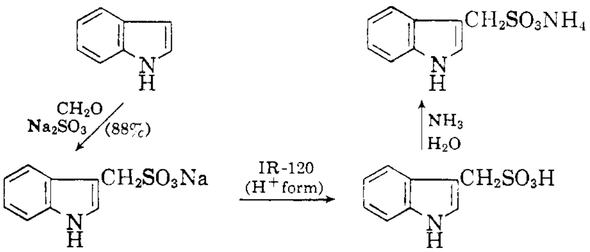
the addition of aqueous ammonia to a solution of the free acid, was found to be comparable in stability to the sodium salt. All efforts to react free 3-indolemethanesulfonic acid or either its sodium or ammonium salt with an alkali cyanide to produce 3-indoleacetonitrile were unsuccessful.



EXPERIMENTAL

Indole (30 g., 0.26 mole) and sodium sulfite (126 g., 1.00 mole) were placed in water (250 ml.) and heated to gentle reflux with stirring. Aqueous formaldehyde (50 ml. 36.2% solution equivalent to 18.1 g. or 0.60 mole) was added and the mixture refluxed gently for 18 hr. The reaction mixture was then cooled and the crystalline precipitate collected by filtration. Several extractions of the product first with ether, then methanol removed the unchanged indole (10 g.). The crystalline residue was dissolved in a minimum amount (800 ml.) of boiling water and saturated sodium bromide solution (200 ml.) added. The resulting solution was cooled to 0–5° and the precipitate of sodium 3-indolemethanesulfonate which formed collected by filtration. After air drying the white crystalline product amounted to 35 g. (0.16 mole, 88% yield at 59% conversion). A second recrystallization from water (300 ml.) and saturated sodium bromide solution (90 ml.) reduced the yield to 29.5 g. (0.13 mole).

Anal. Calcd. for $C_9H_8O_3NSNa$: C, 46.38; H, 3.43; N, 6.01; S, 14.35. Found: C, 46.16; H, 3.86; N, 6.10; S, 14.35.

The Preparation of Diethyl Peroxide. The Use of Dispersing Agents to Increase Yields in Heterogeneous Systems[1]

P. NANGIA AND S. W. BENSON

Chemistry Department, University of Southern California, Los Angeles 7, Calif.

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The difficulties with regard to the preparation of diethyl peroxide have been described by Leadbeater.[2] According to this investigator, the usual yield of "pure" compound obtained after a number of fractionations was about 2–3%. The methods of preparations reported in the literature as also used by Minkoff[3] were employed to prepare this compound needed for kinetic studies. Unfortunately, all attempts using both methods were met with utter failure. With somewhat modified procedural details, we have been able to prepare the pure product in about 28–30% yields. The significant high yield resulted from the use of sodium stearate as a dispersing agent.

Experimental

To a three-neck Pyrex flask (500 ml.), containing 120 ml. of 30% hydrogen peroxide, was added about 50 mg. of sodium stearate dissolved in a few milliliters of distilled water. The flask was kept cool at or below −35° by using a bromobenzene–Dry Ice slush bath (usually, a simple Dry Ice bath proved equally good and handy, and was mostly used in later preparations). A solution of 56 g. of potassium hydroxide dissolved in 60 ml. of distilled water was added dropwise to the flask whose contents were kept stirred during this process. The result was an almost semifluid mass. The flask was transferred to a common salt-ice bath. Ethyl sulfate, 154 g., was added slowly (a few drops at a time, over a period of about 1 hr.), through another inlet tube. The contents became entirely liquid in the course of the addition of the ethyl sulfate. The temperature of the mixture was kept below −10° during the addition. After the addition, the contents were kept stirred overnight (for about 16 hr.) in the ice bath. No attempt was made to study the effect of period of stirring on the yield. The oily layer was extracted with anisole the next day and washed two to three times with distilled water to remove as much alkali as possible. The extract was transferred to a glass-stoppered flask, 1–2 drops of phenolphthalein were added and sulfuric acid (4 *N*) was added dropwise just to the disappearance of pink color. Anhydrous sodium sulfate (Analar grade), 10 g., was added to the extract. After 1 hr. of drying, the contents were vacuum-distilled (pressure = 20 mm.), raising the temperature of the distillation flask slowly to about 60° toward the end of the operation. The receiving set consisted of a series of traps; the first trap cooled in an ice bath could entrap any anisole that distilled, while the peroxide was found in the two successive traps at liquid nitrogen temperature. The peroxide from both the traps was transferred to a 100 ml. round-bottomed flask fitted with a Vigreux column which had a side-water-condenser and a fraction-cutter of four receivers. The product was fractionated using a water bath; the fraction distilling between 62–63° was collected for subsequent analysis. The infrared spectrum of the product was taken on an Infracord (Perkin-Elmer) and it matched with the one reported by Minkoff.[2] The refractive index also agreed with the value reported in the literature, $n^{20}\mathrm{D}$ 1.3698. A yield of 25.6 g. was obtained in one particular trial, and it ranged from 25 to 28 g.

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[1] This work has been supported by a Grant from the Atomic Energy Commission.

[2] R. J. Leadbeater, *Bull. soc. chim. France*, 1285 (1956).

[3] G. J. Minkoff, *Proc. Roy. Society* (London), **A 224**, 176 (1954).

A Stereospecific Photochemical Addition of Acetone to Norbornylene

WILLIAM REUSCH

Kedzie Chemical Laboratory, Michigan State University, East Lansing, Mich.

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Photochemical addition reactions of olefins with carbonyl compounds were reported early in this century,[1] but only in recent years has the scope and variety of these transformations become

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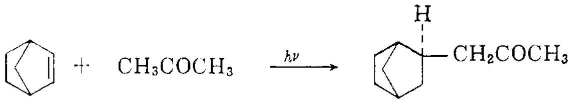
[1] E. Paterno and G. Chieffi, *Gazz. chim. ital.*, **396**, 341 (1909).

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.

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[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]

ERNEST WENKERT[2] AND DONALD P. STRIKE

Department of Chemistry, Iowa State University, Ames, Iowa

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

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[2] Present address: Department of Chemistry, Indiana University, Bloomington, Ind.