Studies in the Norbornane Series. I. A Simple Stereospecific Synthesis of *exo*-2-Norbornyl Methyl Ketone

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The first sterically unequivocal synthesis of *exo*-2-norbornyl methyl ketone has been described by Berson.[1] The procedure consists of five steps and is too lengthy for preparations on a larger scale. This prompted us to investigate a simpler synthesis whose concept is based on the combination of two already known facts: (1) the free-radical addition of aldehydes to olefins yields ketones,[2,3] (2) the first step of the addition of free radicals or ions to the double bond of norbornene almost exclusively follows the "*exo*" course.[4]

Heating the commercially available norbornene with acetaldehyde at 80° for 40 hr. in presence of 0.02 mole of azobisisobutyronitrile[5] yielded 80% *exo*-norbornyl methyl ketone. The *exo* configuration of the ketone was proven by checking its refractive index and the melting point and mixture melting point of its semicarbazone and also by converting the ketone into *exo*-norborneol by reaction with perbenzoic acid. It had been shown previously[6] that the Baeyer–Villiger oxidation proceeds without change of configuration.

The steric uniformity of the ketone was demonstrated by the fact that the semicarbazone of the correct melting point was formed in 96% yield.

Experimental[7]

***exo*-Norbornyl Methyl Ketone.**—Freshly distilled norbornene (47.0 g., 0.5 mole) was dissolved in 132 g. of freshly distilled acetaldehyde containing 0.01 mole of azobisisobutyronitrile. The mixture was heated in an autoclave at 80° for 40 hr. After removing most of the unchanged acetaldehyde at atmospheric pressure the remainder was distilled *in vacuo* to yield 56.7 g. of *exo*-norbornyl methyl ketone, b.p. 79–81° (15 mm.), lit.[1] b.p. 87° (19 mm.), and an unidentified high-boiling residue. The ketone which had $n^{24}\text{D}$ 1.4709, lit.[1] $n^{25}\text{D}$ 1.4710, formed a semicarbazone in 96% yield, m.p. 181.5–182.5°, lit.[1] m.p. 182–183°. The semicarbazone gave no melting point depression upon admixture with a semicarbazone, prepared from authentic *exo* ketone[1]; admixture with authentic *endo* semicarbazone,[1] m.p. 179–180°, resulted in a melting point depression of about 10°. Following the procedure already reported,[1] the *exo* ketone was converted into *exo*-norborneol, m.p. 126–127°; dinitrobenzoate, m.p. 104°.

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[1] J. A. Berson and S. Suzuki, *J. Am. Chem. Soc.*, **81**, 4088 (1959).

[2] M. S. Kharasch, W. H. Urry, and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

[3] K. Ziegler, *Brennstoff-Chem.*, **30**, 181 (1949).

[4] See among others: (a) K. Alder and K. Backendorf, *Ann.*, **535**, 106 (1938); (b) G. Stork, E. E. Van Tamelen, L. J. Friedman and A. W. Burgstahler, *J. Am. Chem. Soc.*, **75**, 384 (1953); (c) L. Kaplan, H. Kwart, and P. von R. Schleyer, *ibid.*, **82**, 2341 (1960); (d) W Reusch, *J. Org. Chem.*, **27**, 1882 (1962).

[5] It should be noted that *replacement of this initiator by other free-radical sources of peroxidic nature drastically reduces the amount of ketone formed in the present case.* Some reasons for this are given in ref. 2 and 3.

[6] R. B. Turner, *J. Am. Chem. Soc.*, **72**, 878 (1950); *cf.* also ref. 1

[7] Melting points were determined using the Kofler hot-stage apparatus.

A 1,3,5-Dioxazine

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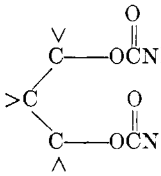
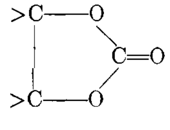
In a recent publication, we described an improved method of synthesis of carbamates of alcohols, thiols, phenols, and oximes using a procedure that involves simply stirring a mixture of the alcohol, thiol or oxime, sodium cyanate, trifluoroacetic acid, and a solvent for a brief period.[1] When this reaction was applied to 1,3-glycols, the biscarbamate (I) was formed; when applied to 1,2-glycols, the cyclic carbonate (II) was the major product.

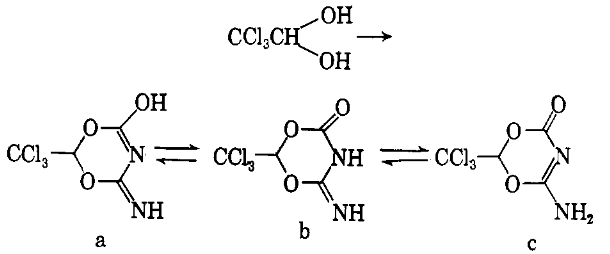


I



II

We now wish to report a novel product prepared by the reaction of a 1,1-glycol, chloral hydrate, under the same reaction conditions. This product, assigned the tautomeric substituted 1,3,5-dioxazine structures (III)



III

is a high-melting, water-insoluble, tasteless crystalline solid—in sharp contrast to the starting material, chloral hydrate, a low-melting, hygroscopic, bitter, amorphous solid. The compound is insoluble in aqueous acid, soluble in and decomposed by aqueous base, and insoluble in most of the ordinary organic solvents other than alcohols. It could not be catalytically reduced with platinum or palladium catalysts at 50 p.s.i.g.

The near-infrared absorption spectra[2] support the assigned structure and suggest that it is mainly in the form IIIb. The n.m.r.[2] shows only a single tertiary C–H; the compound does not absorb in the ultraviolet region (220 to 230 mμ).

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[1] B. Loev and M. F. Kormendy, *J. Org. Chem.*, **28**, 3421 (1963).

[2] We are indebted to Dr. W. Thompson and R. Warren for running these spectra for us. N.m.r. spectra were measured at 60 Mc. on a Varian Associates Model A-60 spectrophotometer, in perdeuteriomethanol solution. Chemical shifts are given with reference to tetramethylsilane. The near-infrared spectra were determined as a mineral oil mull on a Perkin-Elmer Model 137-G.