# An Improved Synthesis for the Isomeric 2,3-Dimethylnorbornanes

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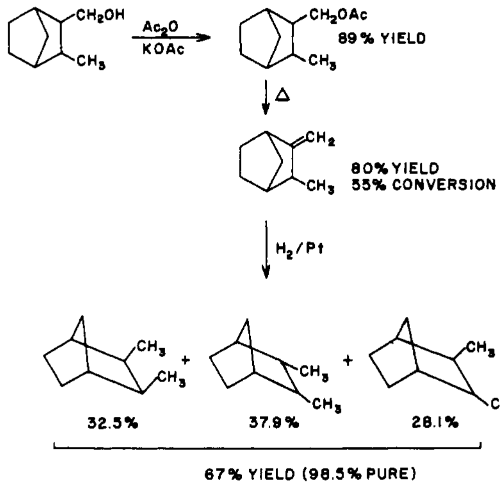
**2-Methyl-3-hydroxymethylnorbornane was converted by acetic anhydride-potassium acetate to 2-methyl-3-acetoxymethylnorbornane (I) in 89% yield. (I) was pyrolyzed at 467° C. to yield a mixture of the *exo-* and *endo*-2-methyl-3-methylenenorbornanes (II) in 80% yield, 55% conversion. (II) was hydrogenated over $PtO_2$ to yield a mixture of the isomeric 2,3-dimethylnorbornanes (III) in 67% yield. The isomers of (III) were separated cleanly by gas chromatography to yield the *trans* isomer (28.1%), *exo-cis* isomer (32.5%), and the *endo-cis* isomer (37.9%).**

THE FOLLOWING REACTION SEQUENCE, proceeding from readily available 3-methylnorcamphane-2-methanol (Eastman Kodak Co.), yielded a mixture of the isomeric 2,3-dimethylnorbornanes in 48% yield. The isomers were cleanly separated by vapor phase chromatography.



Previous methods for preparation of the desired isomeric hydrocarbons either involved many steps, tedious separations, or proceeded from relatively scarce starting materials (*1, 7*).

## EXPERIMENTAL

**2-Methyl-3-Acetoxymethylnorbornane.** The general method of preparation has been described (*8*). Anhydrous potassium acetate (294 grams, 3 moles) was added to a stirred mixture of 2-methyl-3-hydroxymethylnorbornane ($n_D^{20}$ = 1.4802; 420 grams, 3 moles) and acetic anhydride (378 grams, 3.8 moles) in a dry atmosphere. The temperature of the mixture rose to 120° C. during 15 minutes. After 1.25 hours, the temperature of the thick slurry had dropped to 63° C. Water (450 ml.) was added with stirring to dissolve the solids. The organic layer was extracted with ether and washed with several portions of a saturated salt solution. The organic phase was then stirred vigorously with a $4M K_2CO_3$ solution (200 ml.) for an hour. The organic layer was washed with a saturated salt solution until the aqueous phase was neutral. The organic phase was dried over $MgSO_4$, filtered and evaporated at 50° C. and 20 mm. of Hg to yield 532 grams of oil. The oil was distilled through a 10-inch Vigreux column to yield 2-methyl-3-acetoxymethylnorbornane (487 grams, 89% yield), boiling point = 89.5–92° C. at 7 mm. of Hg, $n_D^{20}$ = 1.4610 (literature (*3*) boiling point = 100–102° C. at 12 mm. of Hg).

Analysis for $C_{11}H_{18}O_2$: Calculated: C, 72.5; H, 9.9: Found: C, 72.8, H, 10.2.

**2-Methyl-3-Methylenenorbornane.** PREPARATION OF THE PYROLYSIS COLUMN. A 96% silica column (1-inch outer diameter, 15 inches long) packed with ⅛-inch helices with a total free volume of 110 ml. was filled with a dilute $K_2CO_3$ solution and was allowed to stand for several days. The column was washed thoroughly with water and finally with distilled water until the aqueous washings were neutral. The column was rinsed with several portions of acetone and was purged with nitrogen at 350° to 400° C. until the packing was thoroughly dry.

PYROLYSIS OF THE ACETATE. The pyrolyses of 2,3-bisacetoxymethylnorbornane has been described (*4*). 2-Methyl-3-acetoxymethylnorbornane (36.4 grams, 0.2 mole) was added dropwise to the pyrolysis column at 467° C. (furnace length = 13 inches) at a rate of 0.2 grams per minute with a nitrogen flow of 21 ml. per minute. The condensate was collected in a receiver immersed in an ice water bath. After the addition was complete, the column was allowed to cool, was rinsed with ether (100 ml.) and the ether washings added to the condensate. The ether solution was washed successively with a saturated salt solution, a saturated $NaHCO_3$ solution until the aqueous phase was basic and finally with salt solution until neutral. The organic phase was dried over $MgSO_4$, filtered, and the ether was distilled at atmospheric pressure to yield a liquid. The liquid was distilled through a 6-inch Vigreux column to yield 2-methyl-3-methylenenorbornane (13.4 grams, 55% conversion, 80% yield); boiling point = 47–52° C. at 28 mm. of Hg, $n_D^{20}$ = 1.4709, [reported (*5*): boiling point = 139–141° C. $n_D^{20}$ = 1.4709 for the *exo*-methyl derivative and boiling point = 141–143° C.; $n_D^{20}$ = 1.4708 for the *endo*-methyl derivative]. The gas chromatogram (Perkin-Elmer gas chromatograph, Model 154B) of the product on a 6-foot column of 10% Squalane (Mann Research Laboratories, Inc.) on 38–50 mesh Chromosorb W (94° C. 95 cc. of He per minute) had 13 peaks. Two of the peaks with a combined total area of 93% had retention times of 12 minutes (53%) and 13 minutes (40%). A sample was collected at each of the two main peaks. The infrared spectra (Perkin-Elmer infrared spectrophotometer, Model 21, sodium chloride optics) had characteristic $\alpha$-olefin absorptions at 3070–3080 cm.$^{1}$ (C—H stretch), 870–875 cm.$^{-1}$ (C—H out of plane deformation), and 1660–1670 cm.$^{-1}$ (C=C stretch) (*6*). The liquid residue from the distillation of the olefin was 2-methyl-3-acetoxymethylnorbornane (9.0 grams, 25% recovery). The infrared spectrum and vapor phase chromatogram were identical with those of an authentic sample.

**2,3-Dimethylnorbornane.** A solution of 2-methyl-3-methylenenorbornane (12.5 grams, 0.1 mole) in hexane (40 ml.) was hydrogenated at 25° C. and 24–31 p.s.i.g. with platinum oxide (0.1 gram) in a Parr hydrogenator. Hydrogen (78% of the theoretical amount) was taken up during 0.75 hour. The catalyst was removed by filtration. The liquid was fractionated in a 6-inch Vigreux column to yield 2,3-dimethylnorbornane (8.6 grams, 67% yield); boiling point = 130–145° C.; $n_D^{20}$ = 1.4588 (reported (*2*): boiling point for *trans* form = 41° C. at 20 mm. of Hg, $n_D^{20}$ = 1.4512; for *endo-cis* form boiling point = 50.5° C. at 20 mm. of Hg, $n_D^{20}$ = 1.4643; for *exo-cis* form boiling point = 53° C. at 25 mm. of Hg, $n_D^{20}$ = 1.4596). The gas chromatogram on a 6-foot column of 10% Squalane on 35–80 mesh Chromosorb W (97° C.; 95 cc. of He per minute) had six peaks. Three of the peaks had a combined total area of 98.5%. Peak 3 had a retention time of 10.7 minutes (28.1%). Peak 4 had a retention time of 14.4 minutes (32.5%) and peak 5 had a retention time of 16.2 minutes (37.9%). A sample was collected at each of the peaks. The infrared spectrum of peak 3 was identical with that of authentic *trans*-2,3-dimethylnorbornane, that of peak 4 was identical with that of authentic *exo-cis*-2,3-dimethylnorbornane, and that of peak 5 was identical with that of authentic *endo-cis*-2,3-dimethylnorbornane (*1*).

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# Cyanoethyl Esters of Halocarboxylic Acids

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THE 2-CYANOETHYL TRICHLOROACETATE was reported recently (*1*) to be a selective herbicide. This note concerns some additional esters of ethylene cyanohydrin with halogen-containing carboxylic acids which also possess varying degrees of herbicidal activity. An analogous product, 2-cyanoethyl $\alpha$-chloroacrylate, was reported earlier (*2*) but no indication of its biological activity was given.

The esters described in the table were prepared by direct esterification of the acid (A), transesterification of an ethyl ester (B), acid chloride-pyridine method (C) and chlorination of an unsaturated acid (D).

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(2) Lichty, J., (to Wingfoot Corp.), U.S. Patent **2,322,035** (1943).

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Table I. 2-Cyanoethyl Esters of Halocarboxylic Acids, $RCO_2CH_2CH_2CN$

| | | Yield, | | | | | Calcd., % | | | Found, % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| R | Formula | % | % B.P.$^a$/mm. | | $n_D^{30}$ | $D_{20}^{20}$ | C | H | N | C | H | N |
| $Cl_3C$-$^d$ | $C_5H_4NO_2Cl_3$ | 43 | 99 | 0.5 | 1.4758 | 1.4774 | 27.7 | 1.8 | 6.5 | 27.9 | 1.8 | 6.3 |
| $Cl_2HC$-$^f$ | $C_5H_5NO_2Cl_2$ | 19 | 128 | 6 | 1.4673 | 1.3831 | 33.0 | 2.7 | 7.7 | 33.4 | 2.7 | 7.4$^{b'}$ |
| $ClH_2C$-$^e$ | $C_5H_6NO_2Cl$ | 64 | 123 | 3.5 | 1.4527 | 1.2582 | 40.7 | 4.1 | 9.5$^c$ | 40.9 | 4.7 | 9.1$^{c'}$ |
| $BrH_2C$-$^e$ | $C_5H_6NO_2Br$ | 79 | 133 | 5 | 1.4760 | 1.5740 | 31.3 | 3.1 | 7.3 | 31.9 | 3.2 | 7.7 |
| $CH_3CCl_2$-$^d$ | $C_6H_7NO_2Cl_2$ | 20 | 92 | 1 | 1.4570 | | 36.7 | 3.6 | 7.1 | 37.3 | 3.8 | 7.0 |
| $ClCH_2CHCl$-$^g$ | $C_6H_7NO_2Cl_2$ | 92 | Residue | | 1.4730 | 1.3484 | 36.9 | 3.6 | 7.1 | 36.9 | 3.6 | 7.0 |
| $ClCH_2(CH_2)_4$-$^e$ | $C_9H_{14}NO_2Cl$ | 79 | 165 | 5.5 | 1.4564 | 1.1096 | 53.0 | 6.9 | 6.9 | 53.2 | 6.9 | 7.0 |
| p-Cl-$C_6H_4$-$^e$ | $C_{10}H_8NO_2Cl$ | 55 | 160 | 4 | m.p. 41° | | 57.3 | 3.8 | 6.7 | 56.8 | 3.8 | 7.1 |
| $Cl_2C_6H_{10}$-$^g$ | $C_{10}H_{13}NO_2Cl_2$ | 63 | Residue | | 1.5010 | 1.2422 | 48.0 | 5.2 | 5.6 | 48.5 | 5.6 | 5.2 |
| $Cl_2C_6H_5$-$OCH_2$-$^e$ | $C_{11}H_9NO_3Cl_2$ | 98 | | | m.p. 91–94° | | 48.2 | 3.3 | 5.1 | 48.4 | 3.0 | 5.4 |
| $Cl_2C_6H_3$-$O(CH_2)_3$-$^e$ | $C_{13}H_{13}NO_3Cl_2$ | 98 | Residue | | 1.5269 | | 51.6 | 4.3 | 4.6 | 51.7 | 4.2 | 5.1 |
| $CH_3(CH_2)_7CH$-$ClCHCl(CH_2)_7$-$^g$ | $C_{21}H_{37}NO_2Cl_2$ | 86 | Residue | | 1.4853 | 0.9330 | | | 3.4 | | | 2.9 |

$^a$All temperatures are uncorrected. $^b$%Cl = 37.9. $^{b'}$% Cl = 37.9. $^c$%Cl = 24.0. $^{c'}$%Cl = 24.4. $^d$By Method A. $^e$By Method B. $^f$By Method C. $^g$By Method D.