dried over Na_2SO_4, filtered and concentrated *in vacuo* to the point of crystallization. The flask was warmed to redissolve the crystals, petroleum ether was added, and the flask placed in the ice box overnight. The precipitate of soft needles was filtered and washed with petroleum ether. The yield was 3.3 g. (73%) and it melted at 86–87°. After recrystallization from 75% ethyl alcohol and drying *in vacuo* the melting point was unchanged.

Anal. Calcd. for $C_{23}H_{28}O_5N_2$: C, 66.97; H, 6.84; N, 6.79. Found: C, 66.91; H, 7.06; N, 6.79.

γ-Aminobutyryl-γ-aminobutyric acid. To a solution of 2.1 g. (0.0051 mole) of *N*-carbobenzoxy-γ-aminobutyryl-γ-aminobutyric acid benzyl ester in 35 ml. of methyl alcohol were added 2 drops of glacial acetic acid and 0.7 g. of Palladium black catalyst (Fisher Scientific Co.). Hydrogen gas was bubbled through and after 2 hr., 20 ml. of H_2O were added and the hydrogenation continued for an additional 3 hr. The catalyst was removed by filtration and washed with a small volume of water. The filtrate was concentrated *in vacuo* to a crystalline residue. The solid was recrystallized from absolute ethyl alcohol. The yield was 0.75 g. (79%). Dried *in vacuo* at 80–81° it melted at 178–179°. Another crop (0.2 g.) was recovered from the filtrate. Recrystallized from water–ethyl alcohol it melted at 177–178°. The total yield was practically quantitative.

Anal. Calcd. for $C_8H_{16}O_3N_2$: C, 51.04; H, 8.57; N, 14.88. Found: C, 50.89; H, 8.56; N, 14.76.

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A Convenient Synthesis of Cyclohexyl Methyl Ketone and Cyclohexylmethylcarbinol

WILLIAM K. JOHNSON

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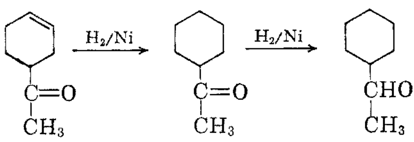
The preparation of a sizable quantity of vinylcyclohexane from cyclohexylmethylcarbinyl acetate[1] required that cyclohexylmethylcarbinol (III) be readily available. This alcohol has been previously prepared by several routes including the reaction of the cyclohexyl Grignard reagent with acetaldehyde,[2,3] the sodium and alcohol reduction of cyclohexen-1-yl methyl ketone[4] and the catalytic hydrogenation of acetophenone.[3,5] The latter method seemed to be the only reported route to III which might be particularly well suited to rather large scale laboratory operation. An investigation of the hydrogenation of acetophenone substantiated the observations of others[3,5] that the hydrogenation of acetophenone is very sensitive to poisons, and the reaction conditions must be controlled extremely carefully. A search for an alternate reliable method of preparing quantities of cyclohexylmethylcarbinol resulted in the development of a procedure based on the Diels-Alder adduct (I) of methyl vinyl ketone and butadiene-1,3.[6] The hydrogenation of I over W-4 Raney nickel was accomplished in two distinct steps, the first being the highly exothermic hydrogenation (25° at 200 p.s.i.g. H_2) of I to cyclohexyl methyl ketone (II) which is further reduced to III under somewhat more strenuous conditions (120° at 1500 p.s.i.g. H_2). The hydrogenation of I to III without isolation of II furnished III in 96% yield. II may also be reduced to III with lithium aluminum hydride, the acetate being isolated to 90% yield.



I II III

EXPERIMENTAL

Cyclohexen-3-yl methyl ketone (I). Equimolar amounts (5.3 moles) of butadiene-1,3 and methyl vinyl ketone[7] were heated at 140° in a sealed reactor during 9 hr. as described by Petrov.[6] The reaction temperature must be approached with caution as in several runs an uncontrollable exothermic reaction was observed. Distillation furnished a 90% yield of ketone; b.p. 78–80° (20 mm.), n_D^{25} 1.4662 [reported b.p. 79.5–80° (20 mm.),[6] n_D^{20} 1.4698[6]].

Cyclohexyl methyl ketone (II). A mixture of I (620 g.; 5 moles) and about 5 g. of W-4 Raney nickel catalyst[8] was treated with hydrogen at 150–200 p.s.i.g. The temperature of the reaction mixture was initially 25° and increased to 60° during 30 min. at which point no further hydrogen was consumed. Distillation furnished 569 g. (89% yield) of II, b.p. 73–74° (17 mm.), n_D^{25} 1.4494 [reported b.p. 72° (18 mm.)[3], $n_D^{25.9}$ 1.44955[3]]. The semicarbazone, after recrystallization from methanol, melted at 177° which is in agreement with the literature value.[4]

Cyclohexylmethylcarbinol (III). A mixture of I (540 g.; 4.35 moles) and about 5 g. of W-4 Raney nickel catalyst in a rocking autoclave pressurized with hydrogen to 900 p.s.i.g. was hydrogenated to II as described above. The temperature of the reaction mixture rose from 20° to 63° in 10 min. and then slowly dropped. Hydrogen was then added until the pressure within the system was 1500 p.s.i.g., and the system heated by an external heater to 120°. By maintaining the hydrogen pressure at about 1500 p.s.i.g. by repressurizations, the hydrogenation of the carbonyl was completed in 1 hr. Distillation furnished 527 g. (96% yield) of alcohol b.p. 85–87° (17 mm.); n_D^{25} 1.4639 [reported b.p. 189.4–189.8°

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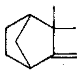
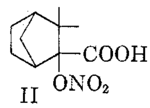
The addition of dinitrogen pentoxide to several simple olefins to produce 1,2-nitronitrates and α- and β-nitro-olefins has been reported.[1] In connection with this study and with the investigation of the dinitrogen tetroxide–camphene reaction,[2] the addition of dinitrogen pentoxide to camphene (I)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


I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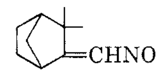
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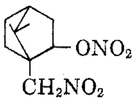
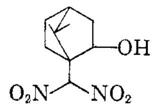
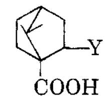

IV


V


VIa. Y = ONO_2
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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(6) Ref. 4, pp. 334, 335.

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(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.