was refluxed at 140° for 30 hr. The mixture was steam distilled and the distillate was made alkaline by aqueous NaOH to give precipitate of 2-styrylpyridine, which was recrystallized from aqueous ethanol: 10 g (18.1%), mp 90.0–90.5° (lit.[4a] 90.0–91.0°).

2-(4′-Nitrostyryl)pyridine.—A mixture of *p*-nitrobenzaldehyde (0.033 mol), 2-picoline (0.051 mol), and acetic anhydride (0.053 mol) was refluxed for 10 hr and further heated without the reflux condenser for 30 min to remove any acetic acid, which was produced, 2-picoline, and acetic anhydride. The filtered product was washed with water and recrystallized from aqueous ethanol, yielding yellow crystals (81.5%): mp 134–135° (lit. 126°,[18] 136°,[4a] 142°[19]); ir (KBr disk) 960 ~ 970 cm^{-1} (characteristic to *trans* –CH=CH– group); uv λ_{max} (MeOH) 338 mμ (log ε 4.50), λ_{max} (protonated by 1 or 2 drops of concentrated HCl in a methanolic solution) 340 mμ (log ε 4.50) [lit.[4b] 355 mμ (log ε 4.48) in MeOH].

Effect of Light on *trans–cis* Isomerization of *trans*-2-(4′-Nitrostyryl)pyridine.—It is known that irradiation causes the *trans–cis* isomerization[20] of 2-styrylpyridine derivatives under nitrogen atmosphere, and also dimerization[20,21] and cyclization[22] *via* the *trans–cis* isomerization in the presence of oxygen. We also observed that 2-(4′-nitrostyryl)pyridine suffered *trans–cis* photoisomerization in methanol or dioxane (10^{-5} *M*) by standing in the diffused light in a room. The change in its uv spectra is listed in Table II. Irrespective of the presence or absence of oxygen the photoisomerization which disturbs the precise rate measurement was avoided by the interception of light with aluminum foil.

TABLE II
EFFECT OF DIFFUSED LIGHT IN A ROOM ON *cis–trans* ISOMERIZATION OF 2-(4′-NITROSTYRYL)PYRIDINE

Solvent	At the moment of dilution, λ_{max} (log ε)	Interception from light (after 6 hr), λ_{max} (log ε)	Standing in diffused light (after 6 hr), λ_{max} (log ε)
Methanol	338 (4.52)	338 (4.54)	323 (4.20)
Dioxane	345 (4.41)	344 (4.43)	330 (4.07)

Rate Measurement.—The rate of reaction was measured by following the extinction at 338 mμ (log ε 4.50) of *trans*-2-(4′-nitrostyryl)pyridine. The reaction was carried out in a 100-ml two-necked flask furnished with a Dimroth condenser, at 135°. Aliquots were taken out at appropriate intervals of time, diluted with methanol, and kept standing in a test tube covered with aluminum foil in the dark; extinctions at 338 mμ were determined. The third-order rate constant, k_3, in eq 1 was calculated by the following equation, $k_3 = 2.303A/(2a + c)(2b + c)(a - b)$, if $a \neq b$, where A is the slope in a plot of $[(2b + c) \log (a - x) + (a + c) \log (b - x) + 2(a - b) \log (c + 2x)]$ *vs.* time, or $k_3 = B/(2a + c)_2$, if $a = b$, where B is a slope in a plot of $[-2 \ln (a - x) + (2a + c)/(a - x) + 2x \ln (b + 2x)]$ *vs.* time. a, b, c, and x are defined in eq 1. The third-order plot showed a good linearity except at an early stage of the reaction at low concentration of acetic acid ($c \sim 0$).

Intermediate Criterion. 1-(4′-Nitrophenyl)-2-(α-pyridyl)ethanol (1).—A mixture of *p*-nitrobenzaldehyde (1 g), 2-picoline (2 ml), acetic acid (0.5 ml), and N,N-dimethylformamide or dimethyl sulfoxide (5 ml) was heated at 135° for 4–5 hr. The reaction mixture was poured into water, made alkaline by aqueous NaOH, and precipitated. The precipitate was dissolved in benzene, treated with saturated $NaHSO_3$ to remove aldehyde, and dried (Na_2SO_4), and the solvent was evaporated. The residue was recrystallized from aqueous methanol, giving yellow crystals (18%), mp 154–160°. The uv spectrum showed a strong resemblance to that of 2-picoline; ir spectrum (KBr) 3140 (OH···N chelation as shown in 1), 2920, 2850, 1465 (CH_2), 1094 cm^{-1} (α-phenyl OH).

Dehydration of 1-(4′-Nitrophenyl)-2-(α-pyridyl)ethanol (1) in Acetic Acid or in Acetic Anhydride.—1 (10 mg) in acetic acid (1 ml) or acetic anhydride (1 ml) was heated at 115° for 2 hr. The reaction mixture was made alkaline with aqueous NaOH, the products being filtered and dried (Na_2SO_4). The yield was 64% (in acetic acid) and 58% (in acetic anhydride): mp 133–133.5°; uv λ_{max} (MeOH) 338 mμ; ir (KBr disk) 960–970 cm^{-1} (*trans* –CH=CH–). The product was *trans*-2-(4′-nitrostyryl)pyridine alone.

Attempted Condensation of 2-Picoline with Benzaldehyde by a Basic Catalyst.—A mixture of 2-picoline (0.1 mol), benzaldehyde (0.1 mol), and tri-*n*-butylamine (0.01 mol) was refluxed for 100 hr. The mixture, after being treated with water, was extracted with benzene. The benzene solution was treated with aqueous HCl and the aqueous layer was neutralized with K_2CO_3 to give precipitate of a mixture of 2-styrylpyridine and 1-phenyl-2-(α-pyridyl)ethanol, 1.7 g (9.2%).

Registry No.—2-Picoline, 109-06-8; acetic anhydride, 108-24-7; *p*-nitrobenzyldehyde, 555-16-8; 1, 20151-01-3; *trans*-2-(4′-nitrostyryl)pyridine, 24470-06-2.

(18) K. Feist, *Ber.*, **34**, 465 (1901).
(19) L. Horwitz, *J. Org. Chem.*, **21**, 1039 (1956).
(20) J. L. R. Williams, S. K. Webster, and J. A. Van Allen, *ibid.*, **26**, 4893 (1961).
(21) J. L. R. Willams, *ibid.*, **25**, 1839 (1960).
(22) C. E. Loader and J. T. Timmons, *J. Chem. Soc., C*, 1078 (1966).

Acid-Catalyzed Decarboxylation of Glycidic Acids. "Abnormal" Products

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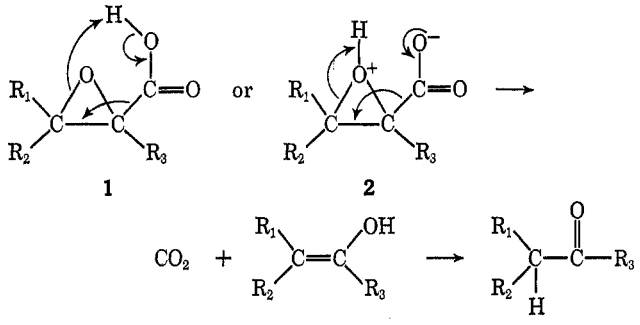
The acid-catalyzed decarboxylation of α-phenylglycidic acids yields carbonyl compounds in which the carbonyl is at the original β carbon of the starting material, and the accepted concerted mechanism for the decarboxylation of glycidic acids must therefore be revised. Consideration of the energy of the two carbonium ions formed by isomerization of the oxirane-protonated species explains the "normal" as well as the "abnormal" behavior of the glycidic acids. The energy of a benzylic carbonium ion adjacent to a carboxyl group is lower than that of a primary or secondary β-alkyl carbonium ion, but is comparable with that of a tertiary β-alkyl carbonium ion since 9 yielded the "normal" as well as the "abnormal" product (11). This latter conversion represents the first example of group migration in the decarboxylation of glycidic acids.

A classical preparative method for aldehydes and ketones utilizes sodium glycidates prepared by Darzens synthesis,[2] followed by Claisen saponification. Decarboxylation and epoxide ring opening take place after acid treatment, usually in the presence of heat. The method has been particularly reliable since no group migration has ever been detected,[3] and the carbonyl in the final product has always been found at the carbon atom bearing the carboxyl in the starting material. The accepted mechanism for the reaction[4,5] involves a *concerted* process in which decarboxylation and epoxide ring opening occur simultaneously, yielding an enol which finally ketonizes. The reacting species

(1) To whom inquiries should be directed.
(2) M. S. Newman and B. J. Magerlein, *Org. React.*, **5**, 413 (1951).
(3) H. H. Morris and M. L. Lusth, *J. Amer. Chem. Soc.*, **76**, 1237 (1954).
(4) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 242.
(5) R. C. Fuson, "Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience Publishers, Inc., 1966, New York, N. Y., p 211.

is often pictured as a glycidic acid (1) which decarboxylates in a cyclic process, although such a species cannot be distinguished kinetically from the oxirane-protonated sodium glycidate 2.[6]

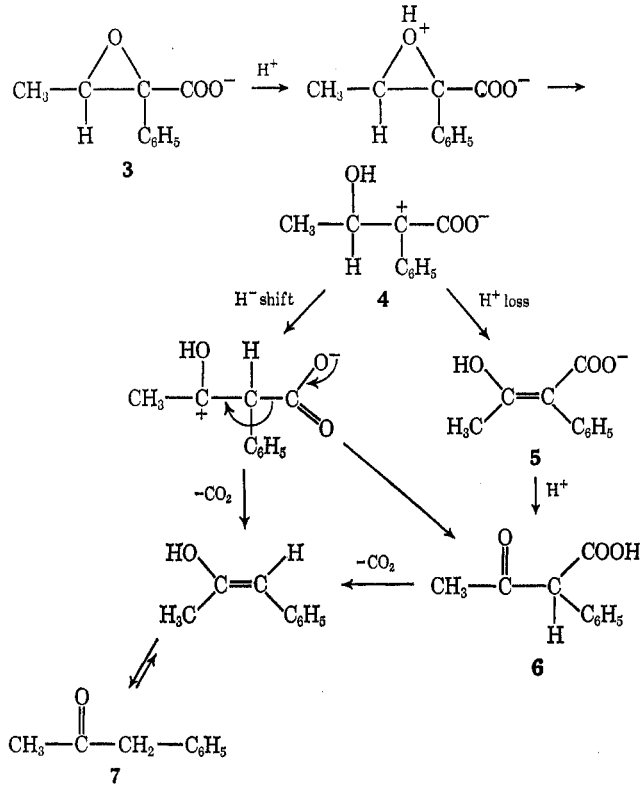


Perhaps the only report in the literature which conflicts with the above mechanism is that of the *thermal* decomposition of dihydro-α-picrotoxininic acid.[7] Since there is no assurance that the same mechanism prevails for the decarboxylation under acid-catalyzed and thermal conditions, we will limit the present discussion to the acid-catalyzed decarboxylation reactions of glycidic acids.

Electrostatic repulsion of like charges usually prohibits the formation of a carbonium ion adjacent to a carbonyl group,[8] but the energy barrier is significantly lowered when the carbonium ion is stabilized by resonance, and we have recently reported[9] our observations concerning the acid-catalyzed isomerization of α-phenylglycidic esters which yield β-keto esters instead of the usual α-keto esters.[10a] We have extended our study to the corresponding glycidic acids, and we now wish to report the first examples of "abnormal" decarboxylation of glycidic acids in aqueous solution. These were found in the sodium α-phenylglycidate series, which is not accessible through the Darzens synthesis.[10b]

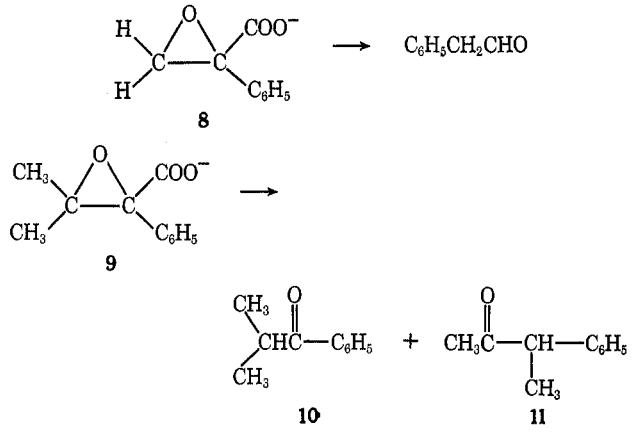
Acid-Catalyzed Decomposition of α-Phenylglycidic Acids.—In a typical experiment, sodium α-phenyl-β-methylglycidate (3) was obtained from ethyl α-phenylcrotonate by epoxidation followed by saponification. The nmr spectrum indicated that there was obtained only one crystalline isomer, of undetermined stereochemistry. It was acidified and refluxed in water for 2 hr, and the nmr and gc-mass spectral analyses of a carbon tetrachloride extract revealed that phenylacetone 7 was the sole neutral reaction product.

We explain this result in terms of the decomposition of the protonated glycidic acid (or its salt) to the resonance-stabilized benzylic ion 4. This protonation is probably taking place intermolecularly at low pH, but an intramolecular process cannot be completely ruled out at this time. Conversion of 4 to the β-keto acid 6, which yields 7 by decarboxylation, or to the enolic form of 7 could occur either through a hydride shift giving the oxygen-protonated form of 6 or through a proton loss yielding the enol 5. We proved this latter mechanism to be correct by carrying out the decomposition in deuterium oxide. If a hydride shift had occurred,



the product 7 should have one hydrogen and one deuterium at the methylene position, in the absence of further exchange *via* acid-catalyzed enolization. If the enol 5 is the intermediate, two deuterium atoms must be present at the methylene position in the product 7. The reaction was carried out to low conversion (10 min reflux), and we observed that 7 contained two deuterium atoms at the methylene position, whereas it still contained 0.45 and 0.75 hydrogen in control experiments with 6 and 7, respectively.

The "abnormal" reaction was also observed in the acid treatment of the congeners of 5 having either no substituent (8) or two alkyl substituents (9) at the β position.

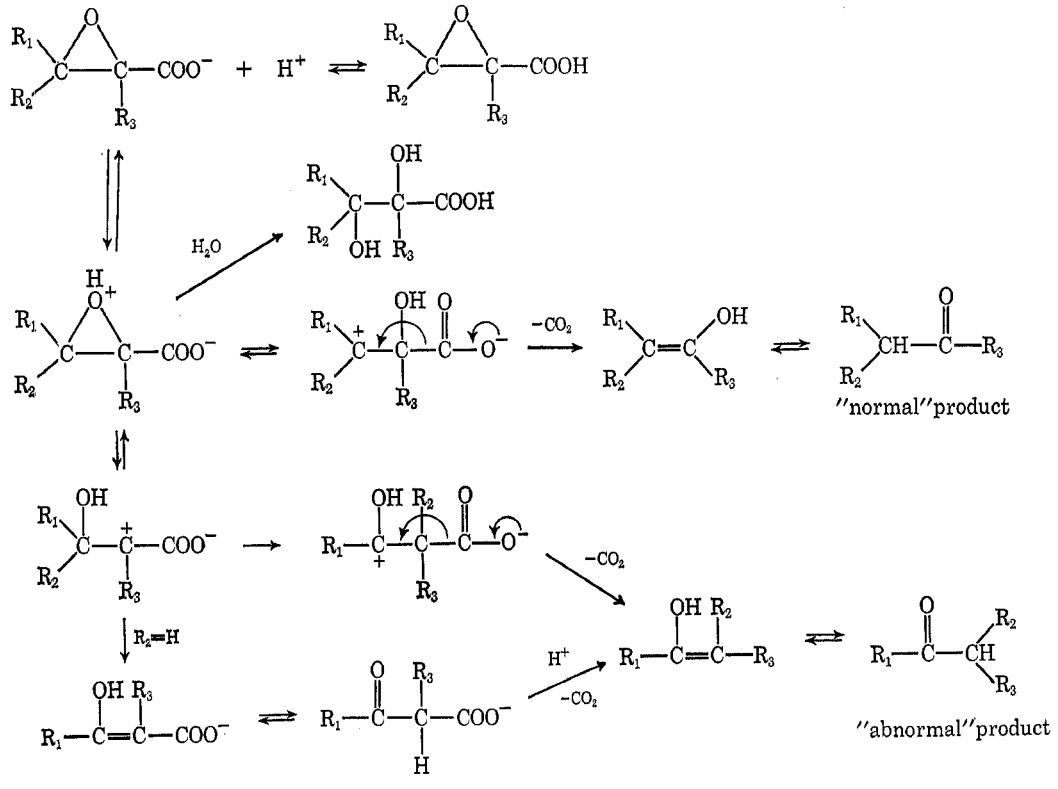


In the case of 8 the alternative to the benzylic carbonium ion intermediate is a very unfavorable primary carbonium ion and, predictably, phenylacetaldehyde was the only neutral decarboxylation product. The decarboxylation of 9, however, yielded two neutral products, 10 and 11, in the ratio 4:1, and the conversion of 9 to 11 represents the first example of group migration in the decarboxylation of glycidic acids. Our

(6) V. J. Shiner, Jr., and B. Martin, *J. Amer. Chem. Soc.*, **84**, 4824 (1962).
(7) H. Conroy, *ibid.*, **79**, 1726 (1957).
(8) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p 199.
(9) S. P. Singh and J. Kagan, *J. Amer. Chem. Soc.*, **91**, 6198 (1969).
(10) (a) H. O. House, J. W. Blaker, and D. A. Madden, *ibid.*, **80**, 6386 (1958), and references cited therein; (b) H. H. Morris, R. H. Young, Jr., C. Hess, and T. Sottery, *ibid.*, **79**, 411 (1957).

SCHEME I

ACID-CATALYZED DECARBOXYLATION OF GLYCIDIC ACIDS

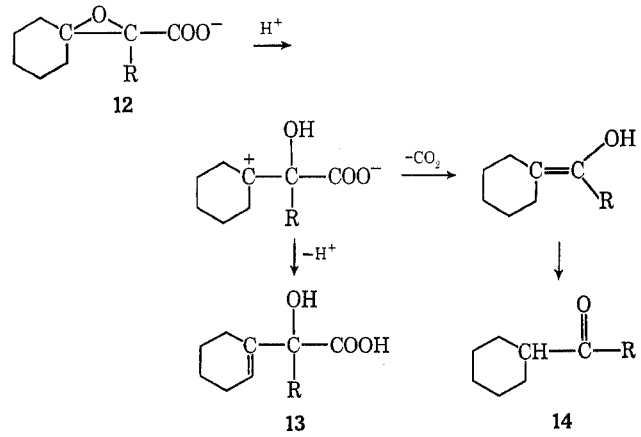


findings also indicate that a tertiary benzylic carbonium ion destabilized by an adjacent carboxyl group is favored over a primary or a secondary aliphatic β-carbonium ion, and that its stability is comparable to that of a tertiary aliphatic β-carbonium ion. These results are in complete agreement with those described by House and his collaborators in the epoxy ketone series.[11]

Mechanism of Decarboxylation of Glycidic Acids.—The results which we have described argue in favor of a carbonium ion intermediate formed by isomerization of the initially oxirane-protonated glycidic acid or of its salt. Furthermore, we believe that the simple consideration of carbonium ion stability satisfactorily explains these three aspects of the behavior of glycidic acids in acidic solution.

(1) Aromatic glycidic acids decarboxylate more easily than aliphatic ones. Although no comparative rate study has been described, the published data[12] as well as our own experience indicate little difficulty in decarboxylating aromatic glycidic acids. In contrast, the decarboxylation of the aliphatic acids has often been reported to be quite difficult and has required the elaboration of alternate procedures, such as the preliminary conversion into the chlorohydrin[13,14] or the pyrolysis of the isolated acid,[15] its sodium salt,[13] or its *t*-butyl ester.[16] In order to illustrate the point, we have compared the extent of decarboxylation of β-methyl- and β-phenylglycidic acids under identical conditions and found that none had taken place in the former when *ca.* 35% of the latter had already decarboxylated.

(2) Among aliphatic acids, the least substituted ones decarboxylate the most reluctantly. For instance, glycidic acid itself does not decarboxylate at all.[17] In the most substituted ones, furthermore, the carbonium ion species need not become neutralized *via* decarboxylation, but, instead, proton loss may occur. Thus, Johnson, *et al.*,[14] observed that **12** (R = H or CH_3) yielded mainly the unsaturated hydroxy acid **13** in addition to some normal product (**14**).



(3) In cases where decarboxylation does not take place readily (which we explain by the high energy of

(11) H. O. House, D. J. Reif, and R. L. Wasson, *J. Amer. Chem. Soc.*, **79**, 2490 (1957); H. O. House and D. J. Reif, *ibid.*, **79**, 6491 (1957); and previous papers in this series.

(12) C. F. H. Allen and J. van Allan, "in Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 733.

(13) W. A. Yarnall and E. S. Wallis, *J. Org. Chem.*, **4**, 270 (1939).

(14) W. S. Johnson, J. C. Belew, L. J. Chinn, and R. H. Hunt, *J. Amer. Chem. Soc.*, **75**, 4995 (1953).

(15) H. H. Morris and R. H. Young, Jr., *ibid.*, **77**, 6678 (1955), and references cited therein.

(16) E. P. Blanchard, Jr., and G. Büchi, *ibid.*, **85**, 955 (1963).

(17) P. Melikoff, *Chem. Ber.*, **13**, 271 (1880).

the required carbonium ions), the competing attack of the protonated epoxy acid form by nucleophiles, typically water or the anion from the mineral acid, predominates. Glycidic acid, for example, is easily hydrated to glyceric acid[17] or converted to chlorolactic acid in presence of HCl.[18] Application of this criterion to the decarboxylation of phenylglycidic acids supports the concept that a benzylic carbonium ion in the α-phenyl series has a higher energy than in the β-phenyl series. In the former, decarboxylation accounted for only *ca.* 10%, while glyceric acids, stable in the experimental conditions, were the major products of the reaction; in the latter, no appreciable formation of glyceric acid took place under the same conditions.

In their careful kinetic study[6] of the decarboxylation of β-phenyl-β-methylglycidic acid in the pH range of 4–5.5, Shiner and Martin concluded that the reaction involved a simple decomposition of a free epoxy acid (in a cyclic fashion as proposed by Arnold[19]) or an acid-catalyzed decomposition of the anion of the acid. They also stated that the difference between the two mechanisms was probably more semantic than real. We believe, however, that the processes are energetically different since inspection of the models indicates that an appreciable strain is required in the intramolecular protonation reaction. Although a more complete discussion will have to await additional kinetic data, especially for the formation of the "abnormal" products, our product analysis illustrates the fact that the decarboxylation mechanism formulated by either Arnold or Shiner and Martin *does not* have a general applicability.

Using Shiner and Martin's findings[6] that only one proton was required in the pH range which they investigated, a general mechanism accounting for both the "normal" and "abnormal" decarboxylation products is outlined in Scheme I. The actual course followed by a given glycidic acid will depend primarily on the energy relationship between the protonated epoxide and the isomeric carbonium ions.[20] Secondary factors, however, such as the energy of the enol intermediate, are undoubtedly significant in determining the extent of the reaction.

A detailed probe of the reaction mechanism is in progress and will be described later.

Experimental Section

The nmr spectra were recorded on Varian A-60A or T-60 spectrometers and are expressed on the δ scale in parts per million downfield from an internal TMS standard. The mass spectra were obtained at 70 and 12 eV on a Perkin-Elmer 270 gas chromatograph–mass spectrometer, using a column of 20% SE-30 on Chromosorb. The melting points were determined in a Thomas–Hoover capillary apparatus. Comparisons of retention times with standards were also performed with SE-52 and DEGS columns in a F & M 402 gas chromatograph. The starting materials were prepared according to the literature showed satisfactory nmr spectra. The epoxidation reactions were carried out with a slight excess of 85% *m*-chloroperoxybenzoic acid in $CHCl_3$ at reflux for 15–20 hr. The solution was cooled, extracted with 5% aqueous bicarbonate, dried, and concentrated. The residue was purified by silica gel column chromatography. Saponification of the ethyl glycidates was performed according to Claisen[22] with 1 equiv of sodium ethoxide and of water. After standing overnight, the solid was filtered, washed thoroughly with ether, and dried. No attempt was made to maximize the yield of decarboxylation products. Identical products were obtained using either hydrochloric or sulfuric acids.

Sodium α-Phenylglycidate (8).—The ethyl ester was prepared from ethyl atropate[23] in 90% yield: nmr (CCl_4) phenyl at 7.20 (5 H, br), epoxide protons at 3.22 and 2.70 (each a d, J = 7 Hz), 4.15 (q, 2 H) and 1.20 (tr, 3 H). Saponification of 1.92 g of ester yielded 1.7 g of **8**: nmr (DMSO-d_6) 7.25 (5 H, br), 3.18 and 2.75 (each a d, J = 6 Hz). Recrystallization from ethanol gave needles which sintered at 260° but did not melt up to 300°. *Anal.* Calcd for $C_9H_7O_3Na$: C, 58.06; H, 3.76. Found: C, 58.06; H, 3.95.

Sodium α-Phenyl-β-methylglycidate (3).—The ethyl ester was prepared as a mixture of isomers from ethyl α-phenylcrotonate[24] (itself a mixture of isomers) in 78% yield: nmr (CCl_4) phenyl at 7.25 (br, 5 H), epoxide proton at 3.5 and 3.0 (each a q, total of 1 H, J = 6 Hz), OCH_2– at 4.20 (m, 2 H), and methyls at 1.25 (m, 6 H). Saponification of 4.12 g of ester yielded 1.8 g of a single crystalline isomer of **3**: nmr (D_2O) 7.30 (br, 5 H), 3.40 (q, J = 6 Hz, 1 H) and 0.94 (d, 3 H, J = 6 Hz). Recrystallization from ethanol gave needles, mp 292–293° dec. *Anal.* Calcd for $C_{10}H_9O_3Na$: C, 60.00; H, 4.50. Found: C, 60.01; H, 4.35.

Sodium α-Phenyl-β,β-dimethylglycidate (9).—Ethyl dimethylatropate[25] was epoxidized in 77% yield: nmr (CCl_4) 7.20 (br, 5 H), 4.2 (q, 2 H) and 1.22 (tr, 3 H), 1.4 and 1.0 (each a s, 3 H). Saponification of 2.2 g of ester yielded 1.2 g of **9**: nmr (D_2O) 7.40 (br, 5 H), 1.48 (s, 3 H) and 1.10 (s, 3 H). Recrystallization from ethanol gave crystals, mp >300° dec. *Anal.* Calcd for $C_{11}H_{11}O_3Na$: C, 61.68; H, 5.14. Found: C, 61.83; H, 4.83.

Decarboxylation of Sodium α-Phenylglycidate.—A solution of 0.5 g of **8** in 10 ml of water was acidified to congo red with 0.2 ml of concentrated H_2SO_4, refluxed for 10 min, cooled, and extracted with 20 ml of CCl_4. The organic layer was dried over $MgSO_4$ and was concentrated to yield 30 mg (9%) of phenylacetaldehyde: nmr (CCl_4) 7.20 (s, 5 H), 9.60 (tr, J = 2.5 Hz, 1 H), 3.60 (d, 2 H, J = 2.5 Hz); gc-mass spectrum identical with an authentic sample (major peaks at *m/e* 120, 92, and 91). The aqueous layer was further extracted thoroughly with ether, which was dried and concentrated to yield 350 mg (72%) of α-phenylglyceric acid, mp 147–148° (lit.[26] mp 149°). The ethyl ester was prepared by ethanol–H_2SO_4 treatment of the previous sample: nmr (DMSO-d_6) phenyl at 7.30 (br, 5 H), α-OH at 5.60 (s, 1 H), β-OH at 4.92 (d of d, 1 H), β protons at 4.10 and 3.55 (each a d of d, 1 H, with J_{gem} = 11 and J_{vic} = 5 Hz), ester at 4.20 (q, 2 H) and 1.15 (tr, 3 H). Upon addition of D_2O, the signals at 5.60 and 4.92 disappeared, and those at 4.10 and 3.55 became doublets, J = 11 Hz.

Decarboxylation of Sodium α-Phenyl-β-methylglycidate.—A solution of 250 mg of **3** in 10 ml of water was acidified with HCl (congo red), refluxed for 2 hr, cooled, and extracted with CCl_4. The extract was concentrated to yield 25 mg (15%) of phenylacetone: nmr (CCl_4) 7.20 (s, 5 H), 3.52 (s, 2 H), and 2.00 (s, 3 H); gc-mass spectrum identical with an authentic sample (major peaks at *m/e* 134, 91, and 43). Extraction of the aqueous layer with ether, which was dried and concentrated, yielded 125 mg (51%) of oily α-phenyl-β-methylglyceric acid which was esterified with diazomethane. The nmr (DMSO-d_6) of the methyl ester showed signals at 7.40 (br, 5 H), 5.60 (s, 1 H), *ca.* 4.35 (complex, 2 H), 3.60 (s, 3 H), and 1.10 (d, J = 6 Hz, 3 H). The signal at 5.60 disappeared and a quartet at 4.30 (J = 6 Hz, 1 H) became clear upon addition of D_2O. Overnight oxidation at room temperature of 200 mg of ester with 460 mg of potassium periodate in 25 ml of 1 *N* H_2SO_4 yielded methyl benzoylformate which was extracted with ether and had a gc-mass spectrum identical with an authentic sample (main peaks at *m/e* 164, 133, 105, 77).

(18) P. Melikoff, *Chem. Ber.*, **13**, 956 (1880).

(19) R. T. Arnold, Abstracts, 10th National American Chemical Society Organic Symposium, Boston, Mass., 1947.

(20) As this manuscript was first ready to be submitted for publication, there appeared a study of the acid-catalyzed decarboxylation–dehydration of a β-hydroxy acid pointing to the intermediacy of a dipolar species.[21] By analogy, the authors suggested a β-carbonium ion intermediate in the "normal" decarboxylation reaction of glycidic acids.

(21) D. S. Noyce and E. C. McGoran, *J. Org. Chem.*, **34**, 2558 (1969).

(22) L. Claisen, *Chem. Ber.*, **38**, 693 (1905).

(23) G. R. Ames and W. Davey, *J. Chem. Soc.*, 1794 (1958).

(24) M. A. Phillips, *ibid.*, 220 (1942).

(25) J. Farakas and J. K. Novak, *Collect. Czech. Chem. Commun.*, **25**, 1815 (1960).

(26) W. C. Craig and H. R. Henze, *J. Org. Chem.*, **10**, 16 (1945).

Decarboxylation of 3 in D_2O.—A solution of 200 mg of **3** in 10 ml of D_2O was acidified with 1 ml of 1 *N* HCl in D_2O, refluxed for 10 min, cooled, and extracted with 10 ml of CCl_4. The organic layer was dried and concentrated, and the phenylacetone showed only two nmr signals (CCl_4) at 7.20 and 2.00 in the ratio of 5:1.5. The above experiment was repeated, keeping all the conditions as above, but replacing **3** by 30 mg of phenylacetone which dissolved completely. The nmr of the recovered product showed signals at 7.20, 3.52, and 2.00 in the ratio 5:0.75:2.5. When the experiment was repeated using 500 mg of sodium α-phenylacetoacetate instead of **3**, the spectrum of the phenylacetone had signals at 7.20, 3.52, and 2.00 in the ratio 5:0.45:0.90.

Decarboxylation of Sodium α-Phenyl-β,β-dimethylglycidate.—A solution of 0.5 g of **9** in 15 ml of water was acidified with 0.2 ml of concentrated H_2SO_4, refluxed for 10 min, cooled, and extracted with 25 ml of CCl_4. The extract was dried and concentrated, yielding 75 mg (21%) of residue which was identified by nmr and by gc-mass spectroscopy as a mixture of four parts isobutyrophenone (major peaks at *m/e* 148, 105, and 77) and one part 3-phenyl-2-butanone (major peaks at *m/e* 148, 105, 79, 77, and 43). Further ether extraction of the aqueous phase and work-up yielded 225 mg (46%) of α-phenyl-β,β-dimethylglyceric acid which was treated with diazomethane. The methyl ester had nmr (DMSO-d_6) at 7.40 (br, 5 H), 5.60 (s, 1 H), 4.42 (s, 1 H), 3.70 (s, 3 H), 1.18 (s, 3 H), and 1.10 (s, 3 H). The signals at 5.60 and 4.42 disappeared in presence of D_2O. Periodate oxidation yielded methyl benzoylformate which had gc-mass spectrum identical with an authentic sample.

Comparative Decarboxylation of β-Phenyl- and β-Methylglycidic Acids.—A solution of 35 mg of sodium β-methylglycidate in 10 ml of water was acidified with 3 ml of 0.1 *N* H_2SO_4. Titration with phenolphthalein as indicator either immediately or after 10-min reflux required 3.0 ml of 0.1 *N* NaOH. In a parallel experiment, a solution of 53 mg of sodium β-phenylglycidate in 10 ml of water consumed 2.01 ml of 0.1 *N* NaOH after a 10-min reflux with 3 ml of 0.1 *N* H_2SO_4.

Registry No.—**3**, 24568-16-9; **8**, 24568-17-0; **9**, 24568-18-1.

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Oxidation of Amine Salts in Dimethyl Sulfoxide[1,2]

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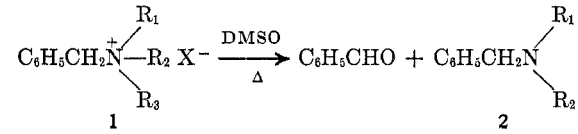
Benzylic amine salts of the type C_6H_5CHRX, when heated in DMSO at 160–180° for 20 hr, undergo oxidation to carbonyl compounds and in some instances elimination to olefins. When R = H and X = $NH_2 \cdot HCl$, $NHCH_3 \cdot HCl$, $N(CH_3)_2 \cdot HCl$, or $N^+(CH_3)_3I^-$, benzaldehyde was formed in varying amounts. With R = CH_2CH_3 and X = $NH_2 \cdot HCl$ the reaction gave isopropenyl phenyl ketone and α-hydroxymethylpropiophenone, while R = CH_2CH_3 and X = $N(CH_3)_2 \cdot HCl$ gave similar oxidation products along with 1-phenylpropene. When R = $CH(CH_3)_2$ and X = $NH_2 \cdot HCl$, the major product was isobutyrophenone, while R = $CH_2C_6H_5$ and X = $NH_2 \cdot HCl$ gave α-hydroxymethyldesoxybenzoin and 2,3,5,6-tetraphenylpyridine and R = $CH_2C_6H_5$ and X = $N(CH_3)_2 \cdot HCl$ produced only *trans*-stilbene. The oxidation reactions which formed carbonyl compounds are explained by an ionic pathway similar to the mechanism for the Pfitzner–Moffatt DMSO oxidation of alcohols. A suggestion was made that olefinic products arose *via* an E1 process. When alkyl groups are on the benzylic carbon, the initial ketone oxidation product undergoes further reaction with formaldehyde (from the acid or thermal decomposition of DMSO) and ammonium chloride. Reactions of the ketone, paraformaldehyde, and ammonium chloride in DMSO under the above experimental conditions gave products similar to the amine salt–DMSO reaction.

During the past 12 years numerous applications of the use of dimethyl sulfoxide (DMSO) as an oxidant have appeared in the literature.[4,5] An alternative nonoxidative reaction with these substrates and DMSO proceeds with elimination and the formation of olefinic products.[4,6] We now wish to report results from the reactions of amine salts in DMSO which occur by oxidation and/or elimination processes.

When benzylamine hydrochloride (0.1 mol), or its various N-methylated derivatives (0.1 mol), was heated in DMSO (0.7 mol) at 165–185° for 20 hr, benzaldehyde was formed in 25–60% yield in addition to a mixture of N-methylated benzylamines. Formation of the latter products may arise from an Eschweiler–Clark reaction since DMSO is known to decompose to produce formaldehyde. A study of this oxidation reaction with various conditions and additives led to the following conclusions. (1) The ammonium ion appears necessary for reaction, and the small amount of oxidation observed with the free base may be attributed to formation of some acid on prolonged heating of DMSO. (2) DMSO is the oxidant. (3) In contrast to the oxidation of benzyl alcohols in DMSO, the benzylamine salt oxidation does not appear to involve a radical process.



1 2

1	Benzaldehyde, %	2, %	2
$R_1 = R_2 = R_3 = H$	60	24	$R_1 = H$; $R_2 = CH_3$
		5	$R_1 = R_2 = CH_3$
$R_1 = R_2 = H$; $R_3 = CH_3$	53	14	$R_1 = H$; $R_2 = CH_3$
		18	$R_1 = R_2 = CH_3$
$R_1 = H$; $R_2 = R_3 = CH_3$	27	51	$R_1 = R_2 = CH_3$
$R_1 = R_2 = R_3 = CH_3$	62		

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