(0.022 mole) of XIV in 100 ml. of methylene chloride. The suspension was stirred at reflux for 7 hours, cooled and evaporated. The oil was washed with 3 N hydrochloric acid, extracted with chloroform and the organic layer dried and evaporated. The resulting oil was treated with 100 ml. of 2 N sodium hydroxide at room temperature for 10 hours. The alkaline solution was washed with methylene chloride, acidified with 6 N hydrochloric acid and extracted with ethyl acetate. The organic layer was evaporated and the resulting solid recrystallized from ethyl acetate and n-heptane to yield 2.01 g. (24.3%) of carbobenzoxy-γ-glutamylglycine, m.p. 158–160°; reported[13] m.p. 159–161°.

2-p-Methoxy-3-phthaloylglycyloxazolidine-5-one (VIIb) from the Dicyclohexylamine Salt of N-p-Methoxybenzylideneglycine. —To 0.75 g. (0.01 mole) of glycine was added 10 ml. of a 1 molar solution of dicyclohexylamine in dioxane. Water was added to dissolve the solid and the solution was evaporated on the rotatory evaporator to near dryness. Anisaldehyde (1.36 g., 0.01 mole) was then added and the Schiff base salt was isolated in the usual manner.

The crude salt was suspended in 100 ml. of methylene chloride and treated with 2.23 g. (0.01 mole) of phthaloylglycyl chloride in 25 ml. of methylene chloride. The suspension was stirred overnight. Work-up in the usual manner afforded 1.35 g. (35.5%) of VIIb, m.p. 165–167°. A mixture melting point with an authentic sample was not depressed.

Carbobenzoxyphenylalanine Amide (X).—Sodium N-p-methoxybenzylidenephenylalanate (IIId, 4.4 g., 0.015 mole) was suspended in 100 ml. of methylene chloride and 2.45 g. (0.015 mole) of carbobenzoxy chloride in 25 ml. of methylene chloride was

added to the stirred suspension. After 10 hours at room temperature the solvent was removed *in vacuo* and the resulting oil carefully dried *in vacuo* over sodium hydroxide. The oil was dissolved in 50 ml. of absolute ethanol and treated with 5 ml. of concentrated ammonium hydroxide. The solution was stirred 6 hours at room temperature, evaporated and the residue dissolved in chloroform. The extract was washed with water, 1 N hydrochloric acid, 5% sodium bicarbonate, sodium bisulfite and water. Removal of the solvent and recrystallization of the residue from chloroform and n-heptane afforded 2.08 g. (88% based on 0.34 g. of recovered Schiff base salt) of X, m.p. 165–166°; $[\alpha]^{24}D$ +11.0° (c 1.0 in chloroform); reported[11] m.p. 167°, $[\alpha]^{20}D$ +12° (c 1.0 in chloroform).

Phthaloylglycyl-D,L-serine from Sodium N-Benzylidene-D,L-serinate.—To 0.75 g. (3.5 mmoles) of sodium N-benzylidene-D,L-serinate suspended in 50 ml. of methylene chloride was added 0.78 g. (3.5 mmoles) of phthaloylglycyl chloride. The mixture was shaken mechanically for 44 hours at room temperature. The solvent was evaporated and the oily residue was steam distilled. The aqueous solution in the distillation flask was evaporated and the residue recrystallized from dilute ethanol to afford 140 mg. (13.7%) of dipeptide, m.p. 192–192.5°; reported[19,20] m.p. 199 and 191°.

Anal. Calcd. for $C_{13}H_{12}N_2O_6$: C, 53.45; H, 4.14; N, 9.56. Found: C, 53.50; H, 4.28; N, 9.46.

(19) F. E. King, J. W. Clark-Lewis and G. R. Smith, *J. Chem. Soc.*, 1046 (1954).

(20) F. E. King, J. W. Clark-Lewis and R. J. Wade, *ibid.*, 880 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

Peracid Reactions. III.[1] The Oxidation of Bicyclo[2.2.1]heptadiene[2]

BY JERROLD MEINWALD,[3] SANTOKH SINGH LABANA AND MOHINDRA SINGH CHADHA

RECEIVED JULY 3, 1962

The peracid oxidation of bicyclo[2.2.1]heptadiene (I) gives bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (VIIIa) rather than the expected epoxide II. Further transformations of this aldehyde establish its structure and stereochemistry, and a mechanism for its formation is suggested. This rearrangement of bicyclo[2.2.1]heptadiene provides ready access to a group of compounds which is otherwise inaccessible.

Introduction

Ever since bicyclo[2.2.1]heptadiene (I) became readily available, there has been extensive interest in its reactions and properties.[4] We were interested in the possibility of preparing its monoepoxide II, and although the peroxidic oxidation of I has been studied in several laboratories, conditions which might have been appropriate for the isolation of II do not seem to have been selected.[5] We wish to report the unusual course of the peracid oxidation of bicycloheptadiene, which promises to be of synthetic usefulness, although not in the way originally intended.

Discussion

One promising approach to our goal was provided by the work of Korach, Nielsen and Rideout,[6] who developed a convenient procedure for the conversion of cyclopentadiene (III) into its monoepoxide IV using peracetic acid and sodium carbonate in a two-phase system. When this technique was applied to I, a neutral *product* with the expected empirical formula,

I   II   III   IV
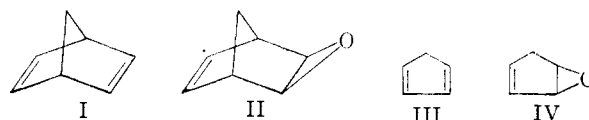
C_7H_8O, was isolated in *ca.* 70% yield. That this product was not the desired one was revealed immediately by the presence of a strong carbonyl stretching band at 5.92 μ in its infrared spectrum. This carbonyl group was part of an aldehydic function, as shown by the presence of a prominent doublet (J = 3 c.p.s.) in the n.m.r. spectrum, centered at 0.70 τ.[7] Chemical confirmation of this conclusion was provided by the smooth silver oxide oxidation of this product to a crystalline acid, $C_7H_8O_2$. This acid readily decolorized bromine and must, therefore, have at least one double bond.

Two possible pairs of structures for the aldehyde and acid which would accommodate these observations may be derived as shown in Chart 1. Epoxidation of I to give II, followed by acid-catalyzed ring opening to give the resonance-stabilized cation V, or direct conversion of I into V without the intermediacy of the epoxide itself, may be pictured as a plausible first step. The contraction of V (focusing on the contributing Va) to give bicyclo[2.1.1]hex-2-ene-5-carboxaldehyde (VI) finds some analogy in epoxide chemistry,[8] although the facile generation of such a highly strained ring system in this particular instance would be rather surprising. Alternatively, the opening of the C_1–C_2 bond in the

(1) For parts I and II of this series, see J. Meinwald, M. C. Seidel and B. C. Cadoff, *J. Am. Chem. Soc.*, **80**, 6303 (1958), and J. Meinwald and E. Frauenglass, *ibid.*, **82**, 5235 (1960).
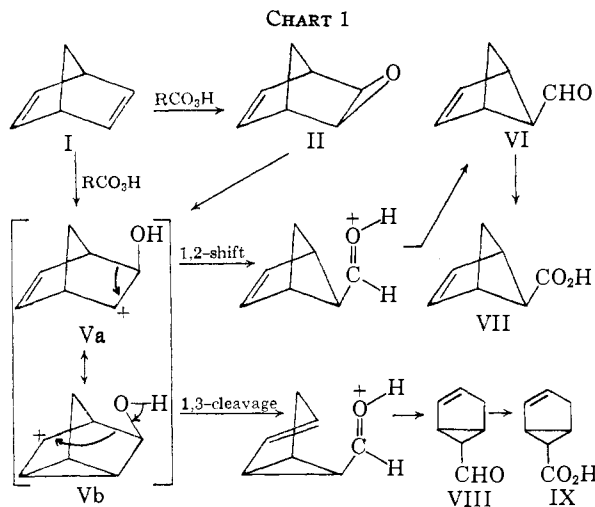
(2) This work was supported in part by research grants from the National Institutes of Health.

(3) Fellow of the Alfred P. Sloan Foundation.

(4) See, for example, G. S. Hammond, N. J. Turro and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961); W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); C. F. Wilcox, S. Winstein and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960); L. Schmerling, J. P. Lewis and R. W. Welch, *ibid.*, **78**, 2819 (1956); also papers cited in ref. 5.

(5) N. A. Milas and P. P. H. L. Otto, *J. Org. Chem.*, **25**, 2225 (1960); J. P. Schaefer, *J. Am. Chem. Soc.*, **82**, 4091 (1960); G. T. Youngblood, C. D. Trivette and P. Wilder, *J. Org. Chem.*, **23**, 684 (1958).

(6) K. M. Korach, R. D. Nielsen and H. W. Rideout, *J. Am. Chem. Soc.*, **82**, 4328 (1960).

(7) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959.

(8) For a convenient review of several early cases of epoxide rearrangement of this type, see S. Winstein and R. B. Henderson in R. C. Elderfield's "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 1.

CHART 1

intermediate ion V (focusing now on structure Vb) in the manner of a "1,3-diol cleavage"[9] would lead to bicyclo[3.1.0]hex-2-ene-6-carboxaldehyde (VIII). Both of these aldehydes should show the aldehydic n.m.r. peak as a doublet, as a consequence of spin–spin coupling with a single α-hydrogen atom.

With these working hypotheses in mind, the structural problem was examined more closely. Since the initial aldehyde was rather unstable, attention was focused chiefly on the corresponding acid (VII or IX). The n.m.r. spectrum of this acid confirmed the presence of two olefinic protons[7] (4.28 τ) in accord with both VII and IX. In the near infrared, a spectral region which we have recently shown to be especially valuable for the detection of tertiary cyclopropyl C–H groups, further support for structure XI was obtained.[10] The near infrared spectrum of the corresponding aldehyde, as well as its somewhat long wave length carbonyl stretching frequency (5.92 μ) and its ultraviolet absorption (apparent λ_{max}^{EtOH} 205 mμ, ϵ 4350), all strengthen this evidence.

To confirm these deductions chemically, an attempt was made to convert the unsaturated acid into the known bicyclo[3.1.0]hexane-2-carboxylic acid (X) by catalytic hydrogenation. Surprisingly, shaking an ethyl alcohol solution of the unsaturated acid with palladium-on-charcoal in a hydrogen atmosphere gave rise to benzoic acid. Using prereduced Adams catalyst in ethyl acetate, however, the reaction took a simpler
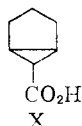

course and gave a new acid, $C_7H_{10}O_2$, m.p, 83–84°, in about 50% yield. Authentic X, prepared as shown in Chart 2 (reaction sequence A),[11] was reported to melt
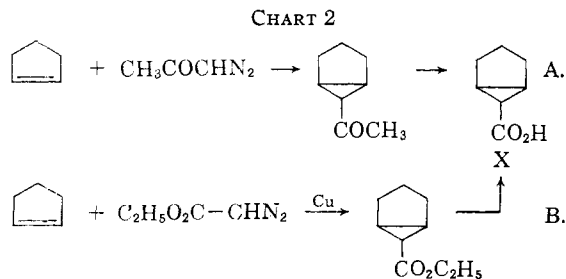
CHART 2

some 20° lower (58°).[11] In order to obtain an authentic sample of this material, we carried out a slightly modified synthesis (Chart 2, B), and obtained X, m.p. 60°, which clearly differed from our hydrogenation product. Since both acids appeared to be bicyclic, and to contain cyclopropyl hydrogens (near infrared evidence), the most likely difference between them appeared to be a stereochemical one. The hypothetical mechanism leading to the aldehyde VIII (Chart 1) would be expected to give rise to the *endo* isomer VIIIa. If there were no
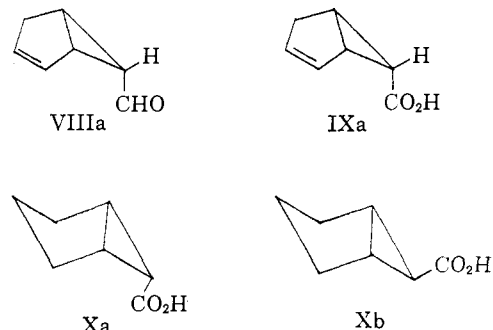
epimerization during the subsequent steps, the unsaturated acid would be IXa, and its hydrogenation product Xa. On the other hand, the addition of diazoacetic ester to cyclopentene might be expected to give the less hindered *exo* isomer preferentially. In the closely related case of the copper-catalyzed addition of diazoacetic ester to cyclohexene, it has been shown recently that this sort of steric discrimination does operate, favoring the *exo* adduct over the *endo* by a 16:1 ratio.[12] Proof that a similar effect was operating in our case was provided when the 83–84° acid was esterified and then epimerized and hydrolyzed to give a product, m.p. 60°, identical with that obtained from the diazoacetic ester addition route. Structure Xa, is, therefore, established for the hydrogenated acid.[13]

Structure IXa, now required for the initial acid, received chemical support from an iodolactonization experiment[14] (see Chart 3). A mixture of δ- and γ-lac-

CHART 3

tones, to which we assign structures XI and XII (showing infrared maxima at 5.75 and 5.65 μ), was obtained

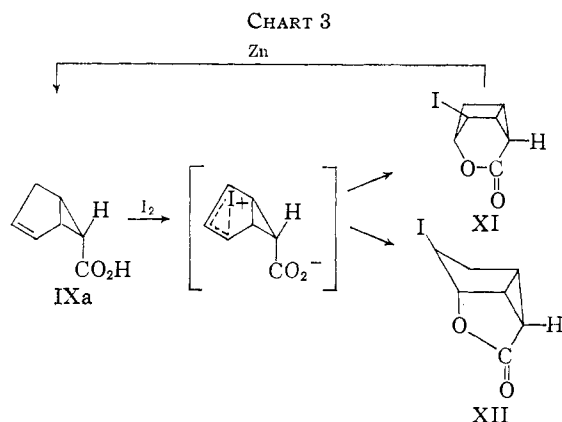(9) J. English, Jr., and F. V. Brutcher, Jr., *J. Am. Chem. Soc.*, **74**, 4279 (1952).

(10) J. Meinwald, A. Lewis and P. G. Gassman, *ibid.*, **84**, 977 (1962). See also P. G. Gassman, Abstr. of Am. Chem. Soc. Natl. Meeting, March, 1962, p. 27-O.

(11) J. Novák, J. Ratuský, V. Šneberk and F. Šorm, *Chem. Listy*, **51**, 479 (1957); see *Collection Czech. Chem. Commun.*, **22**, 1839 (1957).

(12) P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961).

(13) Aromatization of hydroaromatic systems under hydrogenation conditions is a well known process (see, for example, E. A. Braude, R. P. Linstead and P. W. D. Mitchell, *J. Chem. Soc.*, 3578 (1954); H, Wieland, *Ber.*, **45**, 484 (1912); N. D. Zelinski, *ibid.*, **66**, 1420 (1933)). In the case of IXa going to benzoic acid, it must be presumed that the catalyst is also able to effect cleavage of the cyclopropane ring.

(14) E. E. van Tamelen and M. Shamma, *J. Am. Chem. Soc.*, **76**, 2315 (1954). For other examples, see P. I. George and M. M. Lehman, *J. Org. Chem.*, **26**, 2575 (1961); A. W. Schrecher, G. Y. Greenberg and J. L. Hartwell, *J. Am. Chem. Soc.*, **74**, 5669 (1952). Some limitations of this technique have been pointed out recently by J. A. Berson and A. Ramanick, *ibid.*, **83**, 4947 (1961).

by treatment of a sodium bicarbonate solution of IXa with iodine and potassium iodide. The *endo* configuration of the carboxyl group is thus confirmed. It is interesting to note that the δ-lactone XI is formed preferentially, although the fact that both lactones are easily detected means that the energies of the two transition states corresponding to the two directions of opening of the iodonium ion intermediate must not be very different.

Fractional crystallization gave the δ-lactone in pure form, and its structure was confirmed by its reduction to IXa with zinc and acetic acid.

With the structures and configurations of compounds VIIIa, IXa and Xa established, the chief remaining point of interest is whether the aldehyde VIIIa is the direct oxidation product of I, or whether it is formed *via* the epoxide II. Although a variety of experimental conditions was examined, including the use of monoperphthalic acid, perbenzoic acid, *m*-chloroperbenzoic acid[15] and peracetic acid, using appropriate buffers and reaction temperatures down to −78°, no hint of epoxide formation could be detected. On the other hand, yields of about 70% of bicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde (VIIIa) were readily attainable. In view of the fact that the more or less closely related olefins XIII–XV all form monoepoxides smoothly,[16] and that these epoxides are not reported to rearrange to aldehydes, it appears that VIIIa may be the initial reaction product in this case, and that the normal epoxidation reaction course is diverted by transannular intervention involving the second double bond. A scheme of this sort would be especially favored in the case of I, since the opportunity for interaction between the two two-carbon bridges is uniquely good.

The one-step cyclization-plus-cleavage of I allows the facile preparation of a series of 6-*endo*-substituted bicyclo[3.1.0]hex-2-enes and hexanes which would be quite difficult to obtain by any other method. We are continuing to explore the chemistry of these bicyclic compounds, and we hope to present the further results of our work in a subsequent publication.

XIII   XIV   XV
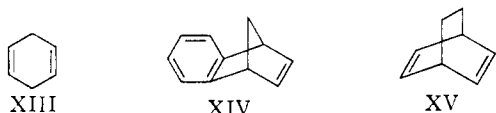
Experimental

Bicyclo[3.1.0]hex-2-en-6-*endo*-carboxaldehyde (VIIIa).—Bicyclo[2.2.1]heptadiene[17] was carefully fractionated (b.p. 89.5–90°) before use.

To a rapidly stirred suspension of 106 g. (1.0 mole) of anhydrous sodium carbonate in a solution of 74.5 g. (0.81 mole) of bicyclo[2.2.1]heptadiene and 650 g. of methylene chloride was added 75.0 g. of 41% peracetic acid (0.405 mole) which had been previously treated with 2 g. of sodium acetate to neutralize any sulfuric acid present. The temperature was maintained at 20° during the addition, which required 45 minutes. After the reaction mixture was allowed to stir for an additional 2 hours, titration of a filtered aliquot showed that all of the peracid had been consumed. The reaction mixture was filtered, and the filter cake washed with methylene chloride. Infrared analysis of combined filtrate and washings revealed strong carbonyl absorption (5.92 μ), and failed to show the presence of epoxide in the 11.7 μ region.[18] The methylene chloride was distilled off and residue fractionated to yield 30.0 g. (70%) of I, b.p. 84–86° (75 mm.), $n^{25}D$ 1.4965; λ_{max}^{EtOH} 205 μ, ε 4350 near infrared (CCl₄): 1653, 1662, 1676, 1713, 1728, 1763 mμ; infrared (neat): 3.32, 3.49, 3.57, 5.92, 6.21, 6.99,

---

(15) We are indebted to the Food Machinery and Chemical Corp. for a generous gift of this material.

(16) M. Tiffeneau and D. Tchoubar, *Compt. rend.*, **212**, 581 (1941); E. E. van Tamelen, *J. Am. Chem. Soc.*, **77**, 1704 (1955); P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960); C. A. Grob and A. Gagneux, *Helv. Chim. Acta*, **42**, 2006 (1959).

(17) We are most grateful to the Shell Development Co. for a generous gift of this compound.

(18) S. B. Soloway and S. J. Cristol, *J. Org. Chem.*, **25**, 327 (1960); G. M. Barrow and S. Searles, *J. Am. Chem. Soc.*, **75**, 1175 (1953).

7.32, 7.50, 8.34, 9.27, 9.58, 10.35, 10.74, 10.92, 11.37, 12.11, 12.76, 13.03, 13.60 μ. This material moved as a single spot on a thin layer chromatoplate (SiO₂).

Anal. Calcd. for C₇H₈O: C, 77.75; H, 7.46. Found: C, 77.60; H, 7.54.

Bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxylic Acid (IXa).—The aldehyde (VIIIa) (2.0 g., 0.019 mole) mixed with 10.8 g. (0.064 mole) of silver nitrate, 25 ml. of water and 10 ml. of 95% ethanol, was stirred vigorously, and to it was added during one hour 3.8 g. of sodium hydroxide in 50 ml. of water.[19] The reaction mixture was allowed to stand overnight. The filtered solution was washed with ether, acidified with 5 N hydrochloric acid and thoroughly extracted with ether. The ether was flash evaporated to give 1.8 g. (87%) of crude product, m.p. 86–90°. This material was crystallized from hexane to give an analytical sample of IXa, m.p. 91.5°; near infrared (CCl₄): 1679, 1711, 1732, 1770, 1896 mμ; infrared (KBr): 2.99, 3.31, 3.48, 3.76, 3.97, 5.90, 6.26, 7.41, 7.80, 8.17, 8.59, 9.01, 9.58, 10.50, 10.78, 11.12, 12.21, 12.60, 13.13, 13.57, 14.47 μ.

Anal. Calcd. for C₇H₈O₂: C, 67.73; H, 6.50; neut. equiv., 124. Found: C, 67.67; H, 6.55; neut. equiv., 126.

Attempted Hydrogenation of Bicyclo[3.1.0]hex-2-ene-*endo*-6-carboxylic Acid (IXa) Using Palladium-on-Carbon.—Palladium-charcoal catalyst (30 mg.) was suspended in 95% ethanol (15 ml.), stirred with a magnetic stirrer and equilibrated with hydrogen gas at atmospheric pressure. The acid IXa (200 mg.), dissolved in 95% ethanol (15 ml.), was added to the catalyst suspension and the hydrogenation continued. The acid absorbed only 15.4 ml. of hydrogen (calculated value: 36.1 ml. for one equivalent). The catalyst was filtered off through a bed of Celite and the solvent evaporated. A sticky solid was obtained which was fractionally sublimed. A liquid sublimed first which was identified as impure cyclohexanecarboxylic acid. Then a fraction appeared which when purified by crystallization (m.p. 121°) from petroleum ether gave infrared spectra identical with that of benzoic acid and showed no depression in mixed melting point with benzoic acid.

In another experiment, the crude products were converted to their methyl esters using diazomethane and were subjected to v.p.c. over a Craig polyester 6-ft. column. It could be resolved into three peaks with the retention times corresponding to those of methyl cyclohexanecarboxylate, methyl bicyclo[3.1.0]hexa-*endo*-6-carboxylate and methyl benzoate.

When the acid IXA was stirred with Pd–C catalyst in 95% ethanol for 6 hours but without hydrogen, the starting material was recovered unchanged.

Bicyclo[3.1.0]hexane-6-*endo*-carboxylic Acid (Xa).—Platinum oxide catalyst (45 mg.) was suspended in 15 ml. of ethyl acetate and reduced with hydrogen gas for about 12 hr. The acid II (250 mg.) was dissolved in 15 ml. of ethyl acetate and was then added to the prereduced catalyst; the hydrogenation continued until 1.2 moles of H₂ per mole of acid was consumed. The solution was filtered and ethyl acetate removed. The crude product was crystallized from hexane to yield 135 mg. (52%) of the acid Xa, m.p. 83–84°. Near infrared (CCl₄): 1682, 1718, 1748, 1893 mμ; infrared (KBr): 3.00, 3.47, 5.95, 6.92, 7.06, 7.50, 8.00, 8.63, 10.46, 11.15, 12.27, 13.16 μ.

Anal. Calcd. for C₇H₁₀O₂: C, 66.64; H, 7.99. Found: C, 66.54; H, 8.09.

Bicyclo[3.1.0]hexane-6-*exo*-carboxylic Acid (Xb).—To a suspension of 0.4 g. of copper powder in 6.8 g. (0.1 mole) of cyclopentene, 5.7 g. (0.1 mole) of ethyl diazoacetate was added dropwise. It was necessary to cool the mixture to keep the resultant exothermic reaction under control. When the reaction had slowed down an additional 5.7 g. of ethyl diazoacetate was added dropwise, again controlling the exothermic reaction. The reaction mixture was finally heated over a steam-bath for 3 hours. The copper powder was filtered off with suction through a bed of Celite and the filtrate was fractionally distilled. A fraction boiling at 58–60° (3 mm.) amounted to 3.0 g. (20%) and showed λ_{max}^{EtOH} 206 mμ, ε 5,140. This fraction could be resolved into 6 different components by v.p.c. on a 6-ft. Craig polyester column maintained at 160°. No attempt was made to isolate pure components, but the whole fraction was subjected to hydrolysis.

The above fraction containing ethyl bicyclo[3.1.0]hexane-6-carboxylate (2.9 g.) was boiled with 30 ml. of 5% sodium hydroxide solution for 2.5 hours. The reaction mixture was then cooled and acidified with 5 N HCl. The acid Xb separated out as white crystals (0.4 g., 16%) m.p. 57–58° (lit. m.p. 58°). The sample was purified by repeated crystallization from hexane to a constant m.p. of 60°; near infrared (CCl₄): 1673, 1707, 1718, 1740–1752, 1895 mμ; infrared (KBr): 2.99, 3.46, 5.94, 6.95, 7.53, 7.82, 8.15, 8.25, 9.21, 9.29, 9.69, 10.01, 11.27, 11.76, 12.32, 14.29 μ.

Methyl Bicyclo[3.2.1]hexa-*endo*-6-carboxylate.—The acid Xa (180 mg.) was dissolved in ether and to this was added an ethereal solution of diazomethane with continuous shaking until the

---

(19) Y. A. A. Goldberg and R. P. Linstead, *J. Chem. Soc.*, 2355 (1928).

yellow color persisted for 2 minutes. Excess diazomethane and ether was then boiled off and the ester used for epimerization without purification.

Epimerization of Xa to Xb.—To a solution of 90 mg. of sodium in 10 ml. of absolute ethanol was added 180 mg. of methyl ester of Xa, and the solution was refluxed for 24 hours. Water (5 ml.) was then added dropwise and the mixture was refluxed for an additional 4 hours. The reaction mixture was then diluted with 10 ml. of water and thoroughly washed with ether. The aqueous layer was then acidified with 5 N hydrochloric acid and the precipitate which formed was collected by filtration and dried under vacuum. This was then sublimed (58°; 0.8 mm.) to give 45 mg. of oily liquid which gave an infrared spectrum identical with that of Xb. This oily liquid was dissolved in 5% NaOH and was reprecipitated by acidification with 5 N hydrochloric in a white, crystalline state, m.p. 58°. This product showed no depression in m.p. when mixed with Xb. It gave an infrared spectrum identical with that of Xb.

Preparation of Iodolactone XI.—A solution of 508 mg. (0.004 mole) of iodine and 2 g. of potassium iodide in 6 ml. of water was added to 248 mg. (0.002 mole) of IXa dissolved in 12 ml. of 0.5 N sodium bicarbonate solution. The mixture was allowed to stand in the dark at room temperature for 24 hours. A light yellow crystalline product formed and was separated by filtration and air-dried. It amounted to 380 mg. (76%), m.p. 97–102°. The infrared spectrum of the crude product showed it to be mainly δ-lactone (5.75 μ) containing a small amount of the γ-lactone (5.65 μ). The δ-lactone, m.p. 105.5°, was obtained in pure state by crystallization from cyclohexane; infrared (CHCl₃): 5.75, 6.95, 7.26, 7.37, 7.50, 8.69, 9.11, 9.23, 9.53, 9.80, 10.00, 10.28, 10.47, 11.24, 11.58, 11.91 μ.

Anal. Calcd. for $C_7H_7O_2I$: C, 33.60; H, 2.80; I, 50.80. Found: C, 33.42; H, 2.82; I, 50.86.

Conversion of Iodolactone XI to Acid IXa.—Iodolactone XI (90 mg.) was dissolved in 30 ml. of glacial acetic acid and cooled to

5°. Zinc dust (400 mg.) previously cooled to 5° was dropped at once into the iodolactone solution. The mixture was vigorously shaken for 5 minutes and quickly filtered through a bed of Celite (prepared by suspending Celite in acetic acid, filtering and washing with acetone). Acetic acid was removed under vacuum and the residue was dissolved in sodium hydroxide solution, extracted with chloroform and acidified with 5 N hydrochloric acid. The solution was extracted three times with ether. The ethereal layer was dried over anhydrous sodium sulfate and the ether removed on the flash evaporator. The product was purified by crystallization from hexane to give 25 mg. (55%) of pure acid, m.p. 90–91°, which showed no depression in mixed melting point with IXa and gave an infrared spectrum identical with that of IXa.

Vapor Phase Chromatography.—Vapor phase chromatography was carried out using a Beckman GC-2 instrument equipped with a 6-ft. Craig polyester column at 160°. Helium at a pressure of 20 p.s.i. was used as carrier gas.

Compound	Retention time, min.
Methyl bicyclo[3.1.0]hex-2-ene-*endo*-6-carboxylate	13.5[a]
Methyl bicyclo[3.1.0]hexane-6-*endo*-carboxylate	11.0[a]
Methyl cyclohexanecarboxylate	7.8[a]
Methyl bicyclo[3.1.0]hexane-6-*exo*-carboxylate	13.5[a]
Pd–C prod. from hydrogenation of IXa	7.8 (1st peak)
	11.0 (2nd peak)
	19.7 (3rd peak)

[a] No detectable impurity.

[Contribution from the Department of Chemistry, University of Wyoming, Laramie, Wyo.]

Decomposition Reactions of Alkyl Chloroglyoxalates[1,2]

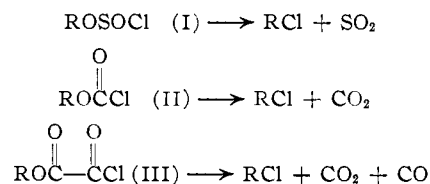By Sara Jane Rhoads and Robert E. Michel[3]

Received September 10, 1962

Alkyl chloroglyoxalates of structure ROCOCOCl (R = C_2H_5, n-C_4H_9, 2-C_8H_{17}, $C_6H_5CHCH_3$) decompose smoothly when heated in the presence of pyridine to yield the corresponding alkyl chlorides, carbon dioxide and carbon monoxide. The decompositions of active 2-octyl chloroglyoxalate (IIIc) and active α-phenethyl chloroglyoxalate (IIId) have been studied as pyridine-induced reactions and as thermal reactions. Both IIIc and IIId undergo the pyridine-induced decomposition to give the corresponding alkyl chlorides with a high degree of inversion of configuration, a result suggestive of an S_N2 process involving the first-formed pyridinium salt. Compound IIIc is resistant toward decomposition when heated alone or in neutral solvents, while IIId decomposes when heated alone or in nitrobenzene to give α-phenethyl chloride with a preponderance of retention of configuration. Relative rates of the first-order thermal decomposition of IIId in tetralin, diglyme and nitrobenzene are 1:2.34:13.6 at 108°. In comparison with the structurally analogous alkyl chloroformates and alkyl chlorosulfinates, the alkyl chloroglyoxalates show an unexpected thermal stability. The mechanistic implications of these findings for the thermal decomposition are discussed in terms of current hypotheses concerning $S_N i$ reactions.

Although the advantages of oxalyl chloride as a reagent for the conversion of acids to acid chlorides have been recognized for many years,[4] its potentiality as a reagent for the corresponding conversion of alcohols to alkyl chlorides appears to have been neglected.[5] In order to explore the possible use of oxalyl chloride for the preparation of alkyl chlorides and also to compare it with reagents more commonly used for this purpose, *e.g.*, thionyl chloride and phosgene, a number of alkyl chloroglyoxalates (III) have been prepared and studied with respect to their decomposition behavior.

The structural parallelism among the alkyl chlorosulfinates I, the alkyl chloroformates II and the alkyl

chloroglyoxalates III led to the expectation that the last would suffer facile decomposition with the formation of an alkyl chloride, carbon dioxide and carbon monoxide. Moreover, it was anticipated that the decomposition of III would respond, ratewise and stereochemically, to changes in intra- and extramolecular environment in much the same manner as do the structural analogs I and II.[6] Finally, on the basis of alkyl–

$$ROSOCl \quad (I) \longrightarrow RCl + SO_2$$

$$\overset{O}{\overset{\|}{RO\text{C}Cl}} \quad (II) \longrightarrow RCl + CO_2$$

$$\overset{O\ \ O}{\overset{\|\ \ \|}{RO\text{C}-\text{C}Cl}} (III) \longrightarrow RCl + CO_2 + CO$$

oxygen bond strengths, it was expected that the alkyl chloroglyoxalates would show a thermal stability inter-

(4) R. Adams and L. H. Ulich, *J. Am. Chem. Soc.*, **42**, 599 (1920).

(5) R. Adams and co-workers, *ibid.*, **37**, 2716 (1915); **38**, 2514 (1916); **40**, 424 (1918), studied the reactions of oxalyl chloride with hydroxylic reagents as preparative routes to esters and olefins.

(6) Summarizing discussions may be found in E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt–Dryden, New York, N. Y., 1959, p. 294, and J. Hine, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1956, p. 114.