(761 mm.)[5], n_D^{20} 1.4643[1], 1.4677[5]]. The α-naphthyl urethane melted at 123° after recrystallization from hexane.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.74; H, 7.80; N, 4.71. Found: C, 76.88; H, 7.79; N (Dumas) 4.69.

Cyclohexylmethylcarbinyl acetate. The ketone II (252 g.; 2 moles) was reduced with lithium aluminum hydride (22.8 g.; 0.6 mole) in 900 ml. of ether in the conventional manner.[9] The crude undistilled alcohol III (255 g.) obtained was treated with 10 drops of concentrated sulfuric acid and acetic anhydride (250 g.) was added dropwise to the stirred mixture which was maintained at 80–90°. The mixture was then heated for an additional 2 hr. at 90°. Distillation furnished 305 g. (90% yield) of ester b.p. 92–93° (18 mm.), n_D^{25} 1.4425 [reported b.p. 136° (93 mm.),[1] n_D^{20} 1.4459[1]].

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Reaction of Camphene and Dinitrogen Pentoxide

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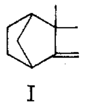
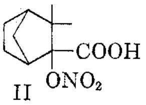
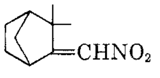
The addition of dinitrogen pentoxide to several simple olefins to produce 1,2-nitronitrates and α- and β-nitro-olefins has been reported.[1] In connection with this study and with the investigation of the dinitrogen tetroxide–camphene reaction,[2] the addition of dinitrogen pentoxide to camphene (I) was examined. An earlier study of this reaction[3] led to the isolation of a nitrato acid assigned structure II.[4]

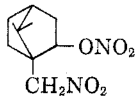

I



II

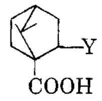


III



IV

V



VIa. Y = ONO2
b. Y = H

Three compounds were isolated from the mixture of products produced in the camphene–dinitrogen pentoxide reaction. The first, m.p. 64–65°, was DL-ω-nitrocamphene[5] (III). The second product, a nitronitrate, m.p. 98–99°, was formulated as 10-nitro-2-nitratocamphane (IV) on the basis of its ready conversion to the known 10,10-dinitro-2-hydroxycamphane (V).[5] The significance of the rearrangement of IV to V has been discussed previously.[2] Formation of IV presumably occurred by addition of NO_2^+ to camphene to give the expected camphenyl-isobornyl cation which then produced the rearranged nitronitrate.

The third compound, a nitrato acid, m.p. 138–140°, undoubtedly was the acid reported previously.[3] In view of the structure IV assigned the nitronitrate, the acid may have structure VIa. Conversion of the nitrato acid to tricyclenic acid was the basis for its formulation as II,[3] but acids such as VI with Y = Br or OH appear to undergo the same conversion.[6] Since it has been shown that an α- or β-nitrato acid has a lower *p*K and higher carbonyl stretching frequency than the unsubstituted acid, these values were measured for VIa and for 1-apocamphane carboxylic acid (VIb). The *p*K of VIa (5.26) was lower than that of VIb (6.02), and the carbonyl frequency of VIa (1700 cm.$^{-1}$) was higher than that of VIb (1690 cm.$^{-1}$). While these values are about what should be expected for a β-nitrato acid such as VIa (the α-nitrato acids have much larger differences[7]) they are not definite evidence for the structure VIa since the corresponding values for an acid related to II were not available.

The camphene–dinitrogen pentoxide reaction also was carried out in the presence of tetraethylammonium nitrate, a process known to reduce the nitration by nitronium ion and to eliminate much of the oxidation in olefin–dinitrogen pentoxide reactions.[1] The products isolated were ω-nitrocamphene (12%) and 10-nitro-2-nitratocamphane (29%). The infrared spectrum of the crude mixture from the reaction conducted in the presence of excess nitrate ion indicated that the two products isolated were the major constituents of the reaction mixture. Apparently some hydrolysis or reaction of IV occurred on the chromatographic column for a considerable amount of the oily material eluted possessed hydroxyl and carbonyl absorption in the infrared that was not present in the original residue. However, the main point is that, in contrast with simple olefins, rearrangement did occur[8] even in the presence of added nitrate ion.

EXPERIMENTAL[9]

Addition of dinitrogen pentoxide to camphene. A solution of 10 g. (0.073 mole) of camphene in 150 ml. of methylene chloride was cooled to −15°, and 0.080 mole of dinitrogen

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(1) T. E. Stevens and W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 6008 (1957).

(2) T. E. Stevens, *Chem. and Ind.* (*London*), 1546 (1957).

(3) N. Demjanov, *J. Russ. Phys. Chem. Soc.*, **33**, 284 (1901) [*Chem. Zentr.*, **72** (2), 346 (1901)].

(4) J. L. Simonsen, *The Terpenes*, 2nd ed., Vol. II, Cambridge University Press, Cambridge, England, 1949, p. 311.

(5) P. Lipp, *Ann.*, **399**, 241 (1913).

(6) Ref. 4, pp. 334, 335.

(7) K. S. McCallum and W. D. Emmons, *J. Org. Chem.*, **21**, 367 (1956).

(8) Addition of dinitrogen pentoxide to *cis*- or *trans*-stilbene, a reaction in which a relatively stable carbonium ion could be produced, has been found to be predominantly a *cis*- process. (Unpublished results from this laboratory.)

(9) All melting points are uncorrected. The infrared spectra of the compounds reported below were consistent with the structural assignments.

pentoxide[1] in 68 ml. of methylene chloride was added over 15 min. while the temperature of the reaction mixture was maintained between −15° and −10°. After addition of the dinitrogen pentoxide the solution was allowed to warm to 3° and stirred for 15 min. The reaction mixture was then quenched with aqueous sodium bicarbonate. The organic layer was washed with water, combined with the organic extracts of the neutralized aqueous washes, and dried over magnesium sulfate. Removal of the methylene chloride at reduced pressure left 15.5 g. of residue. A 3.1-g. portion of this residue was extracted with hot ligroin and the cooled extract was chromatographed on a silica acid–Celite (1:1) column packed in ligroin. Elution of the column with ligroin-ether (30:1) gave 0.43 g. (12%) of 10-nitro-2-nitratocamphane, m.p. 95–97°. Recrystallization of this material from ligroin gave white crystals, m.p. 98–99°.

Anal. Calcd. for $C_{10}H_{16}NO_5$: C, 49.18; H, 6.59; N, 11.47. Found: C, 49.38; H, 6.70; N, 11.14.

From the ligroin-ether (9:1) eluate was obtained 0.35 g. (10%) of the carboxylic acid (II or VIa), m.p. 138–140° reported 140–141°.[3]

The ligroin filtrate from the recrystallization of the nitronitrate was chromatographed on silicic acid–Celite and yielded ω-nitrocamphene, 0.12 g. (4.5%), m.p. 60–62°, m.p. 64–65° after recrystallization from aqueous ethanol, reported 64–65°.[5]

The addition of dinitrogen pentoxide to camphene in the manner described above except that an equivalent of tetraethylammonium nitrate was present[1] led to the isolation of 29% of 10-nitro-2-nitratocamphane and 12.4% of ω-nitrocamphene.

Rearrangement of 10-nitro-2-nitratocamphane. To 10 ml. of 50% ethanol containing 1.2 g. of potassium hydroxide was added 2.30 g. of 10-nitro-2-nitratocamphane. The mixture was warmed and swirled until solution occurred. On cooling in ice, a red salt separated and was removed by filtration. This red salt was suspended in a mixture of 25 ml. of water and 25 ml. of ether and acidified with aqueous hydrochloric acid. The ether layer was separated and the aqueous layer was extracted with ether. Evaporation of the ether left 1.97 g. of a solid, m.p. 155–156°. Two recrystallizations from ligroin gave 10,10-dinitro-2-hydroxycamphane (V) as white needles, m.p. 157–158°, reported 158.5°.[5]

Anal. Calcd. for $C_{10}H_{16}N_2O_5$: C, 49.18; H, 6.59; N, 11.47. Found: C, 49.56; H, 7.11; N, 11.14.

pK determinations. The *p*K's of the nitratoacid (II or VIa) and of VIb were estimated from the titration curves of the acids in 50% ethanol–water at 25°. Under these conditions benzoic acid was found to have a *p*K of 4.50.

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2-Nitro-6-methoxybenzaldehyde[1]

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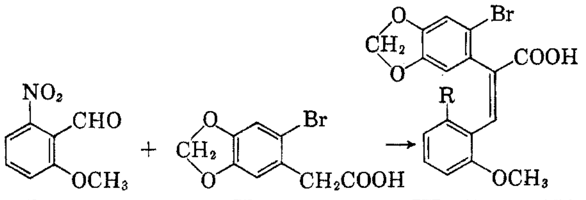
Incidental to another study, it was necessary to prepare *trans*-2-amino-6-methoxy-α-(3′,4′-methylenedioxy-6′-bromophenyl)cinnamic acid (IIIb) from 2-nitro-6-methoxybenzaldehyde (I). Synthesis of I from *m*-nitrophenol by means of a Reimer-Tiemann reaction followed by methylation had already been described by Ashley, Perkin, and Robinson.[2] However, conclusive evidence for the assigned orientation of the formyl group was unavailable since the original structural assignment was made on the basis of color reactions and a physical property.[2,3]

In order to remove any doubt concerning the reliability of the Reimer-Tiemann route to I, a sample for comparison purposes was obtained by the following unequivocal procedure. Conversion of 2,6-dinitrotoluene to 2-methyl-3-nitrophenol was accomplished as previously described.[4,5] Methylation of the phenol followed by chromyl chloride oxidation[6] of the methyl ether afforded an authentic specimen of the aldehyde (I) which was found to be identical with the compound described by Ashley.[2] Reaction of *m*-nitrophenol with chloroform in the presence of sodium hydroxide does indeed yield some 6-nitrosalicylaldehyde.

Condensing[7] I with 6-bromohomopiperonylic acid (II)[8–10] in the presence of triethylamine and acetic anhydride led to *trans*-2-nitro-6-methoxy-α-(3′,4′-methylenedioxy-6′-bromophenyl)cinnamic acid (IIIa). Reduction of IIIa with ferrous sulfate gave the required amino acid (IIIb).



I II IIIa. R = $—NO_2$
b. R = $—NH_2$

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[1] The author is pleased to acknowledge the financial assistance provided by the Coe Research Fund of the University of Maine.

(2) J. N. Ashley, W. H. Perkin, Jr., and R. Robinson, *J. Chem. Soc.*, 382 (1930).

(3) The corresponding phenol, 6-nitrosalicylaldehyde, which was obtained in 3% yield, was shown to be steam volatile and therefore the product of *p*-formylation was excluded as a possible structure. After completion of the present investigation, it was found that additional experimental evidence favoring the 6-nitrosalicylaldehyde structure has been presented by H. Shirai and N. Oda, *Bull. Nagoya City Univ. Pharm. School* No. 4, 30 (1956); *Chem. Abstr.*, **51**, 9522 (1957).

(4) O. L. Brady and A. Taylor, *J. Chem. Soc.*, **117**, 876 (1920).

(5) K. G. Blaikie and W. H. Perkin, Jr., *J. Chem. Soc.*, **125**, 296 (1924).

(6) W. H. Hartford and M. Darrin have recently reviewed the Étard reaction: *Chem. Revs.*, **58**, 1 (1958).

(7) *Cf.*, M. Pailer, A. Schleppnik, and A. Meller, *Monatsh. Chem.*, **89**, 211 (1958).

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