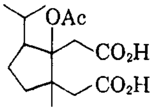
The NMR spectrum of this triol was also consistent with structure II for carotol.

A dicarboxylic acid was obtained by oxidation of the triol with chromic acid in acetic acid. This acid appears to be the same as the one recently reported by Sorm, *et al.*,[6] however, Chiurdoglu and Descamps[7] isolated an α-hydroxyketone by a similar oxidation.

The NMR spectrum of the above acid is consistent with the formula VII proposed by Sorm[6] for this acid. It is interesting that in the NMR spectrum of the acid the isopropyl methyl groups are equivalent and the doublet corresponding to them is found at 55 cps ($\delta = 9.083$), close to the average of the nonequivalent methyls in daucol. A similar situation prevails in carotol itself in which the isopropyl methyls are equivalent or nearly so and fall at 57 cps ($\delta = 9.050$).



VII

EXPERIMENTAL[9]

NMR spectra. The NMR spectra were obtained with a Varian V-4300C high resolution NMR spectrometer operating at 60 mc. in a magnetic field of 14,092 oersteds. Samples were examined in dilute deuterochloroform solution at 33°, contained in cylindrical glass cells 0.195" o.d. and 0.165" i.d. containing 0.4 ml. of solution. The magnetic field was swept through the spectrum at approximately 25 milligauss per minute from low to high field. A trace of tetramethylsilane was added to each sample to serve as an internal reference. The positions of single lines or centers of spin multiplets are designated by the field-independent symbol δ where $\delta = 10.00 - 10^6 \times (\nu - \nu_{\mathrm{SiMe_4}})/\nu_{\mathrm{SiMe_4}}$.

Daucol acetate. Carotol was obtained by distillation of commercial natural carrot seed oil (Magnus Mabee and Reynard, Inc.). The fraction of boiling point 80–81° at 0.1 mm. and n_{D}^{26} 1.4944 was used. Gas chromatography indicated that this fraction contained at least 90% carotol.

Carotol was converted to daucol with either perbenzoic acid or monoperphthalic acid as previously described.[4]

A solution prepared from 262 mg. of daucol (m.p. 117–118°), 2.5 ml. of pyridine, and 0.2 ml. of acetic anhydride was allowed to stand at room temperature for 5 hr., then warmed on the steam bath for 15 min. Daucol acetate, 239 mg., precipitated when the solution was poured on ice. Recrystallization from methanol-water gave colorless needles of constant m.p. 80–81°.

Anal. Calcd. for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41; O, 17.24. Found: C, 73.27; H, 9.87; O, 17.08. $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.78 μ, 8.00 μ. Rotatory dispersion in methanol c 0.494; $[\alpha]_{700\mathrm{m}\mu}$ +4.05°; $[\alpha]_{589\mathrm{m}\mu}$ +10.5°; $[\alpha]_{255\mathrm{m}\mu}$ +170°.

Preparation of acid VII. Carotol was converted to the triol, $C_{15}H_{26}O_3$, m.p. 137–139°, as previously described.[4] The triol, 4.62 g., was dissolved in 400 ml. of acetic acid, 10.3 g. of chromic anhydride added, and the solution maintained at 80° with stirring for 13 hr. The solution was concentrated with the water aspirator and the residue taken up with ether. Extraction of the ether layer with bicarbonate solution followed by acidification of the bicarbonate extract gave 125 mg. of a colorless solid, m.p. 169–170°.

Anal. Calcd. for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05; O, 31.96. Found: C, 60.16; H, 7.93; O, 31.92; neut. equiv., 129. The neutralization equivalent indicates that saponification of the acetate occurred. Rotatory dispersion in methanol c 0.460; $[\alpha]_{700\mathrm{m}\mu}$ −2.6°; $[\alpha]_{589\mathrm{m}\mu}$ −3.0°; $[\alpha]_{305\mathrm{m}\mu}$ −31.3°; $[\alpha]_{255\mathrm{m}\mu}$ +53.9°.

Evaporation of the neutral ether layer gave a viscous oil the infrared spectrum of which showed no O—H band but two carbonyl bands one at 5.63 μ and the other at 5.83 μ.

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[9] All melting points are uncorrected. Microanalysis by Dr. Alfred Bernhardt, Max Planck Institute, Mulheim, Germany.

Generation of Nitroethylene *in Situ* for Use in Diels-Alder Reactions[1a]

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Diels-Alder addition of α,β-unsaturated nitro[2] compounds and conjugated dienes is an important preparative reaction. In a synthesis of derivatives of 3-nitroadipic acid,[3] it became of advantage to prepare 4-nitrocyclohexene. 4-Nitrocyclohexene was first obtained (see Experimental) in the present work in 78–92% yields by condensation of nitroethylene and 1,3-butadiene at 105–107° in either glacial acetic acid or benzene or in the absence of a solvent. The condensation, although adequate, offered the disadvantages that (1) nitroethylene is a viscous lacrymatory liquid which deteriorates on storage and is readily polymerized by heat, light, water, or traces of alkali[4] and (2) preparation of nitroethylene from nitroethanol, either *via* 2-nitroethyl acetate (88% yield from nitroethanol) and subsequent reaction with sodium acetate (considerable polymerization) or by reaction with phthalic anhydride at 170°

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(2) K. Alder, H. F. Rickert, and E. Windemuth, *Ber.*, **71**, 2451 (1938); H. L. Holmes, *Org. Reactions*, **4**, 136 (1948); W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952); E. E. van Tamelin and R. J. Thiede, *J. Am. Chem. Soc.*, **74**, 2615 (1952); W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, **19**, 381 (1954); K. Klager, *J. Org. Chem.*, **20**, 650 (1955); W. E. Noland, H. I. Freeman, and M. S. Baker, *J. Am. Chem. Soc.*, **78**, 188 (1956); and W. E. Noland, *J. Am. Chem. Soc.*, **82**, 2022 (1960).

(3) To be published separately.

(4) (a) H. Wieland and E. Sakellarios, *Ber.*, **52**, 898 (1919); (b) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).

(5) L. Zeldin, Ph.D. dissertation, The Ohio State University, 1951.

(62[5]–67[4b]%yield), is laborious and may be effected only in fair yields. Much simpler and equally (or more) efficient syntheses of 4-nitrocyclohexene involving formation of nitroethylene *in situ* have been found. 2-Nitroethyl acetate and catalytic quantities of sodium acetate at 95–105° or nitroethanol and stoichiometric amounts of phthalic anhydride at 100–150° (preferred) react with 1,3-butadiene to give 4-nitrocyclohexene in 69 and 58–62% yields, respectively. The present techniques of generating nitroethylene (and possibly other conjugated nitroolefins) *in situ* may be of advantage in Diels-Alder reactions of other conjugated dienes.[6]

EXPERIMENTAL

1,3-Butadiene and nitroethylene. 1,3-Butadiene (12 g., 0.22 mole) and nitroethylene[7] (7.3 g., 0.10 mole) were sealed in a Carius tube at −80° and heated for 17 hr. at 107°. The tube was cooled to room temperature, then further cooled in Dry Ice–acetone, opened, and allowed to warm; the excess butadiene was volatilized. The contents of the tube were extracted with ethyl ether, dried with anhydrous sodium sulfate and distilled at reduced pressure to yield, after separation of the lower boiling components, *4-nitrocyclohexene* (10.6 g., 84%); b.p. 73–76° (~9 mm.), n_{D}^{20} 1.4820, d_{20}^{20} 1.114. The physical constants of a redistilled, analytical sample of 4-nitrocyclohexene (colorless) are: b.p. 77° (9–10 mm.), n_{D}^{20} 1.4822, d_{20}^{20} 1.1133, d_{4}^{20} 1.1113; MR_{D} (calcd.) 32.86, MR_{D} (found) 32.63.

Anal. Calcd. for $C_6H_9NO_2$: C, 56.68; H, 7.14; N, 11.02. Found: C, 56.60; H, 6.95; N, 11.13.

The Diels-Alder reaction[7] was also effected in benzene and acetic acid as described above to give 4-nitrocyclohexene in the following yields: (1) mole ratio of 1,3-butadiene to nitroethylene of 1.8:1, benzene (15 ml.), 17 hr., 107°, 87% yield, (2) mole ratio of 1.8:1, benzene (15 ml.), acetic acid (0.2 ml.), 14 hr., 105°, 92% yield, and (3) mole ratio of 2.4:1, glacial acetic acid (15 ml.), 14 hr., 105°, 78% yield.

4-Nitrocyclohexene absorbs bromine and rapidly reduces aqueous potassium permanganate to manganese dioxide. The nitrocyclohexene dissolves slowly in aqueous sodium hydroxide (10%); the alkaline solution, upon acidification in the presence of nitrite ion, gives a pseudonitrole reaction characteristic of secondary nitro compounds.[8] The sodium salt of 4-nitrocyclohexene is precipitated rapidly upon reaction of 4-nitrocyclohexene with sodium ethoxide in ethanol. Infrared analysis of the adduct provides confirmatory evidence for the presence of an unconjugated carbon-carbon double bond (6.0 μ)[9a] and a nitro group attached to a saturated carbon atom (6.45 μ).[9b] The structure of 4-nitrocyclohexene is also consistent with the kinetic data for its rate of neutralization.[10]

1,3-Butadiene, 2-nitroethyl acetate and sodium acetate. 1,3-Butadiene (14.6 g., 0.27 mole), 2-nitroethyl acetate[10,11] (13.0 g., 0.098 mole), sodium acetate (0.3 g.), and benzene were heated at 95–105° in a Carius tube. The tube was cooled to −80°, opened, and allowed to warm to room temperature. The product was extracted with ethyl ether and then filtered. After having been washed with water, aqueous sodium bicarbonate, dilute sodium hydroxide (10 ml., 5%), and brine, the extract was distilled to give crude 4-nitrocyclohexene (9.0 g., 72%), b.p. 76–78° (~10 mm.), n_{D}^{20} 1.4766–1.4796. 2-Nitroethyl acetate (2.5 g., 19% recovery) was present in the residue. The crude adduct in ether was extracted with aqueous sodium hydroxide (5%) until the aqueous layer was colorless, then with water and with brine. Pure 4-nitrocyclohexene (8.5 g., 69% yield) was obtained on distillation; b.p. 74–75° (9–10 mm.), n_{D}^{20} 1.4802–1.4812, d_{20}^{20} 1.113.

The optimum ratio of 2-nitroethyl acetate to sodium acetate was not determined. When less sodium acetate (0.1 g.) was used, the yield of adduct was 51%. In the absence of sodium acetate no detectable reaction occurred and 2-nitroethyl acetate was recovered essentially completely.

1,3-Butadiene, nitroethanol and phthalic anhydride. 1,3-Butadiene (11.3 g., 0.22 mole), nitroethanol[12] (9.1 g., 0.1 mole), phthalic anhydride (15.0 g., 0.1 mole), benzene (10 ml.), and hydroquinone (0.1 g.) were heated in a Carius tube for 0.5 hr. at 100–120°, then for 1 hr. at 120–145°, and finally for 3.5 hr. at 140–150° (the reaction mixture became homogeneous at 140–150°; however, considerable decomposition was evident). The tube was cooled, then cooled in Dry Ice and opened; the excess butadiene was allowed to volatilize. The product (a mixture of a dark brown liquid and a charred brown solid) was extracted with petroleum ether (b.p. 60–90°), filtered to remove the phthalic acid and phthalic anhydride, and dried with sodium sulfate. On distillation, 4-nitrocyclohexene (7.86 g., 62% yield, b.p. 76–80° (9–12 mm.), n_{D}^{20} 1.4826–1.4831) was obtained; in a similar experiment, 4-nitrocyclohexene was obtained in 58% yield.

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[6] H. Feuer, R. Miller, and C. B. Lawyer, Abst. of 136th Meeting of the American Chemical Society, Sept. 13, 1959, p. 45p, report that homologous vicinal nitroalkyl acetates react at elevated temperatures with conjugated dienes in the presence of sodium acetate to give Diels-Alder adducts.

[7] Hydroquinone (0.1 g.) was added to each Diels-Alder reaction mixture.

[8] V. Meyer, *Ann.*, **175**, 120 (1875).

[9] (a) *Catalog of Infrared Spectrograms*, A.P.I. Res. Proj. 44, Carnegie Institute of Technology; Pittsburgh, Pa.; (b) J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955).

[10] P. W. K. Flanagan, Ph.D. dissertation, The Ohio State University, 1957.

[11] (a) H. L. Cates, Jr., Ph.D. dissertation, The Ohio State University, 1951, prepared 2-nitroethyl acetate in 88% yield by adding excess acetic anhydride to nitroethanol and catalytic quantities of concd. sulfuric acid at 30°. Distillation gave 2-nitroethyl acetate as a colorless liquid, b.p. 62–64° (1.3 mm.), n_{D}^{20} 1.4302, d_{20}^{20} 1.2216; lit.,[11b] b.p. 118–119° (30 mm.), d_{4}^{11} 1.2132; (b) L. Henry, *Bull. Acad. Roy. Belg.*, (3), **37**, 162 (1899).

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