Anal. Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.54. Found: C, 61.63; H, 6.47.

The keto-enol acetate solidified in the cold room. It crystallized from methyl alcohol as large prisms, mp 32°.

The phenylosazone of cyclohexane-1,2-dione, mp 149-150° (lit.[22] mp 149-150°), was prepared by refluxing 0.9 g of 2-acetoxycyclohex-2-enone with 1.4 g of phenylhydrazine in 10 ml of ethanol for 2.5 hr.

Reaction of *cis*-2,6-Dibenzoyloxycyclohexanone with Sodium Benzoate.—*cis*-2,6-Dibenzoyloxycyclohexanone, mp 187-188°, (0.8728 g, 0.00258 mole) was dissolved in 10 ml of hot diglyme and 1.55 g of sodium benzoate (0.0108 mole) was added. The mixture was stirred at 105-110° (bath temperature) for 4 hr. Processing gave 93% of 2-benzoyloxycyclohex-2-enone, mp 83-84°.

Reaction of 2α,4α-Dibromocholestan-3-one with Sodium Benzoate.—A mixture of 3.0 g (0.0058 mole) of dibromocholestanone, 4.9 g (0.034 mole) of sodium benzoate, and 30 ml of diglyme was stirred and heated (103-107°, bath temperature) 3.5 hr. The reaction mixture was then poured into water and extracted with ether. After drying and concentration, 2.9 g of oily solid was obtained. Trituration of this material with 10 ml of pentane gave 1.36 g of solid, mp 80-110°.[23] The solid was dissolved in 2 ml of benzene and adsorbed onto a slurry-packed silica gel column (3.5 × 120 cm) eluted with 3% ether in hexane initially. Fractions 1 and 2 were blank. Fraction 3 (1000 ml, 6% ether) gave 0.12 g of solid, mp 165-170°. One crystallization from chloroform-ethanol gave 0.10 g (0.19 mmole or 3%) of **3-benzoyloxycholest-2-en-4-one** (12): mp 175-177°; $[\alpha]^{26}\text{D}$ +31° (lit.[3] mp 177°; $[\alpha]^{20}\text{D}$ +25.9°); $\lambda_{\max}^{\text{MeOH}}$ 233 mμ (ε 18,800). Fraction 4 (1000 ml, 7% ether) gave 0.13 g of solid, mp 135-140°, which appeared to be a mixture of keto-enol benzoates 11 and 12 by nmr analysis. Fraction 5 (2600 ml, 8-10% ether) yielded 0.52 g of solid. Recrystallization from ethanol-chloroform gave 0.40 g (0.8 mmole) of **3-benzoyloxycholest-3-en-2-one** (11), mp 162-163°, further identified by mixture melting point and infrared analysis.

Chromatography of the pentane mother liquors (see above) gave 0.16 g of 11 for a total of 1.111 mmoles (19%).

Attempted Reaction of 2-Acetoxy-4,4-diphenylcyclohexanone with Sodium Benzoate.—A mixture of 2-acetoxy-4,4-diphenylcyclohexanone (0.1 g, 0.37 mmole), sodium benzoate (0.2 g, 1.5 mmoles), and 2 ml of diglyme were heated at 105-115° (bath temperature) for 3 hr with frequent shaking. Only starting material was recovered on processing.

Attempted Rearrangement of 2-Acetoxy-5,5-diphenylcyclohexanone.[24]—A mixture of 2-acetoxy-5,5-diphenylcyclohexanone (0.1 g, 0.35 mmole), sodium benzoate (0.2 g, 1.4 mmoles), and 2 ml of diglyme was heated at 117° (bath temperature) for 3 hr, with magnetic stirring, and then poured into 100 ml of water and 200 ml of ether. The ethereal layer was washed with three 100-ml portions of 5% sodium bicarbonate, dried, and concentrated to about 1 ml. A seed crystal of starting material was added and the solution was cooled to 0°. The first crystalline crop amounted to 0.10 g (mp 116-127°). The infrared spectrum was almost identical with that of the starting material. Thin layer chromatography comparing this crude material with standard mixtures showed that 1% or less of 2-acetoxy-4,4-diphenylcyclohexanone was present. Trituration with hot hexane followed by cooling gave solid material which melted at 130-131°; there was less than a 2% weight loss during this operation.

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[22] A. Kotz, K. Blendermann, R. Rosenbusch, and E. Sirringhaus, *Ann.*, **400**, 55 (1913).

[23] In several preliminary runs it was found that the melting point of the solid depended upon the amount of washing with pentane; when the crude product was triturated with about 25-30 ml of pentane, the melting point was 137-138° (with softening). The nmr spectrum of the product so obtained showed vinyl proton signals corresponding only to the two benzoates (mp 162-163° and 175-177°) obtained when the products were chromatographed.

[24] We wish to thank Mr. Robert Frame for carrying out this experiment.

The Synthesis of 2-Nitrocyclohexanone and the Reaction of Acetyl Nitrate with Cyclohexene

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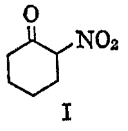
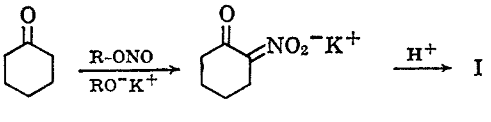
The synthesis of 2-nitrocyclohexanone was accomplished by the chromic acid oxidation of 2-nitrocyclohexanol and by the reaction of acetyl nitrate with cyclohexen-1-ol acetate. The reaction of acetyl nitrate with cyclohexene was shown to produce the previously unreported 4-nitrocyclohexene in addition to the previously reported 2-nitrocyclohexyl acetate, 2-nitrocyclohexyl nitrate, and 3-nitrocyclohexene.

Some of the recent work in this laboratory has centered around the synthesis on a preparative scale of 2-nitrocyclohexanone (I). The only previous synthesis of I was that of Wieland, Garbsch, and Chavan[1] who started with cyclohexanone according to eq. 1.



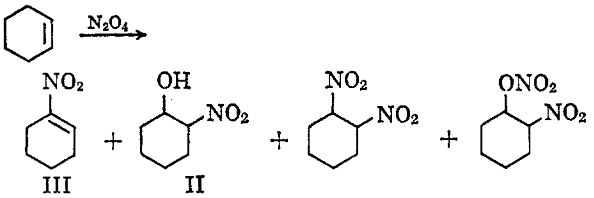
I



(1)

These reactions, however, did not appear to be a suitable preparative route owing to the low over-all yield.

The literature indicated that a possible path to I was by direct oxidation of 2-nitrocyclohexanol (II), whose synthesis was accomplished by the reaction of cyclohexene with dinitrogen tetroxide according to the method of Baldock, Levy, and Scaife.[2] The problems[3] associated with this reaction are apparent even though



(2)

II and III are quite easily isolated. The chromic acid oxidation[4] of II provided a 30% yield of I whose physical properties agreed closely with those given by Wieland, Garbsch, and Chavan.[1]

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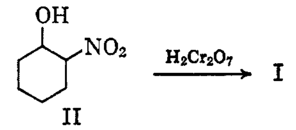
[1] H. Wieland, P. Garbsch, and J. J. Chavan, *Ann.*, **461**, 295 (1928).

[2] H. Baldock, N. Levy, and C. W. Scaife, *J. Chem. Soc.*, 2627 (1949).

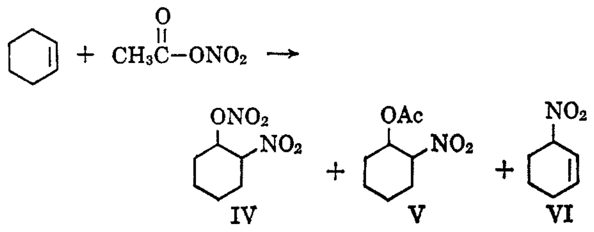
[3] Not only is the number of products excessive, but the reaction temperature must be carefully controlled in order to prevent violent fume-offs in the distillation step.

[4] N. Levy and C. W. Scaife, *ibid.*, 1100 (1946).



(3)

A second and seemingly more convenient preparation of II arose from the work of Bordwell and Garbisch.[5] Their extensive work on the addition of acetyl nitrate to olefins had shown that a general reaction[4] occurs. The reaction with cyclohexene has been repeated and we wish to report somewhat different results which provide further information on the mechanism of the acetyl nitrate addition to olefins.



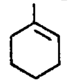
(4)

After repeating the reaction in these laboratories using their method,[5a] 3-nitrocyclohexene (VI), 2-nitrocyclohexyl acetate (V), and 2-nitrocyclohexyl nitrate (IV) were isolated by distillation. The latter two products codistilled and the n.m.r. spectrum of the mixture indicated the presence of 26% of IV. From a synthetic viewpoint, the nitrate ester appeared to offer no problems since Boschan, Merrow, and van Dolah[6] quote data that indicate nitrate esters, as well as acetate esters, readily undergo ester exchange (eq. 5) in the presence of an acid catalyst. The exchange reaction was repeated using the mixture of IV and V.

$$R{-}ONO_2 + CH_3OH \xrightarrow{H^+} ROH + CH_3ONO_2 \qquad (5)$$

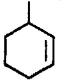
This reaction provided 2-nitrocyclohexanol (II) in 30% yield. Owing to the low yield, this route to II was dropped in favor of a one-step synthesis of I which is discussed later.

Of special interest in the reaction of acetyl nitrate with cyclohexene is the formation of the 3-nitrocyclohexene (VI).[5a] The physical properties which we obtained for this compound were virtually identical with those of Bordwell and Garbisch.[5a] These workers determined the structure of this compound by infrared analysis which was based upon the considerable difference that exists in the asymmetric stretching frequency of the conjugated (III) and nonconjugated nitro group. The inability of this analytical method to distinguish readily between VI and VII caused the presence of 4-nitrocyclohexene (VII) to be overlooked.[7]



III

6.59 μ



VI

6.46 μ

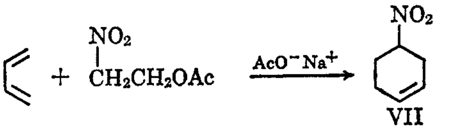
VII

6.45 μ

The n.m.r. spectrum of the olefinic fraction (see Figure 1) gave the first indication of an isomeric mixture as well as the structure of the isomers. The presence of two different types of protons on carbons bearing a nitro substituent is indicated by the multiplets centered at 4.62 and 4.97 p.p.m. The H_a proton of VI is at lower field than the corresponding proton of VII owing to its allylic position. A distinguishing feature of the spectrum is the crude doublet at 2.63 p.p.m. The H_b protons of VII are adjacent to the nitro group as well as being allylic. The combined effects readily explain the observed chemical shift of this methylene group.

VII VI

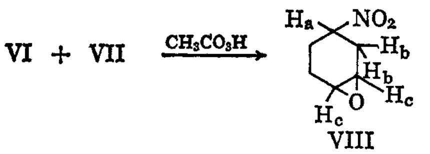
Conclusive proof for structure VII was obtained by synthesis. The reaction[8] of nitroethylene, prepared *in situ* from 2-nitroethyl acetate and base, with butadiene provided VII in low yield. The n.m.r. spectrum (Figure 2) of this product from the Diels–Alder reaction is readily distinguishable in the n.m.r. spectrum of the mixture (Figure 1) from the acetyl nitrate reaction. By subtraction of spectra, a nearly complete spectrum of 3-nitrocyclohexene (VI) is derivable.



VII

(6)

Further support for the structure of VII was obtained from the epoxidation of the nitro olefin mixture. It might be expected[9] that 4-nitrocyclohexene (VII) would be epoxidized more readily than VI owing to the proximity of the highly electronegative group to the double bond. Epoxidation of the olefin mixture yielded an epoxide whose structure was shown to be VIII. The infrared spectrum shows a nitro group on a saturated carbon (6.47, 7.25 μ) as well as epoxide bands (3.32, 11.98 μ). The n.m.r. spectrum shows two epoxide protons, H_c, as a symmetrical multiplet (nine peaks) at 3.07 to 3.36 p.p.m., while H_a appears as a complex multiplet at 4.34 to 4.74 p.p.m. Of interest are the two H_b protons. The apparently equivalent protons occur as a pair of doublets[10] with J_{ab} = 6.0 c.p.s.[11] and J_{bc}



VIII

(7)

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(5) (a) F. G. Bordwell and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **82**, 3588 (1960); (b) *J. Org. Chem.*, **27**, 2322 (1962); (c) *ibid.*, **27**, 3049 (1962); (d) *ibid.*, **28**, 1765 (1963).

(6) R. Boschan, R. T. Merrow, and R. W. van Dolah, *Chem. Rev.*, **55**, 485 (1955).

(7) Since publication of the original work,[5a] Bordwell has observed the formation of γ,δ-unsaturated nitro olefins in the reaction of acetyl nitrate with cyclic olefins: 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1964.

(8) R. B. Kaplan and H. Shechter, *J. Org. Chem.*, **26**, 982 (1961).

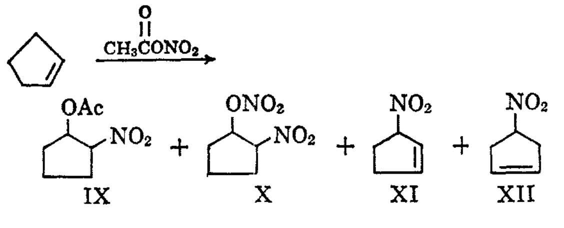
(9) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(10) The coupling constants observed for this multiplet did not change when the n.m.r. spectrum of VIII was obtained using benzene as the solvent.

(11) H. Feltkamp and N. C. Franklin, *J. Am. Chem. Soc.*, **87**, 1616 (1965).

= 2.4 c.p.s.[12] The four remaining protons occur as a narrow multiplet at 1.75 to 2.17 p.p.m. The n.m.r. data can only fit structure VIII as the spectrum of the epoxide of VI would be quite dissimilar.

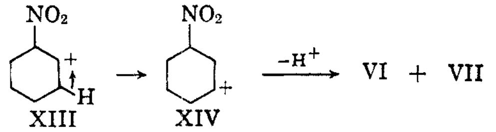
The results obtained with cyclohexene indicated that the same reaction with cyclopentene would provide analogous results. The reaction of acetyl nitrate with cyclopentene did indeed proceed in a like mannér (eq. 8). Esters IX and X were isolated as a mixture,



(8)

as were the nitro olefins XI and XII. The presence of isomeric, nonconjugated nitro olefins was given by the n.m.r. spectrum of the mixture (see Experimental Section).

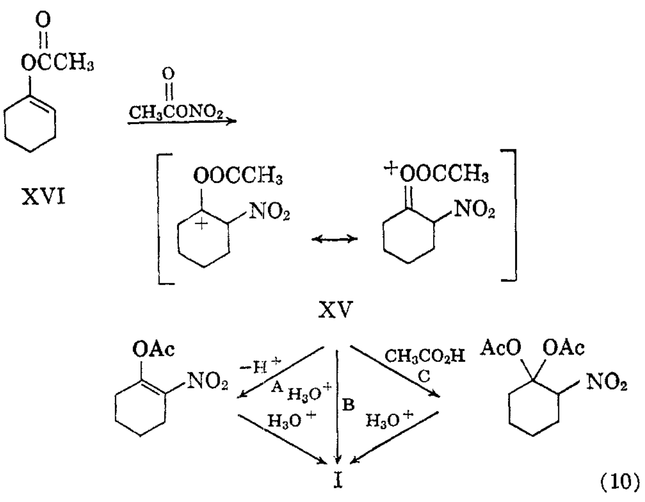
Although much has been written[5a-d] concerning the mechanism of the addition of acetyl nitrate to olefins, the formation of products such as VII and XII suggests that a carbonium ion (XIII) may play a substantial intermediary role. The subsequent formation



(9)

of XIV through a simple hydride shift readily accounts for the observed olefinic products.

The above reactions did not provide a satisfactory route to I, but the previous mechanism suggested a better reaction, *i.e.*, the reaction of acetyl nitrate with an enol ester. According to an electrophilic mechanism, the initial addition of NO_2^+ to an enol ester would lead to an intermediate, XV, which would be stabilized by the acyloxy group. Breakdown of XV by any of the three indicated pathways (A, B, and C) would give the desired α-nitro ketone. When this



(10)

reaction was performed in the laboratory using cyclohexen-1-ol acetate (XVI), the desired 2-nitrocyclohexanone (I) was isolated in 40% yield. The I isolated from this reaction (eq. 10) was identical in every respect with that obtained from the oxidation of 2-nitrocyclohexanol (II). Although this reaction should be general for the preparation of cyclic 2-nitro ketones, it was not extended to other systems since Bachman and Hokama[13] had previously prepared two acyclic 2-nitroketones by a variation of this reaction.

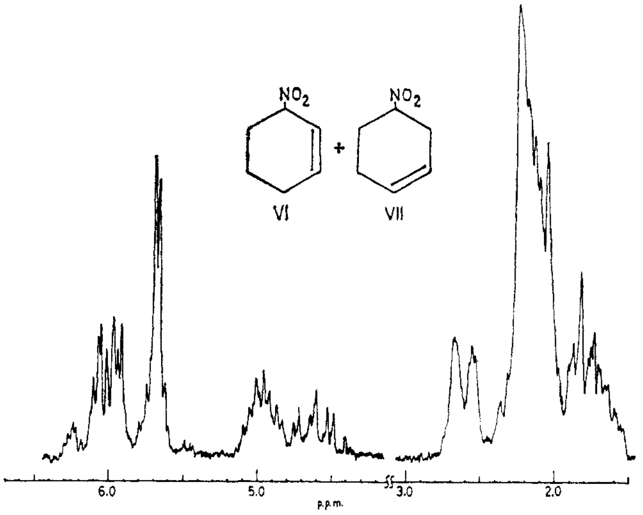


Figure 1.—The 60-Mc. n.m.r. spectrum of the isomeric 3-nitrocyclohexene (VI) and 4-nitrocyclohexene (VII) in deuteriochloroform.

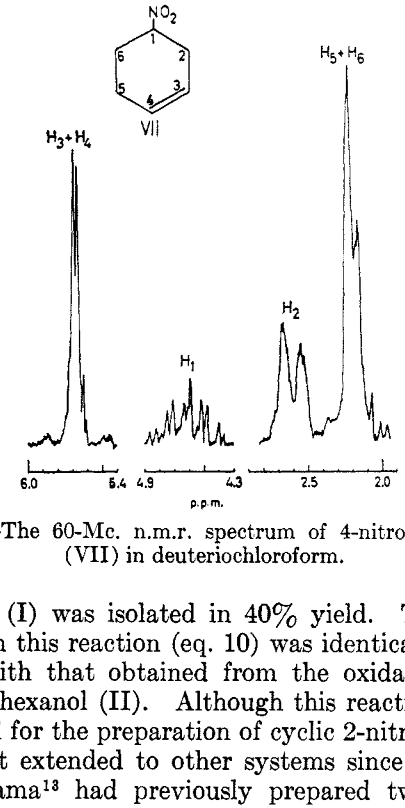


Figure 2.—The 60-Mc. n.m.r. spectrum of 4-nitrocyclohexene (VII) in deuteriochloroform.

Experimental Section

Melting and boiling points are uncorrected. Elemental analyses were performed by the Crobaugh Laboratories, Charleston, W. Va. N.m.r. spectra were determined on a Varian Model A-60 spectrometer. Sample concentrations were *ca.* 5 to 10% (w./v.) in deuteriochloroform unless otherwise indicated. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer.

The Reaction of Cyclohexene with Dinitrogen Tetroxide.[2]—A solution containing 300 g. (3.65 moles, b.p. 83°) of freshly distilled cyclohexene in 2 l. of anhydrous ether was cooled to 0° with an ice–salt bath. A solution containing 335 g. (3.64 moles) of N_2O_4 in 500 ml. of anhydrous ether was slowly added over a 5-hr. period to the cold solution. The addition was made at such a rate as to maintain the temperature below 5°.[3] After

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(12) K. Tori, T. Komeno, and T. Nakagawa, *J. Org. Chem.*, **29**, 1136 (1964).

(13) G. B. Bachman and T. Hokama, *ibid.*, **25**, 178 (1960).

the addition, the ether was removed under reduced pressure and the residue was diluted with 2 l. of distilled water. The two-phase mixture was shaken well and allowed to stand overnight. The organic layer was removed and washed with two 400-ml. portions of water. All of the water fractions were combined for further work-up.

A. **Work-up of the Water-Insoluble Layer.**—The water-insoluble layer was dried over anhydrous sodium sulfate after having been diluted with a small volume of ether. After filtration, the ether was removed under reduced pressure and the residue was distilled under vacuum. A small forerun boiling at 40–110° (2 mm.) was removed. A large fraction (70.2 g.) boiling at 98–120° (1 mm.) distilled before the pressure rapidly increased and the distillation apparatus was disintegrated by a violent fume-off.[3] The first fraction was redistilled through a short Vigreux column giving 14.7 g. of a pale yellow liquid, b.p. 60–61.5° (1.0 mm.) [lit.[2] b.p. 64° (1 mm.)], which was identified as being 1-nitrocyclohexene (III). The infrared spectrum shows $\lambda_{\max}^{\text{neat}}$ 3.41, 3.51, 6.00, 6.45, 6.59, 7.15, 9.43, 10.77, 12.12, 13.52, and 14.37 μ, while the n.m.r. spectrum shows one vinyl proton (three triplets) at 7.15 to 7.36 p.p.m., four allylic protons (complex multiplet) at 2.15 to 2.75 p.p.m., and four saturated protons at 1.35 to 2.00 p.p.m. The second fraction was not redistilled as this has been reported[2] to consist mainly of 1,2-dinitrocyclohexane and 2-nitrocyclohexyl nitrate.

B. **Work-up of the Aqueous Solutions.**—The combined aqueous fractions were saturated with ammonium sulfate, causing an oil to separate. The saturated solution was extracted with three 200-ml. portions of ether which were combined and dried over anhydrous sodium sulfate. After filtration, the ethereal solution was distilled giving 144 g. of a yellow oil, b.p. 97–99° (0.8 mm.) [lit.[2] b.p. 94° (1 mm.)], which was identified as being 2-nitrocyclohexanol (II). The infrared spectrum of II shows $\lambda_{\max}^{\text{neat}}$ 2.93, 3.40, 3.48, 6.47, 7.27, and 9.37 μ.

Oxidation of 2-Nitrocyclohexanol (II) to 2-Nitrocyclohexanone (I).—An 85% sulfuric acid solution (93 g.) was slowly added over a 40-min. period to a stirred solution containing 33.3 g. (0.13 mole) of 2-nitrocyclohexanol, 37.5 g. (0.13 mole) of sodium dichromate, and 23 ml. of distilled water. The temperature of the reaction mixture was maintained at 20–25° by means of an ice bath. The reaction mixture was stirred for 1 hr. after the addition and was then diluted with 150 ml. of water. The resulting solution was extracted with four 60-ml. portions of ether which were combined and dried over anhydrous magnesium sulfate. After filtration, the ether was removed under reduced pressure, leaving 24.8 g. of semisolid residue. The residue was taken up in a small volume of methanol and cooling with a Dry Ice–acetone bath caused precipitation of a crystalline, faintly yellow solid (9.8 g., 30%) that melted at 37.6–38.2° after filtration and air drying. The infrared spectrum of the 2-nitrocyclohexanone (I) shows $\lambda_{\max}^{\text{KBr}}$ 3.37, 3.46, 5.78, 6.40, 7.26, 8.87, 10.55, and 13.50 μ.

Anal. Calcd. for $C_6H_9NO_3$: C, 50.36; H, 6.34; N, 9.79. Found: C, 50.62; H, 6.48; N, 9.84.

The Reaction of Acetyl Nitrate with Cyclohexene.—The preparation of acetyl nitrate followed closely the method of Bordwell and Garbisch.[5a] Freshly distilled acetic anhydride (400 ml.) was cooled to 15°. Colorless, concentrated (70%, 0.3 mole) nitric acid was added to the rapidly stirred anhydride in such a manner that the temperature was maintained at 20°. The addition usually required 5 min. After the addition, the reaction mixture was cooled rapidly to −20°, whereupon 25 g. (0.3 mole) of cyclohexene was quickly added in one portion. The pot temperature rapidly began to rise and, as this occurred, the temperature of the surrounding Dry Ice–acetone bath was lowered to −60 to −70°. The temperature of the reaction mixture usually rose to 8° and remained there for several minutes before dropping. After lowering the temperature to −20°, the reaction mixture was poured into 1 l. of water. The resulting two-phase solution was magnetically stirred in order to hasten the hydrolysis of the acetic anhydride. The pH of this solution was <1. The resulting one-phase system was diluted with 800 ml. of a saturated sodium chloride solution and extracted with three 200-ml. portions of ether. The ether fractions were combined and washed with three 200-ml. portions of water after which the ether was dried over anhydrous magnesium sulfate. After filtration, the ether was removed under reduced pressure, leaving a residue (39 g.) that still contained some acetic acid. Distillation of the residue gave two fractions. The first fraction (11.2 g., 39%) was removed at 55–67° at 0.08 mm. and upon redistillation gave a boiling point of 32–34° (0.07 mm.), $n^{20}\text{D}$ 1.4822. By n.m.r. analysis, this fraction was found to be an isomeric mixture of 3-nitrocyclohexene (VI) and 4-nitrocyclohexene (VII). The infrared spectrum of the mixture shows $\lambda_{\max}^{\text{neat}}$ 3.28, 3.40, 6.05, 6.46, 7.17, 7.28, 7.35, 7.81, 11.81, 12.07, and 12.90 μ. The n.m.r. spectrum of the mixture is shown in Figure 1. The second fraction, b.p. 82–83° (0.13 mm.), 13.5 g., 25%, was a mixture of 2-nitrocyclohexyl acetate (V, 74%) and 2-nitrocyclohexyl nitrate (IV, 26%). The infrared spectrum shows $\lambda_{\max}^{\text{neat}}$ 3.39, 3.48, 5.77, 6.12, 6.47, 7.27, 8.10, 9.60, and 11.50 μ.

Preparation of 2-Nitrocyclohexanol (II) from the Mixture of IV and V.—A solution was prepared containing 20 g. (approximately 0.11 mole) of 2-nitrocyclohexyl nitrate (IV) and 2-nitrocyclohexyl acetate (V, 74%), 100 ml. of absolute methanol, and 1.0 g. of concentrated sulfuric acid. The solution was heated and methanol was slowly distilled off (the distillate showed two peaks by v.p.c.) until the pot temperature began to rise. Attempts were made to distil the residue, but even gentle heating caused loss of vacuum owing to decomposition. The residue was dissolved in ether and percolated through a 1 × 1 in. column of Woelm grade III neutral alumina. The ether was removed under reduced pressure giving a pale yellow residue (8.0 g.) which distilled smoothly giving 2-nitrocyclohexanol (II, 4.8 g., 31%) whose physical properties were identical with those of the II previously prepared.

4-Nitrocyclohexene (VII).—In the following experiment, a 3-l., glass-lined rocker bomb was employed. The charge consisted of 300 ml. of toluene, 40 g. of 2-nitroethyl acetate, 1 g. of sodium acetate, and 0.4 g. of pyrogallol. The bomb was mounted with both an internal and external thermocouple. After charging the above reactants, the bomb was closed and further charged with 66 g. of 1,3-butadiene. The bomb was heated over a 4-hr. period to an internal temperature of 146° (external temperature, 171°) and the pressure rose from 45 p.s.i.g. at the start to 185 p.s.i.g. The bomb was cooled and the residual pressure was released. The resulting solution was dark in color with considerable amounts of black polymer. The polymer was removed by filtration. The toluene was removed under reduced pressure, leaving a residue that provided 9.2 g. of crude product upon distillation. Careful redistillation provided 5.6 g. of pure 4-nitrocyclohexene [VII, $n^{20}\text{D}$ 1.4820, b.p. 36–37° (0.08 mm.)]. The infrared spectrum shows $\lambda_{\max}^{\text{neat}}$ 3.29, 3.43, 3.55, 6.05, 6.45, 7.25, and 15.25 μ. The n.m.r. spectrum is shown in Figure 2.

4-Nitrocyclohexene 1,2-Oxide (VIII).—A stirred solution containing 35 g. (0.28 mole) of the 3- and 4-nitrocyclohexenes and 100 ml. of ethyl acetate was heated to 70° in a hot-water bath. An ethyl acetate solution of peracetic acid[14] (138 ml., 0.38 mole) was slowly added over a 2-hr. period to the hot solution. The amount of peracetic acid present was determined periodically by an iodometric titration of an aliquot. After 12 hr. only 6% of the original peracetic acid remained, and at this point, heating was stopped. The reaction mixture was added dropwise to 200 ml. of ethylbenzene which was distilling at 50 mm. pressure. Distillation was continued until approximately 50 ml. of residue remained in the distillation flask. This residue was distilled giving one main fraction (9.85 g., 24%) which boiled at 57–58.5° (0.3 mm.) and was shown to be 4-nitrocyclohexene 1,2-oxide (VIII). The infrared spectrum shows $\lambda_{\max}^{\text{neat}}$ 3.32, 3.40, 6.47, 7.25, 10.15, 10.25, 11.10, 11.98, 12.50, and 12.72 μ.

Anal. Calcd. for $C_6H_9NO_3$: C, 50.92; H, 6.34; N, 9.79. Found: C, 50.71; H, 6.23; N, 9.50.

2-Nitrocyclohexanone (I) from Acetyl Nitrate and Cyclohexen-1-ol Acetate (XVI).—A solution of acetyl nitrate (0.3 mole) was prepared as in the above reaction with cyclohexene. Cyclohexen-1-ol acetate (XVI, 42.1 g., 0.3 mole) was added in one portion to the acetyl nitrate solution at a temperature of −20°. The reaction mixture began immediately to warm and the temperature of the surrounding Dry Ice–acetone bath was dropped quickly to −60°. The temperature of the reaction mixture rose to −8° before being allowed to drop to −20°. At this point the reaction mixture was poured into 1 l. of cold water. After the acetic anhydride had hydrolyzed, the solution was diluted with 800 ml. of a saturated sodium chloride solution and extraction was made with three 200-ml. portions of ether. The combined ether fractions were washed with five 100-ml. portions

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(14) B. Phillips, F. C. Frostick, Jr., and P. S. Starcher, *J. Am. Chem. Soc.*, **79**, 5982 (1957).

of water before being dried over anhydrous magnesium sulfate. After filtration, the ether was removed under reduced pressure, leaving a residue that still retained traces of acetic acid. The residue (32.3 g.) was dissolved in a small volume of methanol (~50 ml.) and cooled in an Dry Ice–acetone bath. The resulting solid was quickly filtered and washed with cold methanol. After air drying, the solid (17.2 g., 40%) was found to melt at 38°. The infrared spectrum of the product was superimposable on the spectrum of 2-nitrocyclohexanone (I) obtained from the chromic acid oxidation of 2-nitrocyclohexanol (II).

The Reaction of Acetyl Nitrate with Cyclopentene.—The acetyl nitrate reagent was prepared in an identical manner with that used for the cyclohexene reaction. Cyclopentene (20.5 g., 0.3 mole) was added in one portion to the acetyl nitrate at −20°. The temperature of the reaction mixture rose to 4° while the Dry Ice–acetone bath was maintained at −60 to −70°. After allowing the reaction mixture to cool to −20°, it was immediately poured into 1.5 l. of cold water. The solution was allowed to stand for 2 hr. and was then diluted with 800 ml. of a saturated sodium chloride solution. The resulting solution was extracted with four 200-ml. portions of ether which were combined, washed with two 200-ml. portions of water, and dried over anhydrous sodium sulfate. The ether was removed under reduced pressure, giving 23.9 g. of residue. Distillation of the residue provided two fractions. The first fraction [4.1 g., 13%, b.p. 37–38° (0.08 mm.)] was identified as being a mixture of 3-nitrocyclopentene (XI) and 4-nitrocyclopentene (XII). The infrared spectrum of this fraction shows $\lambda_{\max}^{\text{neat}}$ 3.25, 3.44, 3.53, 6.18, 6.45, 7.27, 13.13, and 14.20 μ. Although there is some overlapping of peaks, the n.m.r. spectrum of the mixture shows the spectrum of both XI and XII. The proton on the nitro-bearing carbon of XII appears at 5.14 p.p.m., while the same proton for XI appears at 5.46 p.p.m. Both patterns are complex multiplets. The olefinic protons of XII appear as a virtual singlet (5.70 p.p.m.), while the olefinic protons of XI appear as a highly split AB multiplet at 6.10 p.p.m. The methylenes of XII occur as an unsymmetrical doublet at 2.97 p.p.m., while the methylenes of XI occur as a complex multiplet at 2.48 p.p.m. The second fraction [13.4 g., b.p. 88–90° (0.08 mm.)] was identified[5a] as a mixture of 2-nitrocyclopentyl acetate (IX) and 2-nitrocyclopentyl nitrate (X) by infrared analysis. The infrared spectrum of the mixture shows $\lambda_{\max}^{\text{neat}}$ 5.78, 6.13, 6.44, 7.26, 8.05, and 8.71 μ.

Reactions of 14-Hydroxy-14-azadispiro[5.1.5.2]pentadec-9-ene-7,15-dione and Related Compounds. I. The 3,11-Dimethyl Derivative[1a]

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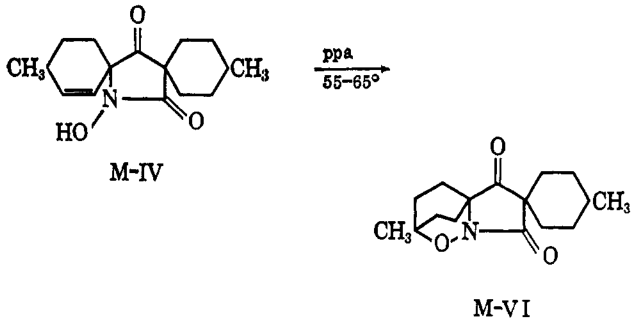
When 3,11-dimethyl-14-hydroxy-14-azadispiro[5.1.5.2]pentadec-9-ene-7,15-dione (M-IV) is heated with polyphosphoric acid at 65–70°, the 9,10 olefinic double bond migrates and the 14-hydroxyl group cyclizes with it to form M-VI, from which a variety of unusual compounds have been obtained. The oxime of M-IV undergoes a Beckmann rearrangement to form a predicted product (M-II) and a cyclized isomer, M-IIa.

The report of Conley and Nowak[2] of abnormal Schmidt reactions of spiro ketones in polyphosphoric acid led us to study the behavior of 3,11-dimethyl-14-hydroxy-14-azadispiro[5.1.5.2]pentadec-9-ene-7,15-dione (M-IV)[3] with sodium azide in this reagent. The product could be either a lactam identical with the Beckmann rearrangement product of M-I (an oxime of M-IV) or abnormal compounds analogous to those obtained by Conley and Nowak.

The product, M-VI, obtained from the attempted Schmidt reaction was not the expected lactam but had the formula, $C_{16}H_{23}NO_3$, as calculated from the elemental analyses and was isomeric with M-IV. Apparently, hydrazoic acid had not taken part in the reaction; so M-IV was heated alone with polyphosphoric acid to form M-VI in 67% yield.



M-IV

M-VI

The infrared spectrum of M-VI has a ketone carbonyl band at 1740 cm.$^{-1}$ and an amide carbonyl band at 1680 cm.$^{-1}$ (Table I) but no absorption for a hydroxyl group, an N–H, or an olefinic linkage. These data were substantiated by the formation of an oxime (M-XI) of M-VI which subsequently underwent a Beckmann rearrangement, a negative ferric chloride test, and the failure of M-VI to acylate.

The disappearance from the infrared spectrum of M-IV of the bands due to the lactam hydroxyl group and the olefinic linkage suggested that cyclization could have taken place between these two groups in a manner analogous to the formation of isoxazolines from α,β-unsaturated ketones in the presence of sulfuric acid.[4]

Cyclization of M-IV at the 11-carbon rather than at the 10-carbon was established by the n.m.r. spectrum of M-VI. The peaks appearing at 1.31 and 0.99 p.p.m. below tetramethylsilane are both assigned to the methyl groups on the basis of their location. The peak at 0.99 p.p.m. is in the typical area for a methyl group α to a saturated cyclic ring. The peak at 1.31 p.p.m. is in the location expected for a methyl group which is β to an oxygen atom, and the line sharpness indicates that there is no proton on the adjacent carbon atom. In addition to the peaks due to the methyl groups at the 3- and 11-positions, the spectrum shows peaks at 2.04 and 1.66 p.p.m. due to aliphatic methylene groups.

Hydrogenation of M-VI over Raney nickel at room temperature and 2 atm. reduced the ketone group to

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(1) (a) Abstract of a portion of the Ph.D. Dissertation of D. N. Heintz, University of Missouri, June 1965. Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964. (b) Gregory Fellow, 1963–1964.

(2) R. T. Conley and R. E. Nowak, *J. Org. Chem.*, **26**, 692 (1961).

(3) Only the numbers I, IV, XV, and XIV correspond to compounds previously described. The prefix M signifies two methyl groups in the 3,11-positions of the azadispiro[5.1.5.2]pentadec-9-enes or -pentadecanes. The compounds having other ring systems also have two methyl groups.

(4) K. von Auwers and H. Brink, *J. Prakt. Chem.*, [2] **133**, 154 (1932).