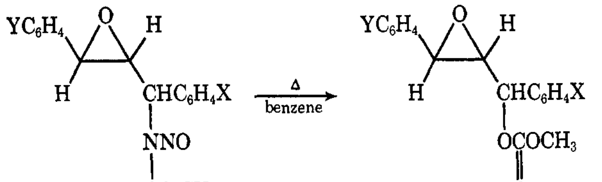
(40) E. H. White, *J. Amer. Chem. Soc.*, **77**, 6011 (1955); **77**, 6014 (1955); **83**, 1174 (1961); **83**, 1179 (1961).

(41) R. Huisgen and H. Reimlinger, *Justus Liebigs Ann. Chem.*, **599**, 183 (1956).

(42) A. Streitweiser and W. D. Schaffer, *J. Amer. Chem. Soc.*, **79**, 2893 (1957).

(43) R. F. Borch and H. D. Durst, *ibid.*, **91**, 3996 (1969).

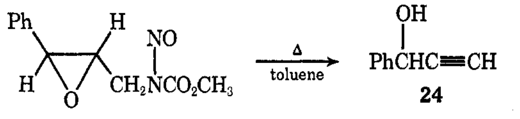
larly, thermolysis of carbamates **19** and **20** gave unscrambled carbonates 22 and 23.



19, X = H; Y = Cl
20, X = Cl; Y = H

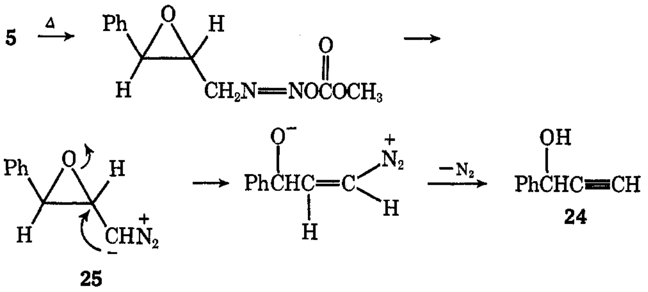
22, X = H; Y = Cl
23, X = Cl; Y = H

Since collapse of the ion pair in nonpolar solvents to form esters should be very fast, epoxide scrambling would have to proceed at a very rapid rate in order to compete. The results indicate that this is not the case. Epoxycarbamates **17**, **19**, and **20** were also treated with base and the epoxy alcohols isolated from the crude reaction mixture were found to be unrearranged. The absence of any significant scrambling of the aryl groups implies that either the collapse of the tight ion pair is very rapid when compared to the rearrangement, or that participation of the epoxide ring is only significant in those cases where a primary carbonium ion is generated adjacent to the epoxide ring. In order to test the latter possibility, we investigated the thermal behavior of epoxycarbamate **5**. The thermolysis of **5** was first attempted using conditions comparable to those used for the diaryl epoxycarbamates. Under this set of conditions only recovered starting material was obtained. However, when **5** was heated at reflux in toluene for 24 hr, a nearly quantitative yield of 3-phenyl-3-hydroxypropyne (**24**) was obtained. The results indicate that the decomposition paths for carbamates **4** and **5** are substantially different. The carbonium ion pathway, found to operate in the decomposition of nitrosocarbamates of secondary carbinamines[30] (such as **4**) is not followed with **5**, presumably because of the relatively high energy of a primary carbonium ion. One intermediate which should be considered as a possible precursor for compound **24** is diazoalkane **25**. *N*-nitrosocarbamates of primary carbinamines are known to decompose to give the corresponding esters *via* a reaction series involving diazoalkane intermediates.[30] This diazo compound would readily account for product **24** by the route shown below. The elevated temperature required for the decomposition of **5** may result in the further decomposition of methyl bicarbonate, thereby precluding its recombination with diazoalkane **25**. The detection of carbon dioxide and methanol from the decomposition of **5** provides support for this suggestion.



5

24



25

24

An alternate path that could also explain the formation of acetylene **24** would involve decomposition of **25** to a carbene followed by bond reorganization. Attempts to trap such a carbene were unsuccessful. The absence of an adduct, however, cannot be taken as definitive evidence against a carbene because bond reorganization may be so fast as to preclude trapping. Unfortunately, the thermal behavior of carbamate **5** does not provide sufficient data to distinguish between these two possibilities, nor do the thermal results aid in understanding the mode of formation of epoxide **13**. Further experiments are underway to clarify this point.

Experimental Section[44]

Methyl *trans*-*N*-(1,3-Diphenyl-2,3-epoxypropyl)carbamate (2).—To a solution of 30 g of *trans*-1,3-diphenylpropene in 30 ml of anhydrous tetrahydrofuran at 0° was added 60 ml of a 1.6 *M* solution of *n*-butyllithium in hexane. After stirring for 5 min, 3 ml of hexamethylphosphorotriamide was added and the mixture was allowed to stir for an additional 2 hr. At the end of this time, an ethereal carbon dioxide mixture was introduced into the reaction flask until the red color disappeared. The resultant solid was hydrolyzed with 600 ml of a 2 *N* sodium carbonate solution followed by 200 ml of dilute ammonium hydroxide. The aqueous layer was extracted with ether and then acidified with concentrated hydrochloric acid. The solid that formed was filtered and crystallized from hexane to give 18 g (56%) of *trans*-2,4-diphenyl-3-butenoic acid, mp 124–126° (lit.[45] 128–129°).

To a solution of 18 g of the above acid in 200 ml of ether at 0° was added 20 ml of thionyl chloride. The mixture was stirred at 0° until all of the acid had reacted (*ca.* 1 hr). The solvent was removed under reduced pressure and the crude acid chloride was used without further purification. To a solution of the acid chloride in 150 ml of anhydrous acetone at −15° was added 14.4 g of sodium azide in 72 ml of water at such a rate so as to maintain the temperature of the reaction between −10 and −15°. The reaction solution was stirred for an additional 30 min at 0° and then poured onto 500 g of cracked ice. The water layer was extracted with ether and the ethereal layer was dried over magnesium sulfate. Anhydrous methanol (200 ml) was then added to the solution and the ether was removed by distillation. The solution was then heated at reflux for 2 hr, cooled, and allowed to stand overnight. The solvent was removed under reduced pressure and the resulting oil solidified upon standing. Crystallization from hexane gave 19.5 g (62%) of methyl *trans*-*N*-(1,3-diphenyl-2-propenyl)carbamate, mp 108–110°.

Anal. Calcd for $C_{17}H_{17}O_2N$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.19; H, 6.34; N, 5.01.

The infrared spectrum exhibited bands at 3.05, 5.91, 6.62, and 10.35 μ.

To a solution of 10.5 g of the above carbamate in 200 ml of methylene chloride at 0° was slowly added 15.7 g of 85% *m*-chloroperbenzoic acid. The mixture was stirred for an additional 2 hr at 0° and was then allowed to warm to room temperature. The *m*-chlorobenzoic acid was filtered and the solution was washed with water and 5% sodium bicarbonate and dried over magnesium sulfate. The solvent was removed under

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[44] All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with the Varian Associates high-resolution spectrometer. Tetramethylsilane was used as an internal standard.

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

reduced pressure to give a solid which was crystallized from hexane–ether to give 6.9 g (64%) of methyl *trans*-*N*-(1,3-diphenyl-2,3-epoxypropyl)carbamate (**2**), mp 101–102°.

Anal. Calcd for $C_{17}H_{17}O_3N$: C, 72.06; H, 6.05; N, 4.94. Found: C, 72.31; H, 6.32; N, 4.66.

The infrared spectrum exhibited bands at 3.05, 5.91, and 6.45 μ. The nmr spectrum ($CDCl_3$) was characterized by multiplets at τ 6.72 (1 H), 6.30 (1 H), and 5.16 (1 H), a singlet at τ 6.35 (3 H), a broad doublet at τ 4.80 (1 H), and a doublet at τ 2.70 (10 H).

Methyl *trans*-*N*-Nitroso-*N*-(1,3-diphenyl-2,3-epoxypropyl)-carbamate (4).—To 4.1 g of the above epoxycarbamate in 50 ml of methylene chloride was added 1.2 g of anhydrous sodium acetate. The resulting mixture was cooled to −25°, a solution of 7.0 g of dinitrogen tetroxide in 50 ml of anhydrous ether was added, and the mixture was allowed to stir at −20 to −25° for 2 hr. At the end of this time the reaction mixture was poured into a cold 5% sodium bicarbonate solution and then extracted with ether. The ethereal extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure to give a yellow solid (4.0 g). Crystallization from methanol gave yellow prisms of methyl *trans*-*N*-nitroso-*N*-(1,3-diphenyl-2,3-epoxypropyl)carbamate (**4**) (78%), mp 95–96°.

Anal. Calcd for $C_{17}H_{16}O_4N_2$: C, 65.37; H, 5.15; N, 8.97. Found: C, 65.29; H, 5.19; N, 8.99.

The infrared spectrum (KBr) exhibited bands at 5.70, 6.57, 6.92, and 9.91 μ. The nmr spectrum ($CDCl_3$) showed a doublet at τ 6.37 (1 H, J = 2.0 Hz), a doublet of doublets at τ 6.07 (1 H, J = 7.0 and 2.0 Hz), a singlet at τ 6.05 (3 H), a doublet at τ 4.36 (1 H, J = 7.0 Hz), and a multiplet at τ 2.71 (10 H).

Methyl *trans*-*N*-(3-Phenyl-2,3-epoxypropyl)carbamate (3).—To a solution of 10 g of 4-phenyl-3-butenoic acid in 100 ml of methylene chloride was slowly added 15 ml of thionyl chloride. The solution was stirred for 2 hr and the solvent and excess thionyl chloride were removed under reduced pressure. The crude acid chloride was dissolved in 100 ml of anhydrous acetone and the solution was cooled to −15°. A solution of 12 g of sodium azide in 50 ml of water was slowly added and the temperature was maintained at −10 to −15°. The reaction solution was stirred for an additional 15 min and then poured into ice water and extracted with ether. The ethereal layer was dried over sodium sulfate. Anhydrous methanol (200 ml) was added to the solution and the ether was removed by distillation. After the ether was removed the methanolic solution was heated at reflux for 1 hr. The methanol was removed under reduced pressure and the residue solidified upon cooling. Crystallization from hexane gave methyl *trans*-*N*-(3-phenyl-2-propenyl)carbamate, 6.2 g (30%), mp 51–52°. The infrared spectrum exhibited bands at 3.02, 5.81, 8.05, and 10.35 μ. The nmr spectrum showed a singlet at τ 6.47 (3 H), a triplet at τ 6.18 (2 H), a broad singlet a τ 4.42 (1 H), a multiplet centered at τ 3.8 (2 H), and a singlet at τ 2.82 (5 H).

To an ice-cooled solution of the above carbamate (0.56 g) in 10 ml of methylene chloride was slowly added 0.65 g of *m*-chloroperbenzoic acid (85%). The mixture was stirred for 1 hr at 0° and the solution was slowly allowed to reach room temperature. The solid precipitate that formed was removed by filtration and the methylene chloride solution was diluted with ether. The ethereal solution was washed with water and 5% sodium bicarbonate solution, and then dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was crystallized from hexane to give 0.48 g (81%) of methyl *trans*-*N*-(3-phenyl-2,3-epoxypropyl)carbamate (**3**), mp 51–52°.

Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.43; H, 6.38; N, 6.81.

The infrared spectrum (CCl_4) showed bands at 3.01, 5.81, and 6.62 μ. The nmr spectrum ($CDCl_3$) showed a multiplet at τ 6.88 (1 H), a multiplet centered at τ 6.42 (3 H), a singlet at τ 6.37 (3 H), a broad singlet at τ 4.33 (1 H), and a singlet at τ 2.77 (5 H).

Methyl *trans*-*N*-Nitroso-*N*-(3-phenyl-2,3-epoxypropyl)carbamate (5).—To a solution of the above carbamate (0.621 g) in 20 ml of anhydrous ether at −78° was added 0.25 g of anhydrous sodium acetate and 0.5 g of dinitrogen tetroxide in 10 ml of ether. The mixture was stirred at −78° for 2 hr and then poured into an ice-cold 10% sodium bicarbonate solution. The aqueous layer was extracted with ether and the etheral extracts were dried over sodium sulfate. The solvent was removed under reduced pressure to give an oil which solidified on standing. Crystallization of the solid from ether–hexane gave 0.54 g of yellow crystals of methyl *trans*-*N*-nitroso-*N*-(3-phenyl-2,3-epoxypropyl)carbamate (**5**), mp 61–62°.

Anal. Calcd for $C_{11}H_{12}N_2O_4$: C, 55.98; H, 5.12; N, 11.86. Found: C, 56.18; H, 5.22; N, 11.81.

The infrared spectrum exhibited bands at 5.68 and 5.92 μ and a doublet at 8.62 and 8.82 μ. The nmr spectrum contained a multiplet at τ 6.38 (1 H, J = 1.8 Hz), a complex multiplet centered at τ 5.96 (2 H), and singlets at τ 5.94 (3 H) and 2.77 (5 H).

Methyl *trans*-*N*-Nitroso-*N*-(1-phenyl-3-*p*-chlorophenyl-2,3-epoxypropyl)carbamate (19).—To a solution of ammonium nitrate (30.4 g) and lithium cyanohydridoborate[43] (1.88 g) in 300 ml of anhydrous methanol was added 5.2 g of *trans*-1-phenyl-3-*p*-chlorophenyl-2,3-epoxypropan-1-one.[46] The solution was stirred for 46 hr at room temperature and then poured into dilute acetic acid. The acidic solution was washed with several portions of ether and was then made strongly basic with ammonium hydroxide. The basic solution was extracted with ether and the ethereal extracts were dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude amine (2.3 g) that was obtained was used without further purification.

To a solution of 2.3 g of the above amine in 50 ml of anhydrous ether was added 0.36 g of sodium hydroxide and 0.86 g of methyl chloroformate. The reaction mixture was stirred for 45 min, then poured into water and extracted with ether. The ethereal layer was washed with dilute hydrochloric acid and water, and then dried over magnesium sulfate. The solvent was removed under reduced pressure to give a crude oil (1.6 g). The oil was crystallized from hexane–ether to give 0.96 g of epoxy carbamate. The infrared spectrum exhibited bands at 3.05, 5.91, 6.51, 8.01, 9.15, 9.65, and 9.85 μ. The epoxycarbamate was used without further purification.

A solution of the above epoxycarbamate (0.95 g) in 20 ml of methylene chloride was cooled to −25° and 0.25 g of anhydrous sodium acetate was added. A solution of 1.0 g of dinitrogen tetroxide in 30 ml of anhydrous ether was cooled to −78° and added to the above solution. The mixture was stirred for 2 hr, poured into a cold 5% sodium bicarbonate solution, and extracted with ether. The ethereal extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. Crystallization of the resulting oil from methanol–water gave yellow crystals of methyl *trans*-*N*-nitroso-*N*-(1-phenyl-3-*p*-chlorophenyl-2,3-epoxypropyl)carbamate (**19**), mp 95–96°.

Anal. Calcd for $C_{17}H_{15}O_4N_2Cl$: C, 58.88; H, 4.36; N, 8.07. Found: C, 59.09; H, 4.22; N, 8.23.

The infrared spectrum exhibited bands at 5.68, 6.58, 6.93, and 9.81 μ. The nmr spectrum consisted of a multiplet at τ 2.65 (9 H), a doublet at τ 4.44 (1 H, J = 7 Hz), a singlet at τ 5.98 (3 H), a multiplet at τ 6.20 (1 H), and a doublet at τ 6.44 (1 H).

Methyl *trans*-*N*-Nitroso-*N*-(1-*p*-chlorophenyl-3-phenyl-2,3-epoxypropyl)carbamate (20).—*trans*-1-*p*-Chlorophenyl-3-phenyl-2,3-epoxypropan-1-one[46] (5.0 g) was subjected to the same reductive amination conditions as described above and yielded 2.3 g of crude amine. To a solution of 2.3 g of the amine in anhydrous ether (30 ml) was added 0.8 g of methyl chloroformate and 0.36 g of sodium hydroxide in 1 ml of water. The reaction solution was stirred for 45 min and then poured into water. The ethereal layer was removed, washed with dilute hydrochloric acid and water, and then dried over magnesium sulfate. The solvent was removed under reduced pressure to give 2.4 g of a white solid. This material was crystallized from hexane–benzene to give 1.7 g of white crystals, mp 141–143°. Recrystallization from hexane–benzene gave analytically pure methyl *trans*-*N*-(1-*p*-chlorophenyl-3-phenyl-2,3-epoxypropyl)carbamate, mp 144–145°.

Anal. Calcd for $C_{17}H_{16}O_3NCl$: C, 64.25; H, 5.08; N, 4.40. Found: C, 64.11; H, 5.03; N, 4.38.

The infrared spectrum exhibited bands at 3.08, 5.91, 6.51, 7.82, 9.13, 9.61, and 9.83 μ. The nmr spectrum consisted of a multiplet at τ 6.7 (1 H), a singlet at τ 6.30 (3 H), a doublet at τ 6.27 (1 H, J = 8 Hz), a multiplet centered at τ 5.08 (1 H), a broad doublet at τ 4.35 (1 H, J = 8 Hz), and a multiplet at τ 2.63 (9 H).

A solution of the above carbamate (2.1 g) in methylene chloride (20 ml) was cooled to −25° and 0.25 g of anhydrous sodium acetate and 2.0 g of dinitrogen tetroxide in 20 ml of ether were added. The reaction mixture was stirred at −20° for 2 hr and

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(46) H. O. House and G. D. Ryerson, *J. Amer. Chem. Soc.*, **83**, 979 (1961).

then poured into a cold 5% sodium bicarbonate solution which was extracted with ether. The ethereal extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure to give 0.82 g of white crystals, mp 103–104.5°. The solid was recrystallized from methanol to give pure methyl *trans*-*N*-nitroso-*N*-(1-*p*-chlorophenyl-3-phenyl-2,3-epoxypropyl)-carbamate (**20**), mp 104–105° dec.

Anal. Calcd for $C_{17}H_{15}O_4N_2Cl$: C, 58.88; H, 4.36; N, 8.07. Found: C, 58.80; H, 4.17; N, 8.15.

The infrared spectrum (KBr) exhibited bands at 5.37, 6.53, 6.92, and 7.31 μ and a doublet at 9.75 and 9.85 μ. The nmr spectrum ($CDCl_3$) consisted of a doublet at τ 6.32 (1 H, J = 1.8 Hz), a multiplet at τ 6.08 (1 H), a singlet at τ 6.0 (3 H), a doublet at τ 4.37 (1 H, J = Hz), and a singlet at τ 2.63 (9 H).

Methyl *trans*-*N*-Nitroso-(1,3-diphenyl-1-deuterio-2,3-epoxypropyl)carbamate (18).—To a solution of 13.6 g of ammonium nitrate and 1.18 g of sodium cyanodeuterioborate[47] in 150 ml of absolute methanol was added 2.0 g of chalcone epoxide. The solution was stirred for 72 hr at room temperature and then poured into dilute acetic acid. The acidic solution was washed with several portions of ether and then made basic by the addition of ammonium hydroxide. The basic solution was extracted with ether and the ethereal extracts were dried over magnesium sulfate. The solvent was evaporated under reduced pressure and the crude amine obtained (0.96 g) was dissolved in 50 ml of anhydrous ether. To this solution was added 0.26 g of sodium hydroxide and 0.3 g of methyl chloroformate. The reaction mixture was stirred for 4 hr, then poured into water and extracted with ether. The ethereal layer was washed with dilute hydrochloric acid and water, and then dried over magnesium sulfate. The solvent was removed under reduced pressure and the residual oil was recrystallized from ether–hexane to give 0.41 g of methyl *trans*-*N*-(1,3-diphenyl-1-deuterio-2,3-epoxypropyl)-carbamate, mp 100–101°. The above carbamate was converted with dinitrogen tetroxide to the corresponding *N*-nitrosocarbamate by the procedure described above. The deuterium content was determined as 85% by mass spectral analysis, which showed the parent ion at *m/e* 313.

Reaction of Methyl *trans*-*N*-Nitroso-*N*-(1,3-diphenyl-2,3-epoxypropyl)carbamate (4) with Sodium Methoxide in Methanol.—A solution of 1.0 g of nitrosocarbamate **4** in 10 ml of methanol was added to an ice-cooled solution of sodium methoxide prepared by dissolving 0.37 g of sodium in 50 ml of anhydrous methanol. Nitrogen evolution (50 ml) was immediate and quantitative. The mixture was stirred for an additional 30 min and then poured into water (500 ml) and extracted with ether (300 ml). The ethereal layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The aqueous layer was acidified with dilute hydrochloric acid and then extracted with ether to give benzoic acid (0.12 g, 30%). The crude oil obtained from the ethereal layer was analyzed by vapor phase chromatography on a DEGS (5% on Chromosorb W, 5 ft × 0.25 in.) or a FS 1265 (6% on Anachrom ABS, 5 ft × 0.25 in.) column. The products were separated by preparative vapor phase chromatography. The products were identified as dimethyl carbonate (90%), benzaldehyde (4%), phenylacetaldehyde (2%), *trans*-1,3-diphenyl-1-hydroxy-2,3-epoxypropane (**8**)[48] (15%), 1,3-diphenyl-1-hydroxypropan-2-one (**6**), mp 113–114°,[49] and 1,3-diphenyl-2-hydroxypropan-1-one (**7**), mp 65–66°[49] (combined yield of **6** and **7**, 40%) by comparison with authentic samples. Keto alcohols **6** and **7** were found to equilibrate and partially decompose to benzoic acid under simulated work-up procedures. Similar treatment of nitrosocarbamate **4** with potassium carbonate in anhydrous ethanol gave mostly **6** and **8**. Under these conditions, negligible (2%) quantities of 1,3-diphenyl-2-hydroxypropan-1-one were detected.

Reaction of Methyl *trans*-*N*-Nitroso-*N*-(1,3-diphenyl-2,3-epoxypropyl)carbamate (4) with Potassium *tert*-Butoxide in Ether.—To a suspension of potassium *tert*-butoxide (0.17 g) in 50 ml of anhydrous ether was added 1.0 g of *N*-nitrosocarbamate (**4**) in 15 ml of ether. Nitrogen evolution was immediate. The mixture was stirred for an additional 30 min and then poured into 500 ml of water and extracted with ether. The ethereal layer was dried over magnesium sulfate. Analysis of the solution by gas chromatography indicated the presence of a mixture of methyl-*tert*-butyl carbonate and di-*tert*-butyl carbonate (80%). The solvent was removed under reduced pressure and the crude oil was analyzed by vpc (5% DEGS on Chromosorb W, 5 ft × 0.25 in.). The isolated products were identified as phenylacetylene (4%), benzaldehyde (8%), phenylacetaldehyde (18%), and a small amount (1%) of 1,3-diphenyl-1-propene. The aqueous layer contained a mixture of benzoic and phenylacetic acid. When benzene was employed as the solvent, the major product was 1,3-diphenyl-1-propene (20%), together with a small amount of benzaldehyde. The identity of all the products was confirmed by comparison with authentic samples.

Reaction of Methyl *trans*-*N*-Nitroso-*N*-(3-phenyl-2,3-epoxypropyl)carbamate (5) with Sodium Methoxide in Methanol.—The reaction conditions used for the decomposition of *N*-nitrosocarbamate (**4**) were used for carbamate **5**. The crude product obtained was analyzed by nmr and the products were isolated by liquid–liquid partition chromatography.[50] The yield of nitrogen was immediate and quantitative. The products were identified as 1-phenyl-2-hydroxypropan-1-one (**9**),[51] 1-phenyl-1-hydroxypropan-2-one (**10**)[51] (combined yield 35%), *trans*-1-hydroxy-3-phenyl-2,3-epoxypropane (**12**)[52] (16%), 1-hydroxy-1-phenyl-2,3-epoxypropane (**13**) (19%), and 1-phenyl-1,2-propanedione (2%). The identity of all compounds was established by spectral data and by comparison with authentic samples.[51,52] Epoxy alcohol **13**, prepared by the sodium borohydride reduction of the known epoxy ketone,[53] showed bands at 2.95 and 9.31 μ in the infrared. Its nmr spectrum consisted of multiplets at τ 7.3 (2 H), 6.9 (1 H), 6.5 (1 H), and 5.5 (1 H) and a singlet at τ 2.72 (5 H).

Thermal Decomposition of Methyl *trans*-*N*-Nitroso-*N*-(1,3-diphenyl-2,3-epoxypropyl)carbamate (5).—Epoxycarbamate **5** (0.3 g) was dissolved in benzene and the solution was heated at reflux for 26 hr. The solvent was removed under reduced pressure and the single product obtained was purified by preparative thick-layer chromatography (3% ethyl acetate–benzene). The structure of the clear oil was established as methyl 1-(1,3-diphenyl-2,3-epoxypropyl)carbonate (**17**). The infrared spectrum contained bonds at 5.71 and 7.93 μ. The nmr spectrum consisted of a multiplet at τ 6.67 (1 H), a singlet at τ 7.27 (3 H), a multiplet centered at τ 6.2 (1 H), a double doublet at τ 4.3 (1 H, J = 6 Hz), and a multiplet at τ 2.7 (10 H). Chemical confirmation of this structure was accomplished by hydrolysis of **17** with sodium hydroxide in aqueous ethanol followed by oxidation to *trans*-chalcone oxide. Compound **17** was independently synthesized by treating *trans*-1,3-diphenyl-1-hydroxy-2,3-epoxypropane with methyl chloroformate.

Thermal Decomposition of Methyl *trans*-*N*-Nitroso-*N*-(3-phenyl-2,3-epoxypropyl)carbamate (5).—Epoxycarbamate **5** (0.5 g) was heated at reflux in 70 ml of toluene for 24 hr. The solvent was removed under reduced pressure and the resulting oil was purified by preparative thick layer chromatography. The major product (>90% by nmr) was identified as 1-phenyl-1-hydroxypropyne (**24**) by comparison with an authentic sample prepared by the method of Jones and McCombie.[54] The infrared spectrum showed bands at 3.04 (exchanges with deuterium oxide), 3.12, 4.71, 9.82, and 10.51 μ. The nmr spectrum ($CDCl_3$) exhibited a doublet at τ 4.62 (1 H, J = 2.3 Hz) and a multiplet centered at τ 2.63 (5 H).

Thermal Decomposition of Chlorophenyl Epoxycarbamates 19 and 20.—Carbamates **19** and **20** were heated separately at reflux in benzene for 24 hr. The solvent was removed under reduced pressure and the crude mixture was chromatographed on a thick layer plate using ether–hexane as the eluent. The carbonates isolated in each instance were found to be at least 95% unrearranged. This was demonstrated by nmr spectroscopy and by comparison with authentic samples obtained from the reaction of the corresponding epoxy alcohols with methyl chloroformate.

The infrared spectrum of the carbonate (**22**) derived from **19** showed absorption at 5.72 and 7.91 μ. The nmr (CCl_4) consisted of multiplets at τ 6.8 (1 H), and 6.15 (4 H), a doublet at τ 6.3 (1 H), and a multiplet at τ 2.6 (9 H). The infrared spec-

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[47] Private communication from Professors R. F. Borch and H. D. Durst.

[48] H. H. Wasserman and N. E. Aubrey, *J. Amer. Chem. Soc.*, **77**, 590 (1955).

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[53] H. O. House, D. J. Reif, and R. L. Wasson, *J. Amer. Chem. Soc.*, **79**, 2490 (1957).

[54] E. R. H. Jones and J. T. McCombie, *J. Chem. Soc.*, 733 (1942).

trum of carbonate **23** derived from epoxycarbamate **20** showed absorption at 5.71 and 7.91 μ. The nmr ($CDCl_3$) exhibited a multiplet at τ 6.67 (1 H), a singlet at τ 6.17 (3 H), a multiplet at τ 6.15 (1 H), a doublet at τ 4.21 (1 H), and a multiplet at τ 2.61 (9 H).

Registry No.—**2**, 33143-41-8; **3**, 33143-42-9; **4**, 24312-28-5; **5**, 24276-26-4; **13**, 33143-44-1; **17**, 33143-45-2; **19**, 33143-46-3; **20**, 33143-47-4; **22**, 33143-48-5; **23**, 33143-49-6; **24**, 4187-87-5; methyl *trans*-*N*-(1,3-diphenyl-2-propinyl)carbamate, 33143-50-9; methyl *trans*-*N*-(3-phenyl-2-propinyl)carbamate, 33143-51-0; methyl *trans*-*N*-(1-*p*-chlorophenyl-3-phenyl-2,3-epoxypropyl)carbamate, 33213-40-0; methyl *trans*-*N*-(1,3-diphenyl-1-deuterio-2,3-epoxypropyl)carbamate, 33143-53-2; sodium methoxide, 124-41-4; potassium *tert*-butoxide, 865-47-4.

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Intermediates in Nucleophilic Aromatic Substitution. XII.[1,2] Interaction of Alkoxide Ions with 3,5-Dinitrobenzonitrile[3]

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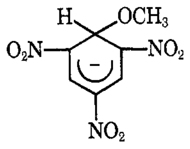
Addition of methanolic methoxide ions to 3,5-dinitrobenzonitrile (**3**) results in the immediate development of an absorption (λ_{max} 490 nm), assigned to the methoxyl σ complex of **3** (**4**), which subsequently decreases rapidly in intensity. The equilibrium constant for the formation of **4** in methanol at 25.00°, $K = 1.9$ l. mol^{-1}, has been obtained from kinetic treatment of the rate of decrease in the absorbance of **4** as a function of methoxide ion concentration. Using the Benesi–Hildebrand equation a value of 1.3 l. mol^{-1} has been obtained for this equilibrium constant under the same conditions. DMSO as a cosolvent increases the stability of **4**. The structure of **4** has been established from the pmr spectra of both the *in situ* generated and isolated complexes. Decomposition of **4** gave 1-methoxy-3-cyano-5-nitrobenzene. Pmr evidence is presented for the *in situ* formation of an analogous complex from 3-cyano-5-nitrobenzonitrile in DMSO-d_6 in the presence of methanolic potassium methoxide. The formation of low concentrations (<1%) of 3,5-dinitrobenzonitrile anion radicals, generated from alkoxide ions and **3** in several dipolar aprotic solvents, has been established using esr spectroscopy. The obtained results are compared to those for related σ, or Meisenheimer, complexes.

1,3,5-Trinitrobenzene has been shown to react extremely rapidly with methoxide ions in methanolic solution to give complex **1**,[6] which subsequently decomposes to produce 3,5-dinitroanisole.[7] The equilibrium constant for the formation of **1** in methanol at 28.0° has been determined to be 15 l. mol^{-1},[7] a value three orders of magnitude smaller than that obtained for the analogous formation of 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide ion (**2**).[8] We have demonstrated recently that substitution of one or two nitro groups by cyano groups in 2,4,6-trinitroanisole profoundly affects the kinetic and thermodynamic parameters for Meisenheimer complex formation.[8,9] More importantly, the unsymmetrical nature of 2-cyano-4,6-dinitroanisole allowed the observation of the preferential initial formation of a 1,3-dimethoxy-2-cyano-4,6-dinitrocyclohexadienylide ion over its 1,5-dimethoxy-2-cyano-4,6-dinitrocyclohexadienylide isomer.[8] As a continuation of our work on the stabilities and structures of Meisenheimer complexes we have, therefore, examined the kinetics for the interaction of methanolic sodium methoxide with 3,5-dinitrobenzonitrile (**3**), isolated crystalline potassium 1-methoxy-2-cyano-4,6-dinitrocyclohexadienylide (**4**) and established its structure together with those of its decomposition products under different conditions. We also wish to report the esr observation of radical anions formed from **3** and alkoxide ions. Pmr parameters for **4** formed *in situ* along with an unspecified amount of 1-hydroxy-2-cyano-4,6-dinitrocyclohexadienylide have been reported recently.[10] However, these authors could not isolate solid salts of **4**.[10]



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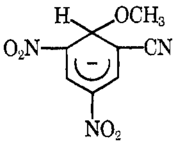

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[1] Part XI: E. J. Fendler, W. Ernsberger, and J. H. Fendler, *J. Org. Chem.*, **36**, 2333 (1971).

[2] For recent reviews on Meisenheimer complexes and their relevance in nucleophilic aromatic substitution see (a) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966); (b) E. Buncel, A. R. Norris, and K. E. Russell, *Quart Rev., Chem. Soc.*, **22**, 123 (1968); (c) P. Buck, *Angew. Chem., Int. Ed. Engl.*, **8**, 120 (1969); (d) J. Miller, "Aromatic Nucleophilic Substitutions," Elsevier, Amsterdam, 1968; (e) M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969); (f) F. Pietra, *Quart Rev., Chem. Soc.*, **22**, 504 (1969); (g) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).

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[4] (a) Texas A & M University; (b) National Institutes of Health Research Career Development Awardee.

[5] (a) LaTrobe University; (b) University of Toledo.

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