glycinate hydrochloride and 3.7 g. (0.02 mole) of tributylamine in 50 ml. of dry dioxane and refluxed with stirring for 5 hr. During this time the initial reactants dissolved slowly and a new precipitate was formed. The progress of the reaction could be followed by the evolution of ammonia and by the gradual decline in intensity of the color reaction of the solution with Fe^{+3} ions. After 5 hr. this test was very weak and the solution was then evaporated to dryness under reduced pressure. The residue was dissolved in hot water, filtered, and left to crystallize in the ice box overnight. A 4.7-g. sample (76%) of product was obtained which was recrystallized from ethanol–water (1:1) and melted at 110°, lit. 113° (for analysis see Table III).

Ethyl N-benzyloxycarbonylglycyl-DL-alanylglycinate was prepared as above from 5.9 g. (0.02 mole) of crude N-benzyloxycarbonylglycyl-DL-alanylhydroxamic acid, 3.0 g. (0.022 mole) of ethyl glycinate hydrochloride, and 4 g. (0.022 mole) of tributylamine. A 5.3-g. sample (73%) of dry product was obtained which was recrystallized from ethanol–water (1:4) and melted at 139° (for analysis see Table III).

Ethyl N-Benzyloxycarbonylglycyl-DL-alanylglycinate (*via* Mixed Carbonic Anhydride).—A 5.6-g. sample (0.02 mole) of N-benzyloxycarbonylglycyl-DL-alanine[11] was dispersed in 145 ml. of sodium-dried tetrahydrofuran and 2.02 g. (0.02 mole) of triethylamine added. The resultant solution was added dropwise to a cooled (ice–water bath) and stirred solution of 2.16 g. of ethyl chloroformate in 25 ml. of tetrahydrofuran during a period of 45 min. After the addition the solution was stirred and cooled for another 25 min. and the precipitate of triethylammonium chloride was then filtered. A cooled solution of 2.8 g. (0.02 mole) of ethyl glycinate hydrochloride and 0.8 g. (0.02 mole) of sodium hydroxide in a minimum amount of water was then added to the filtrate and the resultant clear solution stirred and concentrated by distillation under normal pressure to approximately one-tenth its initial volume. The rest of the solvent was then evaporated under reduced pressure and the residue washed with 30 ml. of 10% sodium carbonate solution and then recrystallized from ethanol–water (1:4). Five grams (68.5%) of white crystalline product was obtained which melted at 139°.

Anal. Calcd. for $C_{17}H_{23}N_3O_6$: C, 55.9; H, 6.3; N, 11.5. Found: C, 55.9; H, 6.0; N, 11.4.

Acknowledgment.—The authors are indebted to Mrs. M. Goldstein and her analytical group for the microanalyses. A grant from the research and development authority of the Hebrew University in support of this work is greatfully acknowledged.

Thermolysis of Azidoformates in Aromatic Compounds. A Synthesis of 1*H*-Azepin-1-yl Carboxylates

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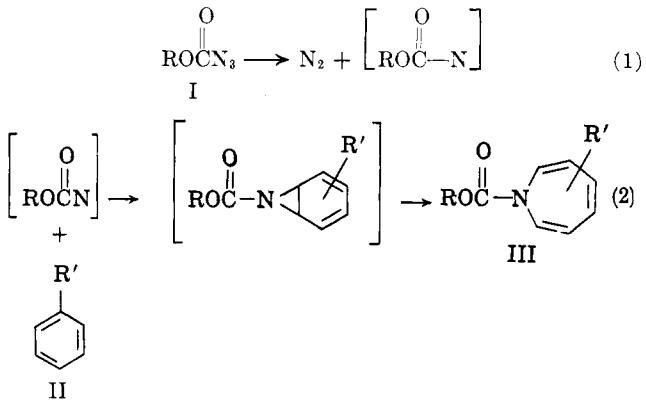
Received October 9, 1963

Two recent reports[1,2] have described the photolysis of ethyl azidoformate to yield carbethoxynitrene, and its subsequent reaction with benzene to yield N-carbethoxyazepine. As part of a study of the chemistry of azidoformates, we have found that simple thermolysis of ethyl and phenyl azidoformates in aromatic compounds also generates the intermediate nitrenes, as evidenced by the isolation of 1*H*-azepin-1-yl carboxylates.

Ethyl azidoformate was synthesized by a published procedure[3] and used for thermolysis without distillation. Phenyl azidoformate[4] was obtained from the reaction of phenyl chloroformate with sodium azide in acetone. The undistilled product from this reaction was found to contain some diphenyl carbonate. However, the use of this crude phenyl azidoformate for thermolysis did not appear to affect the reaction adversely. The presence of unchanged chloroformates in either of these azidoformates was deleterious to the thermolytic reaction. The undistilled azidoformates were generally used for thermolysis because explosions have been encountered when they have been heated excessively on distillation.

Ethyl azidoformate was thermolyzed in dry benzene solution (1–2% by weight) at 125° to yield N-carbethoxyazepine in about 40% yield. Although no exhaustive study of reaction conditions has been performed to maximize the yield, reaction times of 1–2 hr. and concentrations as described above have given satisfactory results. Removal of the benzene yielded a residue from which the azepine derivative could be isolated by distillation. However, better yields were obtained when the residue was chromatographed prior to being distilled. N-Carbethoxyazepine (III, R = $-C_2H_5$, R′ = H)



R = $-C_2H_5$, $-C_6H_5$; R′ = –H, $-CH_3$, –Cl, $-C_6H_5$

is a red-orange liquid stable indefinitely at 0° in sealed glass ampoules. Evidence for its structure was obtained from elemental, infrared, and ultraviolet analyses and from an examination of its nuclear magnetic resonance spectrum (see below). In addition, it was catalytically hydrogenated to N-carbethoxyhexamethylenimine; its properties were identical with those of an authentic sample. Similarly, ethyl azidoformate has been thermolyzed in toluene, chlorobenzene, and biphenyl to yield the respective 1*H*-azepin-1-yl carboxylates (III, R = $-C_2H_5$; R′ = CH_3, –Cl, $-C_6H_5$) of unknown isomeric composition.

Solutions of phenyl azidoformate in benzene (about 1% by weight) were heated at 125° for 2 hr. No study was made of the optimum temperature and time for this reaction, but solutions of higher concentration (about 10% by weight) were found to give noticeably larger amounts of tars. N-Carbophenoxyazepine (III, R = $-C_6H_5$, R′ = H) was isolated as bright yellow crystals by chromatography and sublimation. It is stable when stored in sealed ampoules in a refrigerator. Evidence for its structure was obtained by elemental and spectral analyses. Catalytic hydrogenation of N-carbophenoxyazepine yielded N-carbophenoxyhexamethylenimine which was identical with an authentic sample.

(1) K. Hafner and C. Konig, *Angew. Chem.*, **75**, 89 (1963).

(2) R. S. Berry, D. Cornell, and W. Lwowski, *J. Am. Chem. Soc.*, **85**, 1199 (1963); W. Lwowski, T. Maricich, and T. Mattingly, *ibid.*, **85**, 1200 (1963).

(3) M. Forster and H. Fierz, *J. Chem. Soc.*, (1908) 81.

(4) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3220 (1962).

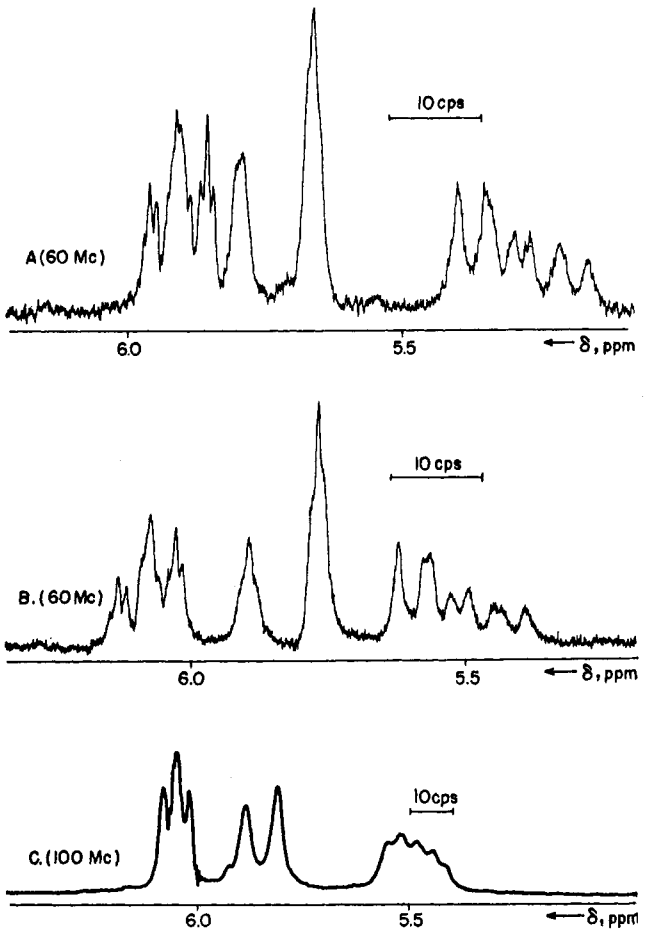
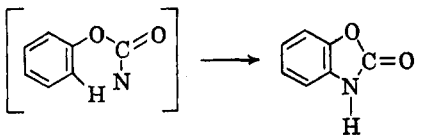


Fig. 1.—N.m.r. spectra of N-carbethoxyazepine: A, ~20% in carbon tetrachloride (60 Mc.); B, ~20% in dimethyl sulfoxide (60 Mc.); C, ~20% in deuteriochloroform (100 Mc.).

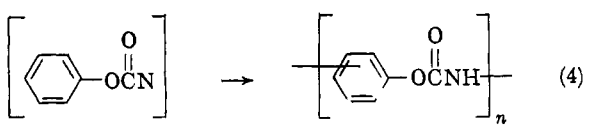
Another product that has been isolated in low yield from this reaction is benzoxazolone-2 (IV).[5] Intramolecular cyclization of carbophenoxynitrene *via* C–H insertion can yield IV. Elemental analyses of the res-



(3)

IV

inous product obtained from this reaction suggests that it is a homopolymer of carbophenoxynitrene. Intermolecular C–H insertion of the intermediate nitrene would lead to V. Thermolysis of phenyl azidoformate



(4)

V

in toluene at reflux under atmospheric pressure also has yielded the azepines (III, R = $-C_6H_5$; R′ = $-CH_3$) of unknown isomeric composition.

The n.m.r. spectra of N-carbethoxyazepine and N-carbophenoxyazepine contained the expected ethyl and phenyl resonances, respectively. In addition, a complex six-proton absorption was observed in the region of δ = 5.0–6.7 p.p.m. below tetramethylsilane, presumably due to the azepine ring hydrogens. The chemical shift of the azepine ring hydrogens, being similar to that of olefinic hydrogens, is in agreement with the lack of aromatic character predicted for the parent azepine.[6] The absorption of the azepine ring hydrogens in III (R′ = H) is somewhat dependent on solvent, as might be expected for a system in which electron delocalization results in the formation of a dipole. Of the three chemically different types of hydrogen on the azepine ring, those α and γ to the nitrogen atom might be expected to lie downfield from those attached to the β-carbon atoms, because hydrogens attached to carbons bearing the higher electron density are found in more shielded positions of the spectrum.[7] Molecular orbital calculations (to be discussed later) demonstrate that the electron density is greater on the β-carbon than on the α and γ carbons. The n.m.r. spectra of solutions of N-carbethoxyazepine in carbon tetrachloride (A) and in dimethyl sulfoxide (B) are presented in Fig. 1. In comparing these spectra, one will observe that the three types of hydrogen expected for the azepine ring are resolved particularly clearly in the spectrum of the dimethyl sulfoxide solution (B). The lower field triplet of finely split bands, the skewed doublet with indications of some secondary splitting, and the upfield multiplet remain nearly the same in the carbon tetrachloride solution spectrum (A) except for their chemical shifts, all of which have changed with solvent. This separation of proton types is shown much more clearly in a 100-Mc. spectrum (C) of a deuteriochloroform solution shown also in Fig. 1.[8] Although it would be beyond the scope of this paper to go into an extensive discussion of this $A_2'B_2'C_2'$ system, a few superficial observations are warranted. The skewed doublet in the center of the resonance might be expected to represent the α-hydrogens, which should be coupled more strongly to the β-hydrogens than any others in the system. This assignment is supported by the fact that this doublet is skewed upfield, indicating coupling to the β-hydrogens (already predicted to be those at highest fields by molecular orbital calculations). By elimination, the triplet of finely split bands at low field is the γ-hydrogens. Thus, to the extent of the analysis of the n.m.r. spectrum available at this time, support is given to structure III (R = $-C_2H_5$, $-C_6H_5$; R′ = H).

1*H*-Azepin-1-yl carboxylates of type III (R′ = H) were unknown[9] until very recently,[1,2] and are currently of theoretical interest because of their relationship to 1*H*-azepine, a monocyclic 8-π electron system.[10] In an attempt to estimate the stability imparted to these azepines by the presence of the carboxylate group, a simple molecular orbital calculation (HMO) was performed using the coulomb integrals, h_N = 1.5, h_O = 2,

(5) G. Young and A. E. Duncan, *J. Chem. Soc.*, (1908) 1052.

(6) A. Streitwieser, "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 280.

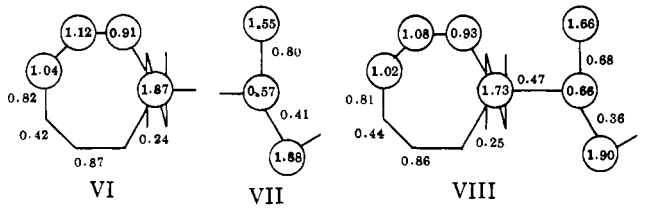
(7) J. Pople, W. G. Schneider, and H. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 256.

(8) Supplied through the courtesy of Dr. N. H. Bhacca of Varian Associates.

(9) K. Dimroth and H. Freyschlag, *Ber.*, **89**, 2002 (1956); **90**, 1628 (1957); R. Huisgen, *et al.*, *ibid.*, **91**, 1, 12 (1958); **92**, 2961 (1959); *Ann.*, **630**, 128 (1960).

(10) M. J. Jorgensen, *J. Org. Chem.*, **27**, 3224 (1962), for leading references.

and $h_O = 1$; and the bond integrals, $k_{C-O} = 0.8$, $k_{C=O} = 1.0$, and $k_{C-N} = 0.8$.[11] The π energies, charge densities, and bond orders for necessary fragments follow.



VI VII VIII

$E_\pi = 8\alpha + 10.34\beta$ $E_\pi = 4\alpha + 7.58\beta$ $E_\pi = 12\alpha + 18.33\beta$

The stabilization possessed by VIII in excess of that possessed by the fragments VI and VII, independently, is 0.41β. Since steric strain may prevent complete planarity of the azepine, the HMO value for extra delocalization energy in VIII should be regarded as an upper limit. In view of the stability of 1*H*-azepin-1-yl carboxylates described here, it might be expected that 1*H*-azepine itself would be capable of existing without the additional stabilization of the carboxylate group.

Experimental

Melting points and boiling points are uncorrected. Infrared spectra were determined on a Beckman IR-5 infrared spectrophotometer. N.m.r. spectra were determined on a Varian Associates Model A-60 spectrometer, except where noted otherwise.

Ethyl Azidoformate.—The method was essentially that of Foster and Fierz.[3] Redistilled ethyl chloroformate, 10.90 g. (0.10 mole), was added to a stirred solution of 7.16 g. (0.11 mole) of sodium azide in 40 ml. water at room temperature. The resulting mixture was stirred at room temperature for 2 hr. and then transferred to a separatory funnel. The bottom, oily layer was drawn off and dried over anhydrous sodium sulfate. Decantation of the oil from the drying agent gave 8.44 g. (73.3%) of ethyl azidoformate which was used directly, without distillation, for thermolysis. The infrared spectrum of this product did not possess any of the strong absorptions of ethyl chloroformate or diethyl carbonate, two of the most probable impurities.

Phenyl Azidoformate.—A mixture made from 15.66 g. (0.10 mole) of phenyl chloroformate, 6.83 g. (0.105 mole) of sodium azide, and 100 ml. of magnesium sulfate-dried acetone was stirred magnetically and held under reflux for 2 hr. It was then stirred at room temperature overnight. The insoluble salt was removed by filtration and the acetone was removed from the filtrate by distillation at 50° under reduced pressure. The residue was fractionally distilled to yield 11.31 g. (69.5%) of phenyl azidoformate, b.p. 63–67° (0.9–1.0 mm.), $n^{25}D$ 1.5290–1.5292. A sample with $n^{25}D$ 1.5291 was analyzed.

Anal. Calcd. for $C_7H_5N_3O_2$: C, 51.54; H, 3.09; N, 25.76. Found: C, 51.77; H, 3.02; N, 25.87.

Phenyl azidoformate has exploded on distillation. The most likely causes are excessive heating and/or contact with contaminated glassware while hot. The residue from the above distillation (2.65 g.) crystallized on cooling and was shown to be mainly diphenyl carbonate by mixture melting point and infrared analysis. It is not necessary to employ distilled phenyl azidoformate for thermolysis, since the crude product obtained after stripping the acetone has been used routinely. Diphenyl carbonate is recoverable unchanged from the thermolyzed reaction mixture by chromatography. However, unchanged phenyl chloroformate in the phenyl azidoformate is deleterious to the thermolysis reaction.

N-Carbethoxyazepine.—A solution of 8.68 g. (0.076 mole) of ethyl azidoformate in 800 ml. of sodium-dried benzene was heated with stirring in an autoclave for 1 hr. at 125° under autogeneous pressure. The reaction solution was filtered and stripped of benzene under reduced pressure at ≲50°. The residue (10.8 g.) in a few milliliters of benzene was chromatographed on a column (5.8 × 12.1 cm.) of 200 g. of silica gel (Davison grade 12, mesh 28–200). Elution with 600 ml. of benzene yielded 1.31 g. of a black, resinous material that was not identified further. Continued elution with 1 l. of benzene–ether (9:1 by volume) gave, on removal of the solvent by vacuum distillation, 5.11 g. (41%) of a red-orange oil. Fractional distillation of this product through a small Vigreux column yielded N-carbethoxyazepine as a red-orange liquid, b.p. 55–56° (0.10 mm.), $n^{25}D$ 1.5222.

Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.15; H, 6.85; N, 8.66. The infrared spectrum of N-carbethoxyazepine (10% in carbon tetrachloride, carbon disulfide) possessed the following significant absorptions: 5.85 (s), 6.05 (m), 6.17 (m), 7.55–7.68 (s), 9.0 (s), 10.82 (m), 13.8 μ (s). Its ultraviolet spectrum (cyclohexane) possessed λ_{max} 216 mμ (shoulder) (ϵ 15,150), 330 (515).

N-Carbethoxyazepine, 0.202 g., was hydrogenated in 40 ml. of benzene using 50 mg. of 10% palladium on charcoal as catalyst. Hydrogen uptake was rapid and amounted to 92% of the theoretical amount. The product was an oil whose infrared spectrum, after short-path distillation, was identical with that of an authentic sample (see below).

N-Carbethoxyhexamethylenimine.—Ethyl chloroformate, 10.85 g. (0.1 mole) was added dropwise to a solution of 19.8 g. (0.2 mole) of hexamethylenimine in 150 ml. of dry benzene and the resulting mixture was held under reflux for 2 hr. The insoluble salt was removed by filtration, and the benzene was stripped from the filtrate under reduced pressure. The residue was fractionated through a Vigreux column to yield 13.41 g. (78.5%) of N-carbethoxyhexamethylenimine, b.p. 46–49° (0.10 mm.), $n^{25}D$ 1.4622.

Anal. Calcd. for $C_9H_{17}NO_2$: C, 63.13; H, 10.01; N, 8.18. Found: C, 62.95; H, 10.03; N, 8.38.

N-Carbophenoxyazepine.—A solution of 15.40 g. of undistilled phenyl azidoformate in 2 l. of dry benzene was heated with stirring in an autoclave for 2 hr. at 125°, under autogeneous pressure. The cooled reaction solution was filtered and stripped of benzene under reduced pressure at ≲50°. The residue (17.38 g.) was mixed with 500 ml. of ethyl ether, filtered, and the ethereal solution was washed with 100-ml. portions of 1% aqueous sodium hydroxide (ten times) and 100-ml. portions of water (three times). After drying over anhydrous sodium sulfate, the ether was removed by vacuum distillation at ≲50° to yield 12.25 g. of an orange residue. A benzene solution of this residue was chromatographed on a column (5.9 × 23.5 cm.) of 360 g. of silica gel (Davison grade 12, mesh 28–200). Elution with 1750 ml. of benzene removed the diphenyl carbonate (see above). Continued elution with 2.5 l. of benzene–ether (9:1 by volume) gave 8.09 g. of an orange oil which crystallized. Sublimation of this product at ≲60° (0.1–0.2 mm.) yielded yellow crystals of N-carbophenoxyazepine, m.p. 65–67°. Resublimation of this material under the above conditions raised the melting point to 66–67°.

Anal. Calcd. for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.28; H, 5.24; N, 6.69.

The infrared spectrum of N-carbophenoxyazepine (10% in carbon tetrachloride, carbon disulfide) possessed the following significant absorptions: 5.80 (s); 6.06 (m), 6.17 (m), 7.5 (s), 7.66 (s–m), 9.32 (m), 10.82 (m), 13.80 μ (s). Ultraviolet spectrum showed λ_{max}^{EtOH} 219.5 mμ (ϵ 20,400), 242 (sh) (5060), 303 (910); $\lambda_{max}^{cyclohexane}$ 325 mμ (ϵ 640).

N-Carbophenoxyazepine, 0.25 g., was hydrogenated in 40 ml. of benzene using 20 mg. of 10% palladium on charcoal as catalyst. Hydrogen uptake was rapid and amounted to 91% of the theoretical amount. The product was an oil whose infrared spectrum and v.p.c. retention time were identical with those of authentic N-carbophenoxyhexamethylenimine, prepared as described below.

Benzoxazolone-2 was isolated from another experiment in which 15.63 g. of undistilled phenyl azidoformate was heated in 1.5 l. of dry benzene. The reaction product was chromatographed on Florisil and eluted with benzene, 1:1 benzene–ether, ether, and 1:1 ether–methanol. The ether eluent yielded 1.37 g. of a partially crystalline residue, which was decolorized with charcoal and recrystallized from ether. There was obtained 0.51 g. of benzoxazolone-2, m.p. 138–140°, which, on admixture with authentic benzoxazolone-2 (m.p. 140–141°),[5] melted at 139–141°. The infrared spectra of these samples were also identical. Concentration of the 1:1 ether–methanol eluent yielded 2.61 g. of a dark, resinous product.

Anal. Calcd. for V, $C_7H_5NO_2$; C, 62.22; H, 3.73; N, 10.37. Found: C, 64.78; H, 4.18; N, 9.67.

(11) Ref. 6, p. 135.

N-Carbophenoxyhexamethylenimine.—This compound was prepared from phenyl chloroformate and hexamethylenimine as described above (see N-carbethoxyhexamethylenimine) in 81% yield, b.p. 128–130° (0.60 mm.), $n^{25}D$ 1.5328.

Anal. Calcd. for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.82; N, 6.39. Found: C, 71.19; H, 7.82; N, 6.61.

Prins Reaction of Norbornene

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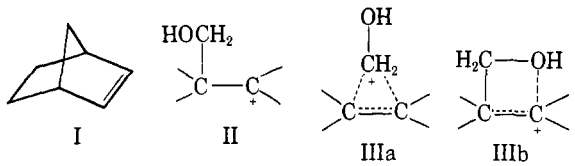
School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey

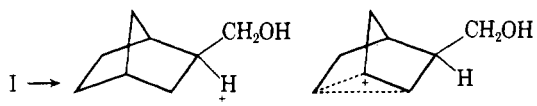
Received August 27, 1963

The course of the Prins reaction of norbornene (I) is of both mechanistic and synthetic interest. Recent work[1] suggests that both open carbonium ions (II) and/or bridged ions (IIIa and/or b) are important intermediates in the reaction. Norbornene, as a substrate in the Prins reaction, offers some interesting possibili-



I II IIIa IIIb

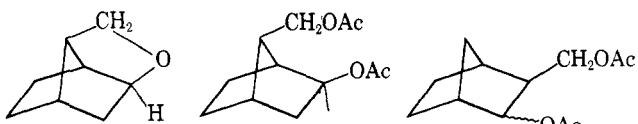
ties for product formation in view of its facile tendency to rearrange during carbonium ion reactions. Specifically, if any of the reaction proceeds *via* open carbonium ions, the norbornyl cation (IVb) should be created with the concomitant production of rearranged prod-



IVa IVb

ucts. Synthetically, simple reactions which lead to 7-carbon substituted norbornane derivatives are rare and hence useful.

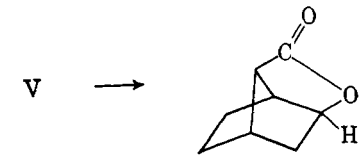
Treatment of norbornene with trioxane in acetic–sulfuric acids led to a complex mixture of products. The low-boiling fraction was shown to contain norbornyl acetate and a new cyclic ether (16%) to which structure V is assigned. The high-boiling fraction (75%) could not be resolved by gas chromatography, but could be shown to contain diacetates VI and VII by further degradation.



V VI VII

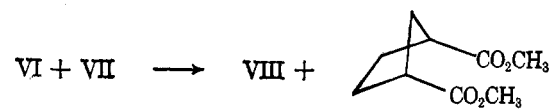
The first clues as to the structures of the $C_8H_{12}O$ ether were provided by the spectral data. No hydroxyl, carbonyl, or unsaturation were evident in the infrared spectrum. The n.m.r. spectrum featured three low-field protons in the ratio of 1:2 centered at 6.0 and 6.4 τ, respectively. The lone proton appeared as a crude triplet with J = 2.5 c.p.s. The other two were apparently the AB part of an ABX system in which J_{AB} = 8.5 c.p.s., J_{AX} = 2.5 c.p.s., and J_{BX} = 0 c.p.s.

Since there are several ethers whose spectra could be described by the above data, it was necessary to obtain chemical evidence on this point. This was provided by the fact that oxidation of the ether with chromium trioxide[2] led to a known[3] lactone, VIII.



VIII

The presence of diacetates VI and VII in the high-boiling fraction was demonstrated in the following manner. The crude product was reduced with lithium aluminum hydride to a mixture of diols. Oxidation of this mixture with potassium permanganate followed by esterification of the acidic products showed only two peaks on the gas chromatogram. They were unambiguously identified as lactone VIII and the dimethyl ester of *cis*-cyclopentanedicarboxylic acid (IX) (see the following). Lactone VIII could only have



IX

formed from acetate VI by oxidation of the primary function to carboxyl followed by lactonization during the esterification. Diester IX could only have arisen from acetate of structure VII.[4] Unfortunately, the low over-all yield (35%) of the oxidation products precludes exact determination of the relative amounts of VI and VII. The observed molar ratio of VIII to IX was 3:2.

The observed products can be readily rationalized by collapse of ions IVa and/or IVb in unexceptional ways.

Experimental

Melting points are corrected and were determined on a Mel-Temp apparatus. Infrared spectra were determined on a Perkin-Elmer Model 21 spectrometer, in carbon tetrachloride unless otherwise noted. N.m.r. spectra were determined on a Varian Model A-60 spectrometer in carbon tetrachloride using tetramethylsilane as internal standard.

Reaction of Norbornene with Trioxane.—To a solution of trioxane (12.0 g., 0.133 mole) in 92 ml. of glacial acetic acid containing 2 ml. of concentrated sulfuric acid was added dropwise a solution of 13.2 g. (0.140 mole) of norbornene in 23 ml. of glacial acetic acid. The temperature was maintained at 65–70° during

(1)(a) L. J. Dolby, C. N. Lieske, D. R. Rosencrantz, and M. J. Schwartz, *J. Am. Chem. Soc.*, **85**, 47 (1963); (b) N. A. LeBel, R. N. Liesemer, and E. Mehmedbasich, *J. Org. Chem.*, **28**, 615 (1963); E. E. Smissman and R. A. Mode, *J. Am. Chem. Soc.*, **79**, 3447 (1957); and A. T. Blomquist and J. Wolinsky, *ibid.*, **79**, 6025 (1957).

(2) H. B. Henbest and B. Nichols, *J. Chem. Soc.*, 227 (1959).

(3) S. Beckmann and H. Geiger, *Ber.*, **94**, 48 (1961).

(4) A similar degradation has been reported by J. Bredt, *Ann.*, **366**, 1 (1909).