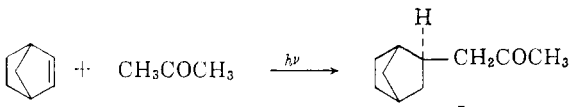
apparent.[2] Thus, direct addition yielding substituted trimethylene oxides,[1,3] allylic addition to give unsaturated carbinols,[4] olefin addition at the α-carbon,[4] and a unique *trans* addition resulting in a saturated 1,4-diol[4] have all been observed.

Norbornylene is an attractive substrate for further investigations in this area because of the presence of a highly reactive double bond and the adsence of activated allylic hydrogen atoms. When an 8% acetone solution of norbornylene was irradiated at reflux for forty-eight hours and subsequently fractionated at reduced pressures, a 45% yield of a sweet smelling, colorless liquid (I) was obtained. This material was characterized by a strong absorption at 5.86 μ in the infrared, a single effluent fraction from a 6-ft 30% silicone column at 190° and two crystalline carbonyl derivatives. Compound I gave a positive iodoform test and was oxidized by chromic acid mixtures or fuming nitric acid to a difficultly separable mixture of organic acids, of which the major component (75%) is 2-exonorbornylcarboxylic acid. The minor acidic component is probably 2-exonorbornylacetic acid, since the retention time of the corresponding methyl ester was identical with that observed for the methyl ester of the acid produced by the haloform reaction of I. The apparent absence of the stereoisomeric 2-endonorbornylcarboxylic acid from the oxidation products[5] suggests that the addition of acetone has been stereospecific, a conclusion buttressed by the nearly quantitative yield (93%) in which the semicarbazone of I is formed.



I

Reflux of acetone solutions of norbornylene in the dark produced no observable change in fifty hours; however, poor yields of I may be obtained if α,α'-azobisisobutyronitrile is added. It thus appears that the photochemical reaction reported here proceeds by chain addition of acetonyl radicals to norbornylene, a process analogous to the addition of cyclohexanone to 1-octene[6] and to cyclohexene.[4]

Experimental

2-*exo*-Acetonylnorbornane (I).—A solution of norbornylene[7] (10 g.) in dry acetone (120 ml.) was irradiated[8] at reflux for 48 hr. The crude organic products were fractionated at reduced pressure to give 5.6 g. (40%) of I, b.p. 94–96°/12 mm., which proved to be homogeneous with respect to vapor phase chromatography on a 6-ft. 30% silicone column at 190°. The forerun (2.1 g.) contained 50% volatile impurities[7] in addition to I.

A semicarbazone, m.p. 194–195° (from methanol), was prepared in excellent yield from I.

Anal.[9] Calcd. for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15; N, 20.09. Found: C, 62.94; H, 9.06; N, 19.95.

The 2-4-dinitrophenylhydrazone of I was crystallized from methanol, m.p. 138–140°.

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07. Found: C, 58.07; H, 6.21.

Oxidative Degradation of I.—Compound I (1.0 g.) was oxidized by a refluxing solution of sodium dichromate (5 g.) in acetic acid (8 ml.) for a 4-hr. period. Extraction in the usual manner gave 400 mg. of recovered I and 250 mg. of semicrystalline acidic material.

A similar oxidation employing an acetic acid solution of fuming nitric acid at steam bath temperatures followed by alkaline permanganate treatment of the crude organic product gave excellent yields of the same acidic material.

Analysis of this acid mixture by vapor phase chromatography indicated it consisted of 75% 2-norbornylcarboxylic acids and 25% of an unknown acid having a greater retention time. Analysis of the corresponding methyl esters confirmed the former assignment and proved both components to be unresolvable by a variety of stationary phases. Furthermore, the infrared spectrum of the methyl ester of the major component was identical with that of known methyl 2-*exo*-norbornylcarboxylate and differed in two respects from the spectrum of the endo isomer.

The crude acid mixture was converted to a low melting *p*-bromophenacyl ester that improved upon several recrystallizations to a point where it was identical with the corresponding derivative (m.p. 91–93°) from a known sample of 2-*exo*-norbornylcarboxylic acid.

A chilled solution of I (1.0 g.) in dioxane (4 ml.) was treated with a cold alkaline bromine solution. The mixture was stirred overnight and, after removing the bromoform, the aqueous portion yielded 800 mg. of a viscous acidic oil. A portion of this oil was converted to a methyl ester which proved to have a retention time identical to that of the methyl ester of the minor acidic oxidation product on the 30% silicone column.

(2) P. de Mayo, "Advances in Organic Chemistry," Interscience, Inc., Vol. II, p. 367 (1960).

(3) G. Buchi, C. G. Inman, and E. Lipinsky, *J. Am. Chem. Soc.*, **76**, 4327 (1954).

(4) P. de Mayo, J. B. Stothers, and W. Templeton, *Can. J. Chem.*, **39**, 488 (1961).

(5) Samples of the *endo* isomer are recovered unchanged from the acidic oxidizing mixtures used to degrade I.

(6) M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **18**, 1225 (1953).

(7) The redistilled norbornylene used in this work was found to contain 15% higher boiling impurities, which pass through the irradiation process unchanged and are easily separated from the products by fractional distillation.

(8) A Pyrex flask containing the solution was suspended 2 in. over a Hanovia type SH mercury lamp.

(9) Spang Microanalytical Laboratory, Ann Arbor, Mich.

Synthesis of 1-Methylbicyclo[3.1.1]heptan-6-one[1]

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During the course of a recent study of the alkali-induced reactions of cyclohexadienones, derived

(1) This work was supported by a research grant from the National Science Foundation.

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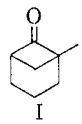
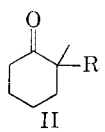
from Reimer-Tiemann reactions,[3] bicyclic four-membered ring ketones were encountered whose curious lability in base was noted. Since the infrequently observed base-catalyzed solvolytic ring cleavage of cyclobutanones is of theoretical interest, especially with regard to the direction as well as stereochemistry of ring scission, the study of the chemical behavior of a simple, but unsymmetrical ketone became of importance. 1-Methylbicyclo-[3.1.1]heptane-6-one (I) was chosen as the model compound and its synthesis attempted.



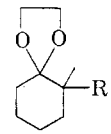
I

2-Methyl-2-cyanocyclohexanone (IIa)[4] was converted to its ethylene ketal IIIa and reduced with lithium aluminum hydride to the amino ketal IIIb. Treatment of the latter with benzenesulfonyl chloride and aqueous base and hydrolysis with aqueous acid afforded a crystalline ketosulfonamide IIb, while alkylation of IIIb with methyl iodide and sodium carbonate in alcohol and acid hydrolysis yielded the ketamine IIc. Exposure of the latter's crystalline methiodide IId to bases under a variety of conditions failed to extrude trimethylamine and yield the desired ketone I, but, at best, merely demethylated the salt back to its amino precursor IIc. As a consequence, a variation of this reaction sequence was tried.



II

a. R = CN
b. R = $CH_2NHSO_2C_6H_5$
c. R = $CH_2N(CH_3)_2$
d. R = $CH_2\overset{+}{N}(CH_3)_3$, $I^{\ominus}$
e. R = $CO_2C_2H_5$
f. R = $CH_2OSO_2C_6H_5$



III

a. R = CN
b. R = CH_2NH_2
c. R = $CO_2C_2H_5$
d. R = CH_2OH

2-Methyl-2-carbethoxycyclohexanone (IIc)[5] was converted to its ethylene ketal IIIc and reduced with lithium aluminum hydride to the alcohol IIId. Treatment of the latter with benzenesulfonyl chloride and pyridine and hydrolysis with aqueous acid led to a crystalline ketosulfonate IIf. Exposure of the latter to sodium hydroxide in aqueous methanol afforded the sought-after cyclobutanone I.

Experimental

2-Methyl-2-cyanocyclohexanone Ethylene Ketal (IIIa).—A solution of 26.0 g. of 2-methyl-2-cyanocyclohexanone (IIa), b.p. 99–101°/15 mm. (lit.,[4] b.p. 94°/13 mm.), 5 mg. of *p*-toluenesulfonic acid, and 50 ml. of ethylene glycol in 500 ml. of sodium-dried benzene was refluxed for 16 hr. in the presence of a water separator. The benzene solution was extracted with 5% sodium hydroxide solution and the aqueous extract extracted with ether. Upon evaporation of the benzene solution nearly to dryness, the residue was distributed between ether and water. The combined ether extracts were dried over anhydrous sodium sulfate, the solvent evaporated, and the residue distilled. Pure liquid ketal IIIa, 18.7 g., b.p. 116–117°/7 mm., infrared spectrum (chloroform): 8.40 (s) and 9.13 (s)μ, was obtained.

Anal. Calcd. for $C_{10}H_{15}O_2N$: C, 66.27; H, 8.34; N, 7.73 Found: C, 65.96; H, 8.18; N, 7.84.

2-Methyl-2-aminomethylcyclohexanone Ethylene Ketal (IIIb).—A solution of 4.0 g. of the cyano ketal IIIa in 40 ml. of ether was added slowly to a stirring cooled suspension of 3.0 g. of lithium aluminum hydride in 150 ml. of ether and the mixture refluxed for 4 hr. The excess hydride was decomposed by the slow addition of a slurry of sodium sulfate saturated with water. The ether solution was decanted and dried over anhydrous sodium sulfate. Evaporation of the solvent and distillation of the residue gave 3.6 g. of the amino ketal IIIb, b.p. 111–113°/8 mm., infrared spectrum (chloroform): 8.50 (m), 9.15 (s), 10.50 (m)μ.

Anal. Calcd. for $C_{10}H_{19}O_2N$: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.57; H, 10.29; N, 7.57.

A mixture of 0.50 g. of the amino ketal and 15 ml. of 10% sodium hydroxide was treated with 1.0 ml. of benzenesulfonyl chloride, stirred and heated on a steam bath for 30 min. The basic solution was extracted with ether, acidified with concd. hydrochloric acid and heated on a steam bath for 30 min. The aqueous mixture was extracted with ether and the extract dried over anhydrous sodium sulfate. Evaporation of the solvent and crystallization of the residue from aqueous ethanol gave 0.52 g. of a solid, m.p. 102–104°. Recrystallization from aqueous ethanol afforded the sulfonamide IIb, m.p. 106–107°, infrared spectrum (chloroform): 5.88 (s), 8.60 (s)μ.

Anal. Calcd. for $C_{14}H_{19}O_3NS$: C, 59.76; H, 6.81; N, 4.98. Found: C, 59.74; H, 6.97; N, 4.98.

2-Methyl-2-dimethylaminomethylcyclohexanone (IIc).—A solution of 13 g. of methyl iodide in 50 ml. of 95% ethanol was added dropwise to a stirring suspension of 20 g. of sodium carbonate in 17.3 g. of the amino ketal IIIb and 400 ml. of 95% ethanol. The mixture was refluxed for 1 hr. Another solution of 13 g. of methyl iodide in 50 ml. of 95% ethanol was added and the refluxing continued for 8 hr. The solvent was removed under vacuum and the residue extracted with ether and water. The ether extract was dried over sodium sulfate, evaporated, and the residue distilled. This led to 13.6 g. of crude dimethylamino ketal, b.p. 105–110°/7 mm. A solution of the product in 100 ml. of 10% hydrochloric acid solution was heated on the steam bath for 30 min. The solution was made alkaline with sodium hydroxide, extracted with ether, and the extract dried over sodium sulfate. Evaporation of the solvent yielded crude ketonic product, which was dissolved in 40 ml. of pyridine and 80 ml. of benzene and treated with 5 ml. of benzoyl chloride. After being heated on the steam bath for 30 min., the solution was evaporated under vacuum nearly to dryness. Dilute sodium hydroxide solution was added to the residue and the mixture extracted with ether. The desired fully *N*-methylated ketone was extracted from the ether solution into 5% hydrochloric acid solution. The latter was made alkaline with sodium hydroxide and extracted with ether. The extract was dried over sodium sulfate, the solvent evaporated, and the residue distilled. This led to 3.9 g. of the ketone IIc, b.p. 86–87°/7 mm., infrared spectrum (chloroform): 5.85 (s)μ.

Anal. Calcd. for $C_{10}H_{19}ON$: C, 70.90; H, 11.32; N, 8.28. Found: C, 70.94; H, 11.02; N, 8.09.

A solution of 0.57 g. of the amino ketone IIc and 10 ml. of methyl iodide in 5 ml. of ether was allowed to stand at room temperature for 12 hr. Filtration of the resulting

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(4) K. von Auwers, T. Bahr, and E. Frese, *Ann.*, **441**, 61 (1925).

(5) M. Yanagita, S. Inayama, and R. Kitagawa, *J. Org. Chem.*, **21**, 612 (1956).

crystalline precipitate and crystallization from absolute ethanol yielded 0.76 g. of the methiodide IId, m.p. 202–204°.

Anal. Calcd. for $C_{11}H_{22}ONI$: C, 42.45; H, 7.13; N, 4.50. Found: C, 42.53; H, 7.14; N, 4.54.

Treatment of the Salt IId with Alkali. A.—An intimate mixture of 300 mg. of the salt IId and 1.0 g. of sodium carbonate was heated at 230° and 7 mm. of pressure for 1 hr. The distillate, collected on a cold finger cooled with Dry Ice–acetone, was dissolved in ether and extracted with 5% hydrochloric acid. The ether solution contained no appreciable quantity of solute. The aqueous extract was made alkaline with sodium hydroxide and extracted with ether. The organic solution was dried over sodium sulfate, evaporated, and the residue, 135 mg., distilled. The product, 100 mg., proved to be the amino ketone IIc, b.p. 85–95°/7 mm.

Anal. Found: C, 71.29; H, 11.30; N, 8.63.

Its methiodide, prepared as before, m.p. 201–203°, mixed m.p. 202–204°.

B.—A mixture of 311 mg. of the salt IId and silver oxide, freshly prepared from 0.2 g. of silver nitrate, was stirred at room temperature for 45 min. The mixture was filtered, the water removed under vacuum, and the residue heated at 230° and 7 mm. of pressure for 30 min. The distillate on the cold finger was dissolved in ether and extracted with 5% hydrochloric acid. Again, no neutral product was found in the ether solution. The acidic solution was made alkaline with sodium hydroxide and extracted with ether. This organic solution was dried over sodium sulfate and evaporated. The residual oil, 40 mg., was converted to its methiodide, 45 mg., m.p. 197–200°, mixed m.p. 198–201°.

2-Methyl-2-carbethoxycyclohexanone Ethylene Ketal (IIIc).—The above ketalation procedure was repeated with 60.4 g. of the keto ester IIe, b.p. 90–91°/4 mm. (lit.,[5] b.p. 85–86°/3 mm.), 5 mg. of *p*-toluenesulfonic acid, 100 ml. of ethylene glycol, and 750 ml. of benzene. It led to 64.1 g. of the ketal IIIc, b.p. 123–124°/8 mm., infrared spectrum (chloroform): 5.77 (s)μ.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 62.80; H, 9.01.

2-Methyl-2-hydroxymethylcyclohexanone Ethylene Ketal (IIId).—The above hydride reduction procedure was repeated with 64.1 g. of the ketal ester IIIc in 250 ml. of ether and 20 g. of lithium aluminum hydride in 500 ml. of ether. It led to 44.2 g. of the hydroxy ketal, b.p. 114–115°/6 mm., infrared spectrum (chloroform): 2.70 (m), 9.15 (s)μ.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.12; H, 10.00.

2-Methyl-2-*p*-toluenesulfonoxymethylcyclohexanone (IIf).—*p*-Toluenesulfonyl chloride, 47.5 g., was added to a solution of 42.3 g. of hydroxy ketal in 470 ml. of dry pyridine at −5°, the mixture stirred and then allowed to stand at −15° for 13 hr. The mixture was added to 1 l. of water and ice and extracted with chloroform. The organic solution was extracted with 200-ml. portions of ice-cold 20% sulfuric acid, until the extract remained acidic. The chloroform solution then was washed successively with water, dilute sodium bicarbonate solution and water and was dried over anhydrous sodium sulfate. Evaporation of the solvent under vacuum gave 70.5 g. of oily crude ketal tosylate. The latter and 1 ml. of concd. hydrochloric acid were dissolved in 635 ml. of acetone and heated on a steam bath for 2 hr. The residue was taken up in water and extracted with ether. The extract was dried over sodium sulfate and evaporated under vacuum. The oily residue was crystallized from petroleum ether–ether cooled in a Dry Ice–acetone bath. Recrystallization gave 19.7 g. of solid, m.p. 55–58°. The oily residues from the crystallizations were retosylated by the above procedure and yielded 7.6 g. more of the same solid product. Several further crystallizations from petroleum ether–ether afforded the ketotosylate IIf, m.p. 57–59°, infrared spectrum (chloroform): 5.85 (s), 7.37 (s), 8.51 (s) μ.

Anal. Calcd. for $C_{15}H_{20}O_4S$: C, 60.78; H, 6.80; S, 10.82. Found: C, 60.94; H, 7.09; S, 10.87.

1-Methylbicyclo[3.1.1]heptan-6-one (I).—A solution of 5.0 g. of the ketotosylate IIf and 0.73 g. of sodium hydroxide in 250 ml. of 1:1 methanol–water was refluxed for 12 hr. The solution was acidified and extracted with ether. The extract was washed successively with water, 5% sodium bicarbonate, and water and was dried over anhydrous sodium sulfate. Evporation of the solvent and distillation of the residue gave 1.57 g. of crude product which on redistillation yielded 1.17 g. of the bicyclic ketone I, b.p. 79–80°/35 mm., spectra: ultraviolet (95% ethanol), λ_{max} 290 mμ (ϵ 30): infrared (chloroform), 5.66 (s)μ.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.54; H, 9.90.

Preparation of Spiran Ring Systems by Intramolecular Alkylation

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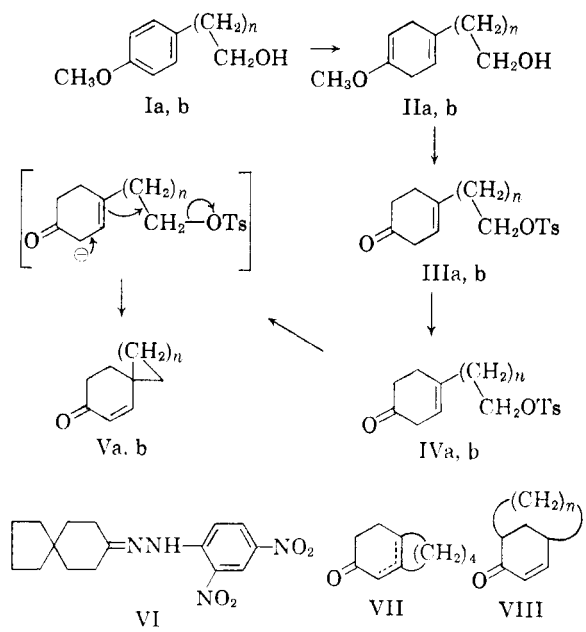
Of the numerous methods for the preparation of carbocyclic spiran ring systems, one of the newer procedures involves intramolecular alkylation. We have prepared the spirans Va and Vb by utilizing an intramolecular alkylation reaction similar to that reported by Winstein and Baird.[2,3]



(1) Department of Chemistry, The Upjohn Company, Kalamazoo, Mich., to whom inquiries should be addressed.

(2) The present work was initiated as an extension of our previous intramolecular alkylations of ketones and esters [N. A. Nelson and G. A. Mortimer, *J. Org. Chem.*, **22**, 1146 (1957)].

(3) S. Winstein and R. Baird, *J. Am. Chem. Soc.*, **79**, 756, 4238 (1957).