charcoal. Addition of light petroleum (b.p. 60–68°) to the filtrate produced a white precipitate (18.1 g., 0.0529 mole, 73%), m.p. 143–144°. Three recrystallizations from methylene chloride–light petroleum (b.p. 60–68°) and three from 95% ethanol yielded the analytical sample of 2-phenyl-3-(1-phenyl-2-nitroethyl)-indole as white crystals, m.p. 144–147°.

3-(1-Amino-2-propyl)-indole (IIIb) Picrate.—A solution of 3-(1-nitro-2-propyl)-indole[2] (1.35 g., 0.00664 mole) in absolute ethanol (100 cc.) was hydrogenated at 2 atm. over Raney nickel (1 teaspoonful), with shaking, for 20 hr. The catalyst was removed by filtration through diatomaceous earth and the solvent was distilled under aspirator pressure. The resulting oily residue was taken up in ether and extracted with 10% hydrochloric acid solution (3 × 67 cc.). The acid extracts were basified with 10% sodium hydroxide solution, extracted with ether, and the ether extract dried over anhydrous sodium sulfate. One-half of the dried ether solution was evaporated and redissolved in benzene (20 cc.) to which picric acid (0.76 g., 0.00332 mole) was added. The precipitate, which formed immediately, was refluxed for an hour and then the orange yellow crystals (0.78 g., 0.00194 mole, 59%), m.p. 223–227°, were filtered off. Five recrystallizations from ethanol, once with a little picric acid, yielded the analytical sample of 3-(1-amino-2-propyl)-indole picrate as orange crystals, m.p. 224–226°, reported m.p. 224°.[11]

Anal. Calcd. for $C_{17}H_{17}N_5O_7$ (403.35): C, 50.62; H, 4.25; N, 17.36. Found: C, 51.18; H, 4.37; N, 17.57.

Tryptamines (IB).—In addition to the hydrogenation of 3-(1-nitro-2-propyl)-indole (IIb) described above, two examples illustrating the hydrogenation of substituted 3-(2-nitroethyl)-indoles are described below:

2-Methyl-3-(1-phenyl-2-aminopropyl)-indole (IVc).—A solution of 2-methyl-3-(1-phenyl-2-nitropropyl)-indole (14.7 g., 0.050 mole) in ethyl acetate (300 cc.) was hydrogenated at 2 atm. over Raney nickel, with shaking, for 15 hr. Filtration of the catalyst and evaporation of the solvent left a residue, which was recrystallized from methylene chloride–light petroleum (b.p. 60–68°), yielding a light tan solid (8.0 g., 0.030 mole, 60%), m.p. 179°. Three recrystallizations from ethanol, with charcoal, yielded the analytical sample of 2-methyl-3-(1-phenyl-2-aminopropyl)-indole as white crystals, m.p. 183–184°.

2-Phenyl-3-(1-phenyl-2-aminoethyl)-indole (IVi).—A solution of 2-phenyl-3-(1-phenyl-2-nitroethyl)-indole (7.8 g., 0.0228 mole) in absolute ethanol (200 cc.) was hydrogenated at 2 atm. over Raney nickel, with shaking, for 24 hr. After filtration of the catalyst, water was added to the filtrate, forming a colloidal suspension. To precipitate the product with an electrolyte, a dilute solution of potassium hydroxide was added and the mixture was set aside in the refrigerator overnight. The resulting curdy precipitate (6.25 g., 0.0200 mole, 88%), m.p. 177–178°, was recrystallized several times from 95% ethanol, yielding the analytical sample of 2-phenyl-3-(1-phenyl-2-aminoethyl)-indole as white needles, m.p. 180–182°.

Phthalimide Derivatives (V) of Tryptamines.—A modification of the method of Manske[22] for 1-methyltryptamine phthalimide was used for preparation of the phthalimide derivatives. Phthalic anhydride (in 20–100% molar excess) was used in place of phthalic acid. The reactants were heated slowly in a Woods metal-bath and held at 210–230° for 1–15 min. The cooled residue was taken up in ether, washed with sodium bicarbonate solution and refluxed with ethanol for an hour. The precipitate which formed on cooling was recrystallized several times from ethanol or methylene chloride–light petroleum (b.p. 60–68°), yielding white to yellow crystals of the phthalimide derivatives.

(22) R. H. F. Manske, *Can. J. Research*, **5B**, 592 (1931).

MINNEAPOLIS 14, MINN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

A Novel Rearrangement in the 5-Nitronorbornene Series[1]

BY WAYLAND E. NOLAND, JAMES H. COOLEY[2] AND PATRICIA A. MCVEIGH[2]

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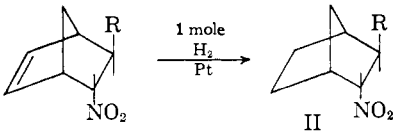
5-Nitronorbornene undergoes a novel rearrangement under acid solvolysis conditions to *cis*-6-cyclopentena[e]tetrahydro-1,2-oxazin-3-one (VII). Reduction of VII yields a dihydro derivative, *cis*-cyclopentana[e]tetrahydro-1,2-oxazin-3-one (XII), and a tetrahydro derivative, *cis*-2-hydroxycyclopentaneacetamide (XIII). Hydrolysis of XIII yielded the known lactone, *cis*-cyclopentana[b]tetrahydrofuran-2-one (XI). Compound VII yielded an unstable nitroso derivative VIII. Compounds VII and XII appear to be the first examples of alicyclic hydroxamic esters and VIII appears to be the first nitroso derivative of a hydroxamic ester. Compound VIII decomposes to an unsaturated lactone, *cis*-5-cyclopentena[b]tetrahydrofuran-2-one (IX), which undergoes hydrogenolysis to cyclopentaneacetic acid. Probable mechanisms involved in the formation of VII and IX are discussed.

Introduction

The failure of salts of the 5-nitronorbornenes (I) to undergo the Nef reaction[3,4] has been noted previously. The action of cold dilute sulfuric acid on the sodium salt of 5-nitro-6-phenylnorbornene (Ic) resulted in a non-ketonic oil, which appeared to be principally unchanged nitro compound.[5,6] Addition of an aqueous solution of the sodium salt of 5-nitro-6-methylnorbornene (Ib) to dilute sulfuric acid did not give nitrous oxide, but an oily material which could not be separated into pure components by crystallization or chromatography.[7] Similarly, when a solution of the sodium salt of 5-nitrobornene (Ia) was added to cold dilute hydrochloric acid no ketonic material could be isolated from the reaction mixture.[8]



II

Ia, R = H
b, R = CH_3
c, R = C_6H_5

(1) Preliminary communication: W. E. Noland, J. H. Cooley and P. A. McVeigh, THIS JOURNAL, **79**, 2976 (1957).

(2) Taken in part from the theses of James H. Cooley, Ph.D., August, 1958, and Patricia A. McVeigh, M.S., October, 1954, both at the University of Minnesota. We are indebted to the Procter and Gamble Co. for financial support provided J. H. C. through a 1955 summer fellowship.

(3) W. E. Noland, *Chem. Revs.*, **55**, 137 (1955).

(4) M. F. Hawthorne, THIS JOURNAL, **79**, 2510 (1957).

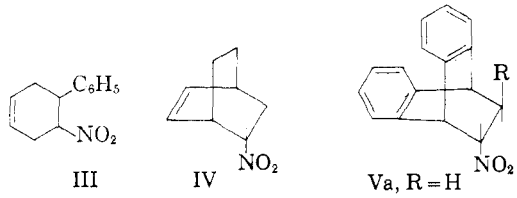
(5) W. E. Parham, W. T. Hunter and R. Hanson, *ibid.*, **73**, 5068 (1951).

(6) W. C. Wildman and R. B. Wildman, *J. Org. Chem.*, **17**, 581 (1952).

(7) E. E. van Tamelen and R. J. Thiede, THIS JOURNAL, **74**, 2615 (1952).

(8) W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952).

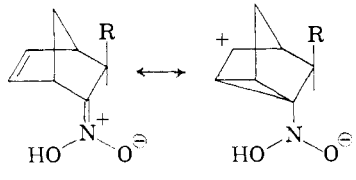
The discovery[7,8] that the Nef reaction proceeds normally with salts of the 2-nitronorbornanes (II), the saturated derivatives of the 5-nitronorbornenes, led to the tentative generalization[7] that the Nef reaction is not applicable to salts of nitro compounds containing an olefinic double bond. That this generalization is not correct, however, is shown by the large number of salts of 4-nitro-5-phenylcyclohexene (III) and its derivatives which successfully undergo the Nef reaction.[6,9-11] Furthermore, the Nef reaction proceeds normally with



III IV Va, R = H
b, R = CH_3
c, R = C_6H_5

5-nitrobicyclo[2,2,2]-2-octene (IV),[12] which is the next higher homolog of 5-nitronorbornene, as well as with the 9,10-dihydro-(11-nitroethano)-anthracenes (V),[13] which are analogous compounds to IV but contain the unsaturation in corresponding positions in fused benzene rings. These results show that a bicyclic ring system alone is not sufficient cause for the failure of salts of the 5-nitronorbornenes to undergo the Nef reaction.

The difference in behavior between the 5-nitronorbornenes (I) and 5-nitrobicyclo[2,2,2]-2-octene (IV) led to the suggestion that homoallylic[14] resonance stabilization involving forms (VIaa) having the known nortricyclene structure may prevent the aci forms (VIa) of the 5-nitronorbornenes from undergoing the Nef reaction.[12] In contrast, it was pointed out that in the bicyclo[2,2,2]-2-



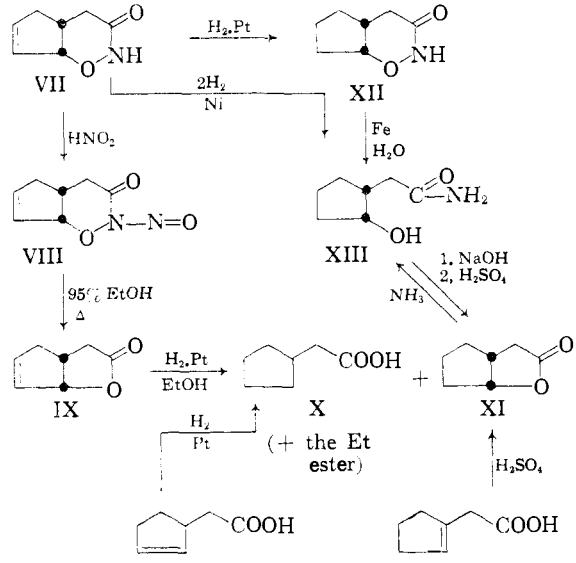
VIa VIaa

octene series, where the Nef reaction does occur, no tricyclic derivatives homologous with nortricyclene are known,[12,15] suggesting that similar resonance stabilization may be lacking in this case. Since it had not been established that the products from attempted Nef reactions on salts of 5-nitronorbornenes were regenerated nitro compounds, we set out to examine carefully the products in the simplest possible case, 5-nitronorbornene (Ia).

(9) J. A. Barltrop and J. S. Nicholson, *J. Chem. Soc.*, 2524 (1951).
(10) W. C. Wildman, R. B. Wildman, W. T. Norton and J. B. Fine, THIS JOURNAL, **75**, 1912 (1953).
(11) A. C. Huitric and W. D. Kumler, *ibid.*, **78**, 614 (1956).
(12) W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, **19**, 381 (1954).
(13) W. E. Noland, M. S. Baker and H. I. Freeman, THIS JOURNAL, **78**, 2233 (1956).
(14) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).
(15) W. C. Wildman and D. R. Saunders, *ibid.*, **76**, 946 (1954).

Results and Discussion

When an ice-cold aqueous methanolic solution of the sodium salt of 5-nitronorbornene (Ia) was added to aqueous hydrochloric acid (9.2% HCl by wt.) at −20 to −10°, a rearrangement product $C_7H_9NO_2$ (VII), isomeric with 5-nitronorbornene, was obtained in up to 42% yield, along with considerable tarry, brownish material. The rearrangement product gave no color change with ferric chloride, but the tarry material gave a positive (cherry-purple) color test. The rearrangement product was found to exist in dimorphic forms, m.p. 104.5–106° and 95.5–96°, which were shown to be interconvertible and to have identical solution infrared spectra. In the crystalline phase, however, the two forms had infrared spectra which were not identical.



The rearrangement product VII decolorized bromine in acetic acid, and aqueous potassium permanganate, indicating the presence of olefinic unsaturation. When ozone was passed through an ethyl acetate solution of VII, 112% of the ozone required for one double bond was taken up and a white solid precipitated. Attempts to obtain crystals, or carbonyl or acid derivatives, from workup of the ozonide were unsuccessful.

Warming of the rearrangement product VII with aqueous 20% sodium hydroxide solution for 2 days on the steam-bath caused the evolution of ammonia and the solution darkened, but some starting material was recovered unchanged at the end of this time. The resistance of the rearrangement product to alkaline hydrolysis is characteristic of hydroxamic esters.[16,17] The action of a small amount of concentrated sulfuric acid on a chloroform solution of VII at room temperature, however, caused the formation of white crystals corresponding in melting point to hydroxylamine sulfate.

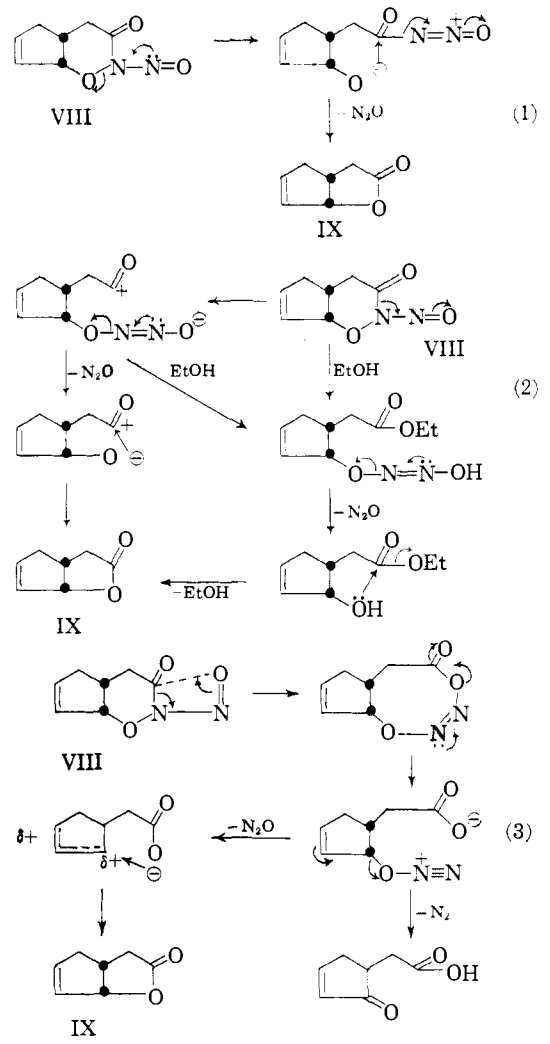
The rearrangement product VII yields an unstable yellow crystalline nitroso derivative VIII. Refluxing of this nitroso derivative with 95% ethanol yielded an unsaturated lactone IX. This unsaturated lactone was regenerated upon acidification of its alkaline solution, showing that it

(16) R. Pieper, *Ann.*, **217**, 1 (1883).
(17) W. Lossen, *ibid.*, **281**, 169 (1894).

is not an enolic lactone. The inability to close a lactone ring from 2-cyclopentanoneacetic acid has been noted previously.[18] The unsaturated lactone underwent extensive hydrogenolysis upon hydrogenation at 1 atm. over platinum in ethanol solution. The products were cyclopentaneacetic acid (X), its ethyl ester and a saturated lactone, *cis*-cyclopentana[b]tetrahydrofuran-2-one (XI). The acid and saturated lactone had infrared spectra corresponding to those of the known compounds, which were synthesized by hydrogenation[19] of 2-cyclopenteneacetic acid[20] and by the lactonization[21] of 1-cyclopenteneacetic acid,[22] respectively.

Although the nitroso derivative VIII decomposes spontaneously as the solid or in solution, its visible and ultraviolet spectrum was estimated by extrapolating the rate of decomposition back to the time of mixing. The maxima in mμ and intensities (in log ϵ) of VIII in 95% ethanol are 261 (3.64), 402 (1.97), 418 (2.11), 439 (2.06). They resemble somewhat those estimated from the published spectrum of a nitrosolactam, N-nitrosopyrrolidone[23]: 252 (3.77), 422 (1.88).

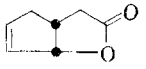
Several alternate pathways may be visualized to account for the decomposition of the nitroso derivative VIII to the unsaturated lactone IX. Pathway 1, the most direct route, finds some analogy in the decomposition of the intermediate diazohydroxide in the reaction of O-alkylhydroxylamines with nitrous acid, which yields nitrous oxide and the corresponding alcohol—without skeletal rearrangement, indicating that the C–O bond has not been broken in the intermediate.[24] Pathway 2 bears direct analogy to the reaction of O-alkylhydroxylamines with nitrous acid. An adverse factor when the decomposition is carried out under solvolysis conditions would be the probable formation of a hydroxyester, which would be relatively stable and might not have lactonized readily under the conditions used. Pathway 3 is analogous in its initial stages to the thermal decomposition of N-nitroso-N-alkylamides[25] and N-nitrosolactams,[23,26,27] in which an intermediate diazoester is proposed. In the present case, however, the diazoester cannot decompose by fission of a C–N bond, but must decompose by fission of an O–N or a C–O bond. Fission of an O–N bond would not give the unsaturated lactone IX, but by analogy with the formation of by-product benzaldehyde in the reaction of O-benzylhydroxylamine with nitrous acid,[24] would be expected to give 3-cyclopenten-2-one-1-acetic acid. While cleavage of the C–O bond has been demonstrated not to occur in the reaction of O-alkylhydroxylamines with nitrous acid,[24] the possibility remains that the additional stabilization provided an incipient carbonium ion by an allylic or benzylic system may reverse the direction of electron flow in the decomposition of an allylic diazohydroxide and permit carbonium ion formation by loss of nitrous oxide. Consequently, it does not appear possible to exclude pathway 3 from consideration in the present case. The fact that the rate of decomposition is increased markedly by daylight suggests that at least part of the decomposition may proceed by a free radical mechanism; alternatively, the effect of light may indicate that some of the modes of decomposition previously outlined may proceed through photochemical as well as thermal excitation.



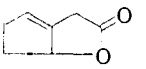
Hydrogenolysis is characteristic of enolic lactones[28,29] and of allyl alcohol derivatives[30,31] including allylic lactones,[32–34] provided that the allylic double bond is not also α,β- to the carbonyl group.[28] Since the enolic possibilities for the

(18) F. A. Kuehl, Jr., R. P. Linstead and B. A. Orkin, *J. Chem. Soc.*, 2213 (1950).
(19) J. F. Eykman, *Chem. Weekblad*, **6**, 699 (1909).
(20) C. R. Noller with R. Adams, THIS JOURNAL, **48**, 2444 (1926).
(21) R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934).
(22) G. A. R. Kon and R. P. Linstead, *ibid.*, **127**, 616 (1925).
(23) R. Huisgen and J. Reinertshofer, *Ann.*, **575**, 174 (1952).
(24) J. E. Leffler and A. A. Bothner-By, THIS JOURNAL, **73**, 5473 (1951).
(25) E. H. White, *ibid.*, **77**, 6011, 6014 (1955).
(26) R. Huisgen and J. Reinertshofer, *Ann.*, **575**, 174 (1952).
(27) G. Nischk and E. Müller, *ibid.*, **576**, 232 (1952).
(28) W. A. Jacobs and A. B. Scott, *J. Biol. Chem.*, **87**, 601 (1930).
(29) J. Meinwald, THIS JOURNAL, **76**, 4571 (1954).
(30) R. Willstätter and E. W. Mayer, *Ber.*, **41**, 1475 (1908).
(31) H. O. L. Fischer and G. Dangschat, *Helv. Chim. Acta*, **17**, 1203 (1934).
(32) (a) W. G. Dauben and P. D. Hance, THIS JOURNAL, **75**, 3352 (1953); **77**, 606, 2451 (1955); (b) R. Adams and M. Gianturco, *ibid.*, **78**, 1922 (1956).
(33) D. H. R. Barton and D. Elad, *J. Chem. Soc.*, 2085 (1956).
(34) Dr. Joseph Wolinsky, private communication, Feb. 24, 1958, concerning the hydrogenolysis of photosantonic acid: E. E. van Tamelen, S. H. Levin, G. Brenner, J. Wolinsky and P. Aldrich, THIS JOURNAL, **80**, 502 (1958).

structure of the unsaturated lactone have been excluded, two allylic possibilities (IX and IXa) remain. While structure IXa has not been rigor-



IX



IXa

ously excluded,[35] it seems improbable on mechanistic grounds and because the β,γ-double bond might have been expected to rearrange to the position α,β- to the carbonyl group under the alkaline conditions used for lactone opening. Consequently, structure IX is assigned to the unsaturated lactone.

In the hope of preparing the unsaturated lactone, and by means of hydroxylamine possibly the rearrangement product itself, 2-cyclopenteneacetic acid[20] was brominated in acetic acid solution. In contrast to the report of Eykman[19] that a bromolactone, m.p. 76°, was formed in about 30% yield, the infrared spectrum indicated that our principal product, 2,3-dibromocyclopentaneacetic acid, was contaminated with only a small amount of lactone. Similar results were obtained from brominations in carbon disulfide, and in chloroform solution with added aluminum bromide.[36] The action of sodium carbonate[37] or sodium hydroxide on 2,3-dibromocyclopentaneacetic acid failed to give the unsaturated lactone. Esterification produced a new compound, ethyl 2,3-dibromocyclopentaneacetate, but an attempt to produce amide-ester interchange with hydroxylamine was unsuccessful.

When the rearrangement product VII was hydrogenated at 2 atm. over platinum in absolute ethanol, one mole of hydrogen was consumed and a dihydro derivative (XII) was obtained. The failure of a hydroxamic ester (dibenzoylcanalin) to undergo hydrogenolysis in the presence of hydrogen and platinum black has been reported previously.[38] Under similar conditions, however, the free alkoxylamine derivative (canalin) did undergo hydrogenolysis of the N–O bond.[38] The rearrangement product VII, its nitroso derivative VIII and its dihydro derivative XII appear to represent new classes of compounds; we have not encountered any previous reports of alicyclic hydroxamic esters, nor of nitroso derivatives of any kind of hydroxamic ester. As is true with hydroxamic esters[39] the rearrangement product VII and its dihydro derivative XII do not give a color change with ferric chloride and they are weakly acidic; they can be extracted with ether from aqueous 10% sodium bicarbonate solution but not from 20% sodium hydroxide; they are regenerated upon acidification. Evaporation of the dihydro derivative with concentrated hydrochloric acid by warming on a steam-bath gave a residue of ammonium chloride. Dichromate oxidation gave glutaric acid, consistent with the possibility of an oxygenated cyclopentane ring in XII.

Hydrogenation of the rearrangement product VII at 2 atm. over Raney nickel or chemical reduction of its dihydro derivative XII with iron powder and water containing ammonium chloride yielded a crystalline tetrahydro derivative (XIII). This tetrahydro derivative gave no color change with ferric chloride, evolved a gas on treatment with nitrous acid, and liberated ammonia under alkaline saponification conditions, indicating the presence of a primary amide group. Alkaline permanganate oxidation[40] of the tetrahydro derivative gave glutaric acid, suggesting, as in the case of the dihydro derivative, the presence of an oxygenated cyclopentane ring. The formation of a phenylurethan derivative indicates the presence of an alcoholic hydroxyl group. Alkaline saponification of the tetrahydro compound, followed by acidification, gave the saturated lactone, *cis*-cyclopentana[b]-tetrahydrofuran-2-one (XI), identical as shown by infrared spectra with samples prepared by hydrogenation of the unsaturated lactone IX and by lactonization[21] of 1-cyclopenteneacetic acid.[22] The action of concentrated ammonium hydroxide solution on the saturated lactone regenerated the tetrahydro derivative XIII of the rearrangement product, thus constituting a proof of its structure by synthesis. The action of hydroxylamine failed to open the saturated lactone to the hydroxamic acid or to yield the cyclization product of the latter, which would be the dihydro derivative XII of the rearrangement product. The failure of hydroxylamine to open γ-lactones to hydroxamic acids has been noted previously in the case of 3-methyloctahydrobenzfuran-2-one.[41]

The isolation of a lactone from hydrolysis of the tetrahydro derivative of the rearrangement product permitted the formulation of a mechanism for the rearrangement, which correctly predicted the structures of the lactone XI as well as its precursors (VII, XII and XIII) in advance of their determination and aided greatly in their elucidation. The mechanism proposed to account for this novel fission of the norbornene ring system begins with protonation of 5-nitronorbornene (Ia) anion to yield the acid form VIa. Further protonation yields the cation VIb, which undergoes *exo* hydrolysis at C_2 with concerted shift of the double bond to C_3–C_4, fission of the C_4–C_5 bond, and elimination of water to form the nitrile oxide VIc. This bond fission step is seen to be a vinylic example of Grob's "Principle of Ethylogy,"[42] in which a nitrogen atom

(35) The rearrangement product VII has been examined recently with the aid of nuclear magnetic resonance spectroscopy by Mr. LeRoy F. Johnson of Varian Associates, Palo Alto, Calif. When dissolved in deuteriochloroform and referenced against benzene in an external annulus, compound VII produced the following signals: −200 c.p.s. (NH proton), +20 and +45 c.p.s. (two protons, one on each of the double bond carbon atoms), +83 c.p.s. (proton on the carbon atom adjacent to the double bond in the 5-ring and oxygen in the 6-ring), and complex signals at ~200+ c.p.s. (all other protons in the molecule). These data definitely support structure VII and, consequently, structure IX for the unsaturated lactone derived from it. The alternative structure for the rearrangement product, isomeric with VII but containing the double bond in the 5-ring in the other position allylic to the oxygen atom, as well as structure IXa for the unsaturated lactone derived from it, are now rigorously excluded.

(36) Some evidence has been obtained to show that aluminum bromide promotes lactone formation in brominative lactonization: Walter P. Miller, Ph.D. thesis (with S. W. Fenton and R. T. Arnold), University of Minnesota, 1957, pp. 84–85, 154–155.

(37) R. Fittig and C. Geisler, *Ann.*, **208**, 48 (1881).

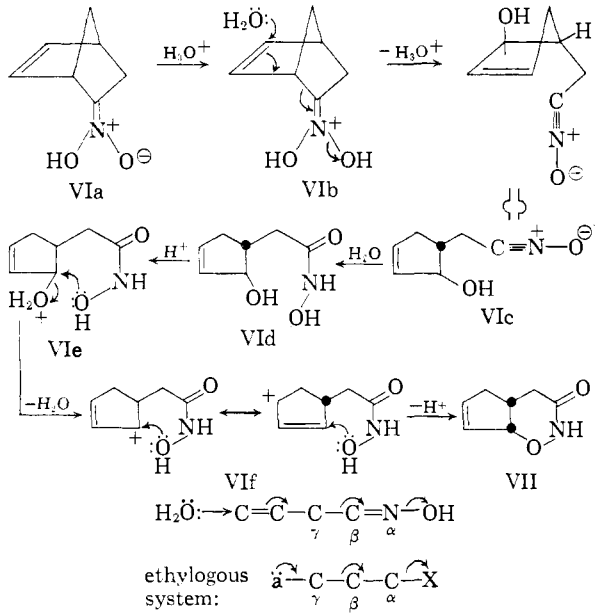
(38) M. Kitagawa and S. Monobe, *J. Biochem. (Tokyo)*, **18**, 333 (1933).

(39) H. L. Yale, *Chem. Revs.*, **33**, 231 (1943).

(40) In our preliminary communication (ref. 1) dichromate is stated incorrectly to be the agent used for this oxidation.

(41) G. R. Clemo and W. Cocker, *J. Chem. Soc.*, 30 (1946).

(42) C. A. Grob, *Experientia*, **13**, 126 (1957).



has replaced the α-carbon atom of the usual ethylogous system.

Hydrolysis of the nitrile oxide VIc could yield the hydroxamic acid VId. In support of the argument for nitrile oxide hydrolysis is the fact that hydrolysis of an ether solution of benzonitrile oxide takes place with concentrated hydrochloric acid at room temperature to yield benzoic acid and hydroxylamine hydrochloride.[43] It seems likely that the strong acid hydrolysis of primary nitroalkanes may involve a nitrile oxide intermediate[3]

$$RCH_2NO_2 \xrightarrow[\text{slow}]{H^+} RCH{=}NO_2H \xrightarrow{H^+} RC{\equiv}\overset{+}{N}{-}\overset{\ominus}{O} \xrightarrow[H^+]{H_2O} RC(=O)NHOH \xrightarrow[H^+]{H_2O} RCOH + H_3\overset{+}{N}OH$$

In the reaction of primary nitroalkanes it has been shown that the intermediate hydroxamic acid can be isolated under essentially anhydrous conditions,[44] thus tending to support the postulation of intermediate VId. Protonation of VId would yield the conjugate acid of the allylic alcohol VIe. Concerted displacement with inversion (as in VIe) or solvolysis of the protonated hydroxyl to an allylic carbonium ion (VIf), in either case with *cis* ring closure (to the probably thermodynamically more stable *cis* form) produced by the hydroxylamino hydroxyl acting as the nucleophile, would yield the rearrangement product VII.

Experimental

Unless otherwise specified, melting points were determined in capillary tubes using a calibrated thermometer.

5-Nitronorbornene (Ia).—A solution of nitroethylene[45,46] (~40 g., 0.6 mole) in dry ether (60 cc.) was added dropwise, with stirring and cooling in an ice-bath, over a half-hour to a solution of cyclopentadiene (54.3 g., 0.82 mole) in dry ether (50 cc.). The solution then was allowed to warm to room temperature and stirring was continued overnight. Ether and unreacted cyclopentadiene were evaporated under aspirator pressure at room temperature. Distillation of the residual oil gave 5-nitronorbornene (77.6 g., 0.557 mole, ~90%), b.p. 64° (2 mm.), m.p. 37–40°; reported,[47] semisolid at room temperature; ν_{NO_2} 1536, 1375 in Nujol, 1375 in CS_2.

It has been reported previously[47] that no suitable procedure has been found for determination of the *endo–exo* isomer ratio in 5-nitronorbornene. The unsaturated nature of the nitro substituent is assumed, however, to result in a predominance of the *endo* isomer in the Diels-Alder adduct.

Regeneration of 5-Nitronorbornene from Alkaline Solution. (A) With Acetic Acid.—5-Nitronorbornene (0.5 g.) was dissolved in a solution of sodium hydroxide (0.2 g.) in water (5 cc.) and ethanol (5 cc.), and then the solution was cooled for 1 hr. in an ice-bath. A solution of acetic acid (0.5 cc.) and urea[48] (0.5 g.) in water (2 cc.), previously cooled in the ice-bath, was added dropwise, with swirling, to the alkaline solution. After about three fourths of the acetic acid solution had been added, the previously alkaline solution suddenly became cloudy and a white solid appeared. After addition of the acid was complete the mixture was allowed to stand for 5 min. and then was filtered. The precipitate was a waxy solid (0.3 g., 60%), m.p. and mixed m.p. with the starting material, 31.5–32.5° (on a Kofler micro hot-stage).

(B) With Strong Acid.—5-Nitronorbornene (2.78 g.) was dissolved in a solution of sodium hydroxide (1.6 g.) in water (16 cc.) and ethanol (16 cc.), and then the solution was cooled for 1 hr., in an ice-bath. An aqueous 20% hydrochloric acid solution, previously cooled in the ice-bath, was added dropwise, with swirling, to the alkaline solution. At an apparent *p*H of about 8.5 the solution suddenly became quite milky, and at an apparent *p*H of about 7.5 a precipitate appeared. Addition of acid was continued to an apparent *p*H of about 7 and then the mixture was allowed to stand for 0.5 hr. in the ice-bath. The coagulated precipitate was filtered, washed with water, and dried (1.12 g., 40%), m.p. 30–31°, mixed m.p. with the starting material, 30–31.5° (on a Kofler micro hot-stage).

After 2 hr. the clear, light yellowish filtrate was extracted with ether (3 × 10 cc.), saturated with sodium chloride, and extracted again with ether (3 more times). The ether extracts were dried over sodium sulfate and evaporated, leaving a small amount of *cis*-6-cyclopentena[e]tetrahydro-1,2-oxazin-3-one.

cis-6-Cyclopentena[e]tetrahydro-1,2-oxazin-3-one (VII).—5-Nitronorbornene (30 g., 0.215 mole) was dissolved in methanol (160 cc.) and aqueous sodium hydroxide solution (20% by wt., 90 g.) was added. The solution was cooled in an ice-bath and shaken occasionally. After one hour white needles of sodio-5-nitronorbornene began to precipitate. After precipitation had continued for 20 minutes, the salt was dissolved by adding water (160 cc.) and the solution was kept in the ice-bath for an additional 40 minutes. The formation of the sodium salt is slow and the best yield of product was obtained when 5-nitronorbornene was kept in contact with sodium hydroxide for two hours, as described. We have no evidence that the salt formation will not proceed equally well at room temperature; precipitation is, however, a useful measure of the success of the conversion.

A solution of concentrated hydrochloric acid (56 cc.) in water (200 cc.) was cooled with Dry Ice until it became a mush (−20°). The cold alkaline solution was added rapidly, with stirring, to the acid solution, but at a rate such that the temperature did not rise above 0°. The addition time was 10–90 minutes, depending on the initial temperature. The yield of product was higher when the temperature was lower. When the temperature was kept at −10° or lower, a very pale blue color developed and persisted for half an hour. Stirring was continued for 3 hours, during which time the solution slowly warmed up to room temperature.

The excess acid was neutralized with solid potassium carbonate and the largely aqueous solution was extracted with chloroform (3 100-cc. portions). The chloroform extracts were evaporated and the residue was extracted repeatedly with light petroleum (b.p. 90–100°) to remove the product from the tarry, brownish material. The latter gave a

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cherry-purple color with ferric chloride solution. Chromatography of the tarry material on alumina (by Richard H. Mumma) gave first a small amount of yellow to brown oil which did not give a ferric chloride test. This was followed by a larger, but still small amount of crystalline *cis*-6-cyclopentena[e]tetrahydro-1,2-oxazin-3-one, after recrystallization from methylene chloride–light petroleum (b.p. 60–68°) m.p. 93–95°, no depression in mixed m.p. with the sample from the light petroleum (b.p. 90–100°)—extracted main portion. Finally, a large amount of black tar was obtained, which did give a positive ferric chloride test.

The product crystallized from the combined light petroleum extracts as a white solid. Recrystallization from a very small volume of acetone yielded colorless, transparent cubes (12.6 g., 0.0904 mole, 42%), m.p. 102.5–107°. Recrystallization from water or sublimation at 85° (1 mm.) gave the analytical sample of *cis*-6-cyclopentena[e]tetrahydro-1,2-oxazin-3-one, m.p. 104.5–106°.

Anal. Calcd. for $C_7H_9NO_2$ (139.15): C, 60.42; H, 6.52; N, 10.07. Found: mol. wt. (Rast), 150; C, 60.71; H, 6.63; N, 10.04. The ultraviolet spectrum shows only rising end absorption: in 95% EtOH at 220 mμ log ε is 3.22 and at 215, 3.42; ν_{NH} 3390, 3160 in $CHCl_3$, 3380, 3140 in CS_2, 3130 in Nujol, 3130 in KBr disk; $\nu_{C=CH}$ 3040 in $CHCl_3$, 3040 in CS_2, 3040 in Nujol, 3040 in KBr disk; $\nu_{C=O}$ ~1675 in $CHCl_3$, 1698, 1674 in CS_2, 1670 in Nujol, 1670 in KBr disk; $\nu_{C=C}$ 1621 (shoulder) in $CHCl_3$, 1620 in Nujol, 1618 cm.$^{-1}$ in KBr disk.

The use of methanol or ethanol as cosolvent with water in the preparation of sodio-5-nitronorbornene is not essential. In an experiment in which methanol was replaced by dioxane, the product was obtained in about 30% yield.

The product was also obtained in a lower melting dimorphic form, m.p. 95.5–96°. The mixed m.p. with the higher melting form was 96–98°. The lower melting form was usually obtained from rapid crystallization. The two forms were shown to be interconvertible and to have identical solution infrared spectra in $CHCl_3$ or CS_2. In the crystalline phase, however, the spectra differed in the region 1195 to 650 cm.$^{-1}$ in Nujol and 1425 to 685 cm.$^{-1}$ in KBr disks.

Anal. Found: mol. wt. (Rast), 184, 175, 175, av. 178; C, 60.47; H, 6.67; N, 10.20.

Test Reactions with *cis*-6-Cyclopentena[e]tetrahydro-1,2-oxazin-3-one. (A) Salt Formation with 20% Sodium Hydroxide Solution.—*cis*-6-Cyclopentena[e]tetrahydro-1,2-oxazin-3-one (0.2 g.) was dissolved in aqueous 20% sodium hydroxide solution and set aside for 18 hr. at room temperature. The solution then was saturated with sodium chloride and extracted with ether (3 × 10 cc.), but evaporation of the ether extracts left no residue. The aqueous solution was acidified with aqueous 20% hydrochloric acid, saturated with sodium chloride and extracted with ether. Evaporation of the ether left a residue which, after recrystallization from light petroleum, gave no depression in mixed m.p. with the starting material.

In similar experiments in which the aqueous 20% sodium hydroxide was replaced with 10% sodium bicarbonate or 20% hydrochloric acid solutions, the unchanged starting material was extracted with ether directly from the sodium bicarbonate or hydrochloric acid solutions.

(B) **Partial Hydrolysis with Warm 20% Sodium Hydroxide Solution.**—When *cis*-6-cyclopentena[e]tetrahydro-1,2-oxazin-3-one (16.2 g., 0.116 mole) was warmed with sodium hydroxide solution (20% by weight, 100 cc.) on a steam-bath for 2 days some ammonia was evolved and the solution darkened. Acidification of the reaction mixture with concentrated hydrochloric acid, extraction with chloroform (3 × 25 cc.), evaporation of the chloroform, and crystallization of the residual oil from light petroleum (b.p. 90–100°) gave slightly impure starting material, m.p. 91–92°. The infrared spectrum in chloroform was the same as that of the starting material except for a small lactone band at 1757 cm.$^{-1}$.

(C) **Action of Sulfuric Acid.**—Concentrated sulfuric acid (3 drops) was added to a solution of *cis*-6-cyclopentena[e]tetrahydro-1,2-oxazin-3-one (0.30 g.) in chloroform, causing the solution to darken around the interface of the sulfuric acid drops. The mixture was allowed to stand overnight at room temperature and then ether and light petroleum (b.p. 90–100°) were added to the cloud point. Cooling to −20° caused crystallization of white needles, m.p. 160–170° with gas evolution; reported for hydroxylamine sulfate, m.p. 170° dec.

***cis*-2-Nitroso-6-cyclopentena[e]tetrahydro-1,2-oxazin-3-one (VIII).**—An ice-cold solution of sodium nitrite (6.9 g., 0.10 mole) in water (50 cc.) was added to a solution of concentrated hydrochloric acid (8.5 cc., 0.10 mole) in water (50 cc.) cooled to −20°. This cold nitrous acid solution was added dropwise, with stirring, to a solution of *cis*-6-cyclopentena[e]tetrahydro-1,2-oxazin-3-one (6.85 g., 0.0492 mole) in water (50 cc.) cooled in an ice-bath. As soon as the addition of nitrous acid was complete, a yellow solid (1.5 g., 0.0089 mole, 18%) floated to the surface of the solution. One recrystallization from chloroform and one from ether, both at −40°, yielded yellow crystals of *cis*-2-nitroso-6-cyclopentena[e]tetrahydro-1,2-oxazin-3-one, m.p. 67–69.5°; $\nu_{C=O}$ 1748, $\nu_{C=C}$ 1619, $\nu_{N=O}$ 1517 cm.$^{-1}$ in $CHCl_3$.

Anal. Calcd. for $C_7H_8N_2O_3$ (168.15): C, 50.00; H, 4.80; N, 16.66. Found: C, 50.02; H, 5.03; N, 16.58.

This compound decomposes spontaneously at room temperature as the solid or in solution. The decomposition was studied spectrophotometrically in 95% ethanol at room temperature. It involved a decrease in absorption with time; no new absorption appeared in the region studied. The rate of decomposition was increased markedly by daylight and the first-order rate "constants" appeared to be less with higher initial concentrations. By use of the observed first-order rate "constants," which were reasonably constant (with some tendency to decrease) over the first 200 min. of reaction, the first observed absorbancies were extrapolated back to the time of mixing and the intensities of the absorption maxima estimated.

c, mole/l.	k_1, min.$^{-1}$	λmax, mμ	Intensity log ε
0.35×10^{-3}	0.029	261	3.64
7.80×10^{-3}	.0018	402	1.97
7.80×10^{-3}	.0018	418	2.11
7.80×10^{-3}	.0018	439	2.06

***cis*-5-Cyclopentena[b]tetrahydrofuran-2-one (IX).**—*cis*-2-Nitroso-6-cyclopentena[e]tetrahydro-1,2-oxazin-3-one was prepared as previously described from the reaction of a solution of nitrous acid (0.26 mole) in water (100 cc.) with a solution of 6-cyclopentena[e]tetrahydro-1,2-oxazin-3-one (13.5 g., 0.097 mole) in water (300 cc.), except that the product was separated from the reaction mixture by extraction with ether (5 × 75 cc.). The ether solution was dried over sodium sulfate and the ether evaporated at room temperature under reduced pressure. The residual yellowish brown oil was refluxed in 95% ethanol (25 cc.) for two days. Evaporation of the ethanol left a brown oil. Distillation under reduced pressure yielded a fraction (7.6 g., 0.061 mole, 63%), b.p. 76–83° (1 mm.). Redistillation yielded the analytical sample of *cis*-5-cyclopentena[b]-tetrahydrofuran-2-one, b.p. 83° (1 mm.), $n^{25}D$ 1.4881, m.p. −10 to −9°. The ultraviolet spectrum shows only rising end absorption: in 95% EtOH at 220 mμ log ε is 1.59 and at 215, 1.73, $\nu_{C=CH}$ 3040, ν_{C-O} 3500 (overtone), 1760, $\nu_{C=C}$ 1612 cm.$^{-1}$ on the liquid.

Anal. Calcd. for $C_7H_8O_2$ (124.13): C, 67.73; H, 6.50. Found: C, 67.41; H, 6.76.

Test Reactions with *cis*-5-Cyclopentena[b]tetrahydrofuran-2-one. (A) Regeneration from Alkaline Solution.—*cis*-5-Cyclopentena[b]tetrahydrofuran-2-one (1 g.) was dissolved in 10% sodium hydroxide solution (10 cc.), causing the solution to darken rapidly. After a day the solution was extracted with ether, but evaporation of the ether left no residue. The alkaline solution was acidified with concentrated hydrochloric acid and extracted with ether. Evaporation of the ether left a brown oil, which was distilled under reduced pressure, giving a sample, $n^{25}D$ 1.4885, having an infrared spectrum identical with that of the starting material.

(B) Legal Test.—*cis*-5-Cyclopentena[b]tetrahydrofuran-2-one gave a negative test[18] for an enol lactone. A dilute solution of sodium nitroprusside in ethanol was added to an ethanol solution of the product (0.25 drop per cc.). Addition of 1% sodium bicarbonate solution (0.25 cc.) to 1 cc. of the solution gave no color while addition of 20% sodium hydroxide solution (1 drop) to another 1-cc. portion gave a pale yellow color.

Catalytic Hydrogenation of *cis*-5-Cyclopentena[b]tetrahydrofuran-2-one. (A) At Atmospheric Pressure on a Small Scale.—*cis*-5-Cyclopentena[b]tetrahydrofuran-2-one (0.163 g., 0.00131 mole) in 95% ethanol (10 cc.) with platinic oxide (0.1 g.) was hydrogenated at atmospheric pressure and room temperature. The hydrogen uptake was 85 cc. (0.0034 mole), corresponding to 2.6 molecules. Filtration of the catalyst and evaporation of the solvent left an oil which turned blue litmus pink and evolved carbon dioxide on treatment with 5% sodium bicarbonate solution. The infrared spectrum of this oil was most like that of cyclopentaneacetic acid, but weak bands attributable to *cis*-cyclopentana[b]tetrahydrofuran-2-one also appear. With the exception of a weak band at 1360 cm.$^{-1}$ the spectrum can be fully accounted for as a composite of these two compounds.

(B) **At One Atmosphere on a Larger Scale.**—*cis*-5-Cyclopentena[b]tetrahydrofuran-2-one (6.28 g.) in 95% ethanol (25 cc.) with platinic oxide (0.2 g.) was hydrogenated at 15 p.s.i. and room temperature for 26 hours, but there was no pressure drop after the first two hours. Filtration of the catalyst, removal of the solvent by distillation and distillation of the residual oil gave a fraction, b.p. 102–105° (27 mm.), n^{27}D 1.4483. The infrared spectrum contained carbonyl bands at 1779, 1736 (strongest) and 1713 cm.$^{-1}$, attributable to a γ-lactone, an ester and an acid, respectively.

The liquid mixture was dissolved in ether and extracted with 10% sodium hydroxide solution. Evaporation of the ether layer and distillation gave a fraction, b.p. 225–230°, n^{28}D 1.4383, having carbonyl absorption at 1737 cm.$^{-1}$; reported for ethyl cyclopentaneacetate: b.p. 74–75° (12 mm.), n^{20}D 1.4357[49] and b.p. 91° (27 mm.), n^{20}D 1.435.[50] This ester fraction was refluxed with 20% sodium hydroxide solution for about an hour until it became homogeneous. The alkaline solution was washed with ether, acidified with concentrated hydrochloric acid, and extracted with ether. Evaporation of the ether left an oil having the odor of cyclopentaneacetic acid. After distillation under reduced pressure, the sample had n^{27}D 1.4537 and carbonyl absorption at 1710 cm.$^{-1}$. The infrared spectrum appeared to be that of slightly impure cyclopentaneacetic acid; reported: n^{18}_f 1.4548, n^{33}_f 1.4482[19,51] (f = 5876 Å.).

The sodium hydroxide solution remaining from separation of the ester was acidified with concentrated hydrochloric acid and extracted with ether. The ether extracts were extracted with 5% sodium bicarbonate solution and the bicarbonate extracts re-extracted with ether. The combined ether extracts were evaporated and the residual oil distilled at 27 mm., giving a sample, n^{28}D 1.4700, having an infrared spectrum identical with that of *cis*-cyclopentana[b]tetrahydrofuran-2-one.

The sodium bicarbonate extracts were acidified with hydrochloric acid and extracted with ether. Evaporation of the ester and distillation of the residue gave cyclopentaneacetic acid, b.p. 130–132° (28 mm.), n^{27}D 1.4514, m.p. 13–14° (uncor.) and mixed m.p. with an authentic sample 12.5–13.5° (uncor.). The infrared spectrum was identical with that of an authentic sample.

Cyclopentaneacetic Acid (X).—2-Cyclopenteneacetic acid[20] (4.57 g.) in absolute ether (30 cc.) with platinic oxide (0.2 g.) was hydrogenated at 2 atmospheres of pressure and room temperature. Filtration of the catalyst, evaporation of the ether and distillation of the residual oil gave cyclopentaneacetic acid, b.p. 132° (23 mm.), n^{27}D 1.4507, m.p. 13–14.5° (uncor.); ν_{OH} ~2760 (broad), $\nu_{C=O}$ 1705 cm.$^{-1}$ on the liquid; reported: b.p. 133–134° (23 mm.),[19,50] n^{18}_f 1.4548 and n^{34}_f 1.4482[19,51] (f = 5876 Å.), m.p. 13–14°.[19]

Ethyl 2,3-Dibromocyclopentaneacetate.—A solution of bromine (38 g., 0.238 mole) in carbon disulfide (100 cc.) was added dropwise[52] with stirring over a period of one hour to an ice-cooled solution of 2-cyclopenteneacetic acid[20] (30 g., 0.238 mole) in carbon disulfide (90 cc.), placed under a reflux condenser. The bromine color was discharged rapidly at first, but toward the end of the addition the solution became red. Some hydrogen bromide was evolved during the addition. The solution was stirred for an hour after bromine addition was complete. The solvent was evaporated, causing the red color to disappear and leaving a pale yellow oil (68 g., 0.238 mole, 100%). The infrared spectrum of this oil contained a shoulder at ~1772 on the acid carbonyl band at 1700 cm.$^{-1}$, suggesting a bromo-γ-lactone impurity.

The oil was dissolved in ether and extracted with sodium bicarbonate solution. The bicarbonate extract was acidified with 10% hydrochloric acid and extracted with ether. The ether extract was dried with magnesium sulfate, evaporated, and the residue dried at 1 mm. pressure. The residual oil, assumed to be crude 2,3-dibromocyclopentaneacetic acid, could not be distilled without decomposition. Its infrared spectrum showed broad acid OH absorption centered at ~2670, a weak shoulder at ~1780, and a strong acid carbonyl band at 1705 cm.$^{-1}$.

A solution of crude 2,3-dibromocyclopentaneacetic acid (40.5 g., 0.142 mole), concentrated sulfuric acid (1 cc.) and ethanol (81.5 cc., 1.4 moles) was refluxed for 5 hours. Ethanol (~25 cc.) was removed under reduced pressure and the residue dissolved in ether (50 cc.), washed with water (2 × 75 cc.), and finally with saturated sodium bicarbonate solution. Evaporation of the ether and distillation gave a fraction (26.7 g., 0.0850 mole, 60% based on 2,3-dibromocyclopentaneacetic acid), b.p. 98–100° (0.15–0.8 mm.). Redistillation yielded the analytical sample of ethyl 2,3-dibromocyclopentaneacetate, b.p. 100° (0.2 mm.), n^{27}D 1.5141, $\nu_{C=O}$ 1729 cm.$^{-1}$ on the liquid.

Anal. Calcd. for $C_9H_{14}O_2Br_2$ (314.03): C, 34.42; H, 4.49. Found: C, 34.10; H, 4.66.

Bromination of 2-cyclopenteneacetic acid in acetic acid solution, or in chloroform solution with aluminum bromide as catalyst[36] gave results similar to those in carbon disulfide solution; in each case the major product was an acid (ν_{OH} ~2670–2720, $\nu_{C=O}$ 1702–1710 cm.$^{-1}$), with a shoulder at 1772–1777 cm.$^{-1}$ in the infrared suggesting the presence of the bromolactone, *cis*-6-bromocyclopentana[b]tetrahydrofuran-2-one, as an impurity.

***cis*-Cyclopentana[e]tetrahydro-1,2-oxazin-3-one (XII).**—*cis*-6-Cyclopentena[e]tetrahydro-1,2-oxazin-3-one (0.30 g. 0.00221 mole) in absolute ethanol (10 cc.) with platinic oxide (0.1 g.) was catalytically hydrogenated at 2 atmospheres of pressure. The uptake of hydrogen corresponded to one molecule. Filtration of the catalyst and evaporation of the solvent under reduced pressure left *cis*-cyclopentana[e]tetrahydro-1,2-oxazin-3-one as a colorless oil (0.29 g., 0.00205 mole, 93%), n^{25}D 1.5065, m.p. 43–46° (but readily supercools); ν_{NH} 3180, 3070; $\nu_{C=O}$ 1668 cm.$^{-1}$ on the supercooled liquid. Impure samples showed an additional weaker carbonyl band at 1750–1786 cm.$^{-1}$ and had low carbon analyses.

Anal. Calcd. for $C_7H_{11}NO_2$ (141.17): C, 59.55; H, 7.85; N, 9.92. Found: C, 59.41; H, 7.79; N, 9.68.

Test Reactions with *cis*-Cyclopentana[e]tetrahydro-1,2-oxazin-3-one. (A) Salt Formation with 20% Sodium Hydroxide Solution.—*cis*-Cyclopentana[e]tetrahydro-1,2-oxazin-3-one (0.2 g.) was dissolved in aqueous 20% sodium hydroxide solution and set aside for 18 hr. at room temperature. The solution then was saturated with sodium chloride and extracted with ether (3 × 10 cc.), but evaporation of the ether extracts left no residue. The aqueous solution was acidified with aqueous 20% hydrochloric acid, saturated with sodium chloride, and extracted with ether. Evaporation of the ether left regenerated starting material, as shown by mixed m.p. determination.

In similar experiments in which the aqueous 20% sodium hydroxide was replaced with 10% sodium bicarbonate or 20% hydrochloric acid solutions, the unchanged starting material was extracted with ether directly from the sodium bicarbonate or hydrochloric acid solutions.

(B) Tollens Test and Hydroxylamine Test.—*cis*-6-Cyclopentena[e]tetrahydro-1,2-oxazin-3-one gave a positive Tollens test (silver mirror) and a positive test for hydroxylamine with salicylaldehyde and copper acetate.[53]

(C) Action of Concentrated Hydrochloric Acid.—Evaporation of *cis*-cyclopentana[e]tetrahydro-1,2-oxazin-3-one (0.2 g.) with concd. hydrochloric acid (2 cc.) by warming on a steam-bath gave a residue of ammonium chloride, as indicated by the odor and basicity of the gas evolved on alkaline treatment of the salt, and by formation of an immediate precipitate with silver nitrate solution.

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(50) H. Moureu, P. Chovin, G. Bloch and G. Rivoal, *Bull. soc. chim. France*, 475 (1949).

(51) J. F. Eykman, *Chem. Weekblad*, **8**, 651 (1911).

(52) R. Fittig and C. Geisler, *Ann.*, **208**, 37 (1881).

(53) F. Feigl, "Spot Tests," Vol. I, "Inorganic Applications," 4th ed., Elsevier Publishing Co., Houston, Texas, 1954, p. 228.

Anal. Calcd. for NH_4Cl: C, 0; H, 7.54. Found: C, 0.91, 0.94; H, 7.47, 7.37.

(D) **Dichromate Oxidation.**—Potassium dichromate (2.0 g.) was added to a solution of *cis*-cyclopentana[e]tetrahydro-1,2-oxazin-3-one (0.5 g.) in concentrated sulfuric acid. A vigorous reaction occurred, with heat evolution. The solution was poured into water (10 cc.) and extracted with ether. The ether was then extracted with 5% sodium bicarbonate solution, the bicarbonate extract acidified with sulfuric acid, and the acidified solution extracted with ether. Evaporation of the ether left a white solid (~0.1 g.). Recrystallization from benzene–light petroleum (b.p. 90–100°) and vacuum sublimation gave a sample, m.p. 92–97.5°, mixed m.p. with glutaric acid of m.p. 95.5–99°, 94–98°.

cis-**2-Hydroxycyclopentaneacetamide (XIII).** (A) **From *cis*-6-Cyclopentena[e]tetrahydro-1,2-oxazin-3-one by Catalytic Hydrogenation over Raney Nickel.**—*cis*-6-Cyclopentena[e]tetrahydro-1,2-oxazin-3-one (2.15 g., 0.0154 mole) dissolved in absolute ethanol (10 cc.) with Raney nickel catalyst (0.25 teaspoonful) was hydrogenated at 2 atmospheres of pressure. The hydrogen uptake corresponded to 0.029 mole or 2 molecules. Filtration of the catalyst and evaporation of the solvent left *cis*-2-hydroxycyclopentaneacetamide (2.03 g., 0.0142 mole, 92%), m.p. 91.5–96°. Recrystallization five times from chloroform and finally from benzene gave the analytical sample as white crystals, m.p. 95.5–96°. The ultraviolet spectrum shows only rising end absorption: in 95% EtOH at 220 mμ log ε is 2.25 and at 215, 2.35; ν_{OH} ~3470 in $CHCl_3$, 3340 in Nujol; ν_{NH} 3390, 1589 in $CHCl_3$, 3340, 3180, 1626 in Nujol; $\nu_{C=O}$ 1668 in $CHCl_3$, 1686 cm.$^{-1}$ in Nujol.

Anal. Calcd. for $C_7H_{13}NO_2$ (143.18): C, 58.72; H, 9.15; N, 9.78. Found: mol. wt. (Rast), 139; C, 58.79; H, 8.98; N, 9.86.

(B) **From *cis*-Cyclopentana[e]tetrahydro-1,2-oxazin-3-one by Chemical Reduction.**—A solution of *cis*-cyclopentana[e]tetrahydro-1,2-oxazin-3-one (10.8 g., 0.0765 mole) in 95% ethanol (44 cc.) was mixed with 1 *N* aqueous ammonium chloride (22 cc.) and reduced iron powder (22 g.) and refluxed for one hour. The solids were filtered off and washed with ethanol (20 cc.). The combined filtrate and ethanol wash were evaporated and the residual oil crystallized from chloroform–light petroleum (b.p. 60–68°), yielding a white solid (2.60 g., 0.0181 mole, 24%). Sublimation gave a sample, m.p. 94–95°. A mixed m.p. with the sample prepared in part A was undepressed (m.p. 95–97.5°).

Anal. Found: C, 58.80; H, 8.98; N, 9.60.

(C) **From *cis*-Cyclopentana[b]tetrahydrofuran-2-one by Reaction with Ammonia.**—*cis*-Cyclopentana[b]tetrahydrofuran-2-one (0.6 g.) was dissolved in concentrated ammonia water (10 cc.) by shaking for 2 hours.[54] The solution was evaporated to dryness in a vacuum desiccator over concentrated sulfuric acid, leaving a white solid. Recrystallization from chloroform–light petroleum (b.p. 60–68°) gave a sample, m.p. 93–95°, mixed m.p. with the sample prepared in part A, 95–97°. The infrared spectra in Nujol and chloroform were identical with those of the samples described in parts A and B, respectively.

Test Reactions with *cis*-2-Hydroxycyclopentaneacetamide. (A) **Action of Nitrous Acid.**—The action of cold dilute nitrous acid on *cis*-2-hydroxycyclopentaneacetamide caused evolution of a colorless, odorless gas. Extraction of the acidic aqueous solution with ether removed an oil having a strong infrared absorption band at 1753 and a weaker band at 1703 cm.$^{-1}$.

(B) **Identification of Ammonia from Alkaline Hydrolysis.**—*cis*-2-Hydroxycyclopentaneacetamide (0.3 g.), benzoyl chloride (0.3 g.) and 20% sodium hydroxide solution (4 cc.) were shaken for a few minutes until a precipitate formed. After filtration, washing with 5% sodium bicarbonate solution and recrystallization from benzene the precipitate had m.p. 126–129°. Vacuum sublimation gave a sample, m.p. 130°, mixed m.p. with benzamide, 129.5–130°. The infrared spectra of the two samples in Nujol were identical.

(C) **Permanganate Oxidation.**—A solution of *cis*-2-hydroxycyclopentaneacetamide (2.5 g.) and sodium hydroxide (0.7 g.) in water (10 cc.) was warmed on a steam-bath until evolution of ammonia was complete. Sodium permanganate[40] (5 g.) was added, resulting in a rapid oxidation and complete discharge of the permanganate color. Filtration of the precipitated manganese dioxide, evaporation of the filtrate under aspirator pressure, acidification of the residue with concentrated sulfuric acid, trituration of the acidified residue with ether, and evaporation of the ether left an acidic solid (~0.5 g.). Four recrystallizations from benzene gave a sample, m.p. 90–93°, mixed m.p. with glutaric acid of m.p. 95.5–99°, 92–96°.

Anal. Calcd. for $C_5H_8O_4$ (132.11): C, 45.45; H, 6.10. Found: C, 45.10; H, 5.69.

Phenylurethan derivative of *cis*-2-hydroxycyclopentaneacetamide white crystals from carbon tetrachloride, m.p. 151.5–153.5°; ν_{NH} 3360 (shoulder), 3320, 3170, 1632 or 1601, 1536; $\nu_{C=O}$ 1696, 1650 cm.$^{-1}$ in Nujol.

Anal. Calcd. for $C_{14}H_{18}N_2O_3$ (262.30): C, 64.10; H, 6.92; N, 10.68. Found: C, 64.10; H, 6.89; N, 10.67.

cis-**Cyclopentana[b]tetrahydrofuran-2-one (XI).**—(A) **From Hydrolysis of *cis*-2-Hydroxycyclopentaneacetamide.**—By procedures previously described, 5-nitronorbornene (30.0 g., 0.216 mole) was converted to *cis*-6-cyclopentena-[e]tetrahydro-1,2-oxazin-3-one (12 g., 0.086 mole, 40%), which was hydrogenated over Raney nickel catalyst at 2 atmospheres of pressure to *cis*-2-hydroxycyclopentaneacetamide. The product was hydrolyzed with 20% sodium hydroxide solution (17 g. of solution containing 3.5 g. of sodium hydroxide), acidified with 20% sulfuric acid (by volume), extracted with chloroform (3 × 20 cc.), and the chloroform evaporated. Vacuum distillation yielded three fractions, b.p. 65–69° (0.4 mm.), $n^{25}D$ 1.4727, the last of which, b.p. 68–69° (0.4 mm.), $n^{25}D$ 1.4727, m.p. −13.5 to −12°, was selected as the analytical sample of *cis*-cyclopentana[b]-tetrahydrofuran-2-one; $\nu_{C=O}$ 3520 (overtone; sample was shown to be pure by vapor phase chromatography), 1759 cm.$^{-1}$ on the liquid.[55–57]

Anal. Calcd. for $C_7H_{10}O_2$ (126.15): C, 66.64; H, 7.99. Found: C, 66.54; H, 7.67; mol. wt. (Rast), 144.

(B) **From Lactonization of 1-Cyclopenteneacetic Acid.**—Crude 1-cyclopenteneacetic acid[22] (25 cc.) was warmed with 60% sulfuric acid (by volume, 100 cc.) at 90–100° for 20 minutes.[21] The solution was cooled, saturated with ammonium sulfate, washed with ether (3 × 50 cc.), partly neutralized with sodium hydroxide, and finally fully neutralized with excess sodium bicarbonate. Evaporation of the ether washes left a residue which did not smell like the lactone. The neutralized sodium bicarbonate solution was extracted with chloroform (2 × 50 cc.) and ether (2 × 50 cc.). The chloroform–ether extracts were washed with sodium bicarbonate solution (10 cc.), dried over magnesium sulfate, and distilled, giving a fraction, b.p. 70° (0.7 mm.), $n^{25}D$ 1.4728, m.p. −13 to −12°, mixed m.p. with the sample described in part A, −12 to −9°. The infrared spectra of the two samples were identical.

Attempted Catalytic Hydrogenation of *cis*-Cyclopentana-[b]tetrahydrofuran-2-one.—*cis*-Cyclopentana[b]tetrahydrofuran-2-one (0.303 g.) in absolute ethanol (20 cc.) with platinic oxide (0.2 g.) was subjected to hydrogen at atmospheric pressure and room temperature, but there was no uptake of hydrogen. Filtration of the catalyst and evaporation of the ethanol left an oil having an infrared spectrum identical with that of the starting material.

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