drolyzed by the addition of water to the corresponding amides; see L. G. Makarova and A. N. Nesmeyanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 887 (1954); *Chem. Abstr.*, **50,** 5548 (1956).

(5) (a) R. R. Schmidt, W. Schneider, J. Kang, and O. Burkert, *Chem. Ber.*, **103,** 1634 (1972); (b) R. R. Schmidt and W. Schneider, *Tetrahedron Lett.*, 5095 (1970); (c) J. M. Birchall, R. N. Haszeldine, J. N. Kokavouras, and E. S. Wilks, *J. Chem. Soc. C*, 562 (1971); (d) R. C. Petterson, unpublished observations.

(6) (a) The diazotizations of *o*-phenylenediamine to give benzotriazole[6b] and *o*-aminothiophenol to give benzothiadiazole,[6c] respectively, could be considered examples which fit this type of reaction. In these cases, the nitrogen of the diazo group is not lost but instead cyclizes onto the adjacent amino and thiol group, respectively. (b) P. Ladenburg, *Ber.*, **9,** 219 (1876); A. O. Fitton and R. K. Smalley, "Practical Heterocyclic Chemistry," Academic Press, New York, N. Y., 1968, p 47 ff. (c) P. Jacobson, *Ber.*, **21,** 3104 (1888); P. Jacobson and H. Janssen, *Justus Liebigs Ann. Chem.*, **277,** 218 (1893).

(7) N. M. Bikales, U. S. Patent 3,211,718 (1965); *Chem. Abstr.*, **64,** P845*f* (1966).

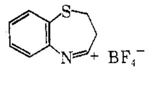
(8) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution NMR Spectra Catalog," Vol. I, Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 191.

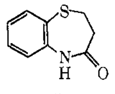
(9) (a) For a detailed discussion and interpretation of the pmr spectra of related 1,2-disubstituted ethane derivatives, see R. C. Hirst and D. M. Grant, *J. Chem. Phys.*, **40,** 1909 (1964); (b) E. O. Bishop in "Nuclear Magnetic Resonance for Organic Chemists," D. W. Mathieson, Ed., Academic Press, New York, N. Y., 1967, Chapter 7, pp 103–127.

(10) For examples of fragmentation patterns of arylthio ethers, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 286 ff.

(11) Summaries of the Baltz–Schiemann reaction have appeared: (a) A. E. Pavlath and A. J. Leffler, "Aromatic Fluorine Compounds," Reinhold, New York, N. Y., 1962; (b) H. Suschitzky, *Advan. Fluorine Chem.*, **4,** 1 (1965); (c) P. Roe, *Org. React.*, **5,** 193 (1949).

(12) (a) It should be noted that no products, which could be derived from the imino carbocation (i), arising from intramolecular cyclization of the cyanoethyl moiety, were obtained. For example, aqueous hydrolysis of i would undoubtedly lead to ii. Thin layer chromatographic analysis of the


i


ii

reaction mixture and of a pure sample of ii[12b] proved that none of ii was present among the reaction products.[12c] (b) W. H. Mills and J. B. Whitworth, *J. Chem. Soc.*, 2738 (1927). (c) We have decomposed **2** in a variety of other organic solvents, in hopes that the intramolecular cyclization might be observed. Thus far, only complex mixtures of products, largely derived from reactions of the solvents with **2**, have been obtained.

(13) The fate of the cyanoethyl moiety in the conversion **7** → **4** is not known with certainty. Decyanoethylation of **7**, for example, may conceivably occur by (a) elimination as acrylonitrile, (b) elimination as β-fluoropropionitrile from attack of BF_4^- at the carbon which is β to the cyano group in **7**, or (c) β-hydroxypropionitrile formed during the hydrolytic work-up. In a single experiment, we have identified (glc) acrylonitrile (route a) in the reaction mixture, prior to hydrolysis. However, it is not known whether pathways b or c are also involved or at what stage (before hydrolysis or during hydrolysis) decyanoethylation actually occurs.

(14) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1964, p 27.

Preparation of Some Bicyclo[3.3.1]nonane Derivatives from Adamantanone

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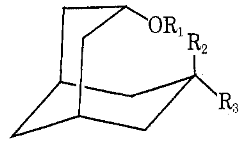
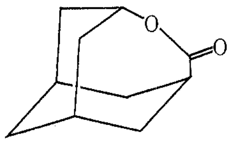
In connection with syntheses in these laboratories, the compound **1** was desired. In an attempt to prepare it the following approach was adopted; however, this gave the epimeric compound **6**.

Addition of slightly more than 1 equiv of methylmagnesium iodide to the lactone **2**,[1] obtained by Baeyer–Villiger oxidation of adamantanone, gave a monoadduct in 80% yield. The infrared spectrum showed absorptions at 3370 and 1720 cm^{-1} consistent with the structural formula **3**. The nmr spectrum was more consistent with a mixture of **3** and the cyclic hemiacetal **4** (in the ratio 1:4). Attempts to acetylate or benzoylate this product in pyridine gave a mixture of unchanged starting material and a liquid product in both cases. The spectral properties of the new product were consistent with the structure **5**: ν_{max} 1650 cm^{-1} (enol ether); nmr (CCl_4) δ 4.62 (methylene group).





1, $R_1 = R_3 = H$; $R_2 = CH_3\underset{|}{C}{=}CH_2$

2

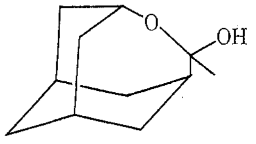
3, $R_1 = R_3 = H$; $R_2 = COCH_3$

6, $R_1 = R_2 = H$; $R_3 = CH_3\underset{|}{C}{=}CH_2$

7, $R_1 = R_2 = H$; $R_3 = COCH_3$

8, $R_1 = R_3 = COCH_3$; $R_2 = H$

9, $R_1 = COCH_3$, $R_2 = H$; $R_3 = CH_3\underset{|}{C}{=}CH_2$



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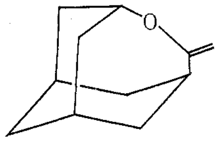

5

A Wittig reaction[2] on the ketol **3** using methylenetriphenylphosphorane in ether was incomplete even after 48 hr. However, a compound having spectral properties consistent with the structure **1** could be isolated in 60% yield: ν_{max} 3350, 3080, 1640, and 885 cm^{-1}; nmr (CCl_4) δ 4.66 (methylene protons), 3.95 (proton next to oxygen), 3.14 (hydroxylic proton), and 1.68 (vinylic methyl group).

Because of the sluggishness of the Wittig reaction, epimerization at the center C_7 in the ketol **3** may have occurred prior to reaction. Therefore doubt existed as to whether the compound formed had structure **1** or structure **6**. The configuration of the isopropenyl side chain was established in the following manner.

Equilibration[3] of the ketol **3** with sodium methoxide in methanol gave a mixture of epimers in approximately a 1:1 ratio which could be separated by preparative tlc. The compound of lower R_f was the new epimer **7** which was readily converted to the acetate **8**. Moreover, the Wittig reaction on the ketol **7** was complete in less than 15 hr and gave a compound identical in all respects with that prepared from the ketol **3**. Furthermore, this compound from the Wittig reactions was converted to its acetate **9** and the double bond in the molecule was cleaved by ozonolysis to give a compound which was identical by melting point and mixture melting point to the compound **8** prepared above. This establishes that the product of each Wittig reaction is the compound **6**, the C_7 epimer of compound **1**.

Experimental Section

General Melting points were recorded on a Kofler hot stage and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer. Nmr spectra were recorded on a Varian T-60 spectrometer using TMS as an internal standard. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6D spectrometer. Elemental analyses were performed by the Australian Microanalytical Service, Melbourne. All preparative tlc plates were prepared from 50% Kieselgel G and 50% HF 254 applied to the glass plates as a suspension in water, and activated at 120°.

***endo*-7-Acetyl-*endo*-3-hydroxybicyclo[3.3.1]nonane (3).** Methylmagnesium iodide (6 ml, 2.33 *M*, 0.013 mol) was added slowly under nitrogen to a stirred solution of the lactone **2** (1.8 g, 0.01 mol) in ether (20 ml) and after the addition stirring was continued for a further 2 hr at 20°. The mixture was cooled, treated with saturated ammonium chloride solution (10 ml), and extracted with ether (3 × 15 ml). The combined ethereal extracts were washed with water (2 × 20 ml), dried (Na_2SO_4), and evaporated to dryness to afford a white, crystalline solid. Purification by preparative tlc gave the compound **3** (1.8 g, 85%): mp 100–101°; ν_{max} (Nujol) (3370, 1720 cm^{-1}; nmr (CCl_4) δ 4.36 (br), 4.06 (br) (total 1 H) in ratio 1:4, 3.18 (br, exchangeable, 1 H, OH), 1.45 [s, *ca.* 2.5 H, $OC(CH_3)OH$] superimposed on 2.8–1.0 (complex, methylene envelope) (ratio of 4.06 to 1.45, 1:3); *m/e* 164 ($M^+ - H_2O$). *Anal.* Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.94. Found: C, 72.32; H, 9.68.

The ketol **3** (70 mg, 0.39 mmol) was stirred with acetic anhydride (0.5 ml) and pyridine (1 ml) for 15 hr under nitrogen. Water (5 ml) was added to the reaction mixture and the resulting solution was extracted with ether (3 × 8 ml). The combined ethereal extracts were washed with HCl (10%, 4 × 5 ml), water (5 ml), and saturated sodium bicarbonate (2 × 5 ml), dried (Na_2SO_4), and evaporated to give a colorless liquid (40 mg, 57%) with the probable structure **5**: ν_{max} (film) 1650 cm^{-1}; nmr δ 4.62 (2 H, s, $C{=}CH_2$), 4.28 (1 H, s, HCOC), and 1.0–2.3 (13 H, complex, methylene envelope).

***endo*-3-Hydroxy-*exo*-7-isopropenylbicyclo[3.3.1]nonane (6) and Its Acetate (9). A.** A suspension of methyltriphenylphosphoniumiodide (1.3 g, 3.3 mmol) and potassium *tert*-butoxide (0.34 g, 3.0 mmol) in anhydrous ether (10 ml) was stirred at 18° under nitrogen for 1 hr. A solution of the ketol **3** (0.18 g, 1 mmol) in dry ether (10 ml) was added and the ethereal layer was separated. The aqueous layer was extracted with ether (2 × 15 ml) and the combined ethereal extracts were dried (Na_2SO_4) and evaporated to leave a pale yellow oil. The crude product was purified by preparative tlc (70% ether–petroleum ether). The band of lower R_f afforded a white, crystalline solid (0.11 g, 58%): mp 34–35°; ν_{max} (Nujol) 3350, 3080, 1640, and 885 cm^{-1}; nmr (CCl_4) δ 4.66 (2 H, s, $C{=}CH_2$), 3.95 (1 H, m, HCOH), 3.14 (1 H, br, exchangeable, OH), 1.68 (3 H, s, $CH_3C{=}C$) superimposed on 1.0–2.2 (13 H, complex, methylene envelope); *m/e* 180 (M^+). *Anal.* Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.83; H, 11.16. The material of higher R_f showed identical R_f and spectral data with the starting material.

B. A solution of the Ketol **7** (0.18 g, 1 mmol) in dry ether (10 ml) was added to the Wittig reagent prepared as in part A and the mixture was stirred for 15 hr, at which time tlc showed that no starting material was present. Water (50 ml) was added and the ethereal layer was separated. The aqueous layer was extracted with ether and the combined ethereal extracts were dried (Na_2SO_4) and evaporated to leave a pale yellow oil. Purification by preparative tlc (70% ether–petroleum ether) afforded a white, crystalline solid (0.15 g, 84%), mp 35–37°. This compound had identical spectral properties with those of that prepared in part A. The mixture melting point with the compound from part A was 35–37°. Acetylation of compound **6** with acetic anhydride in pyridine for 15 hr at 20° gave the compound **9** (74%): mp 58–59°; ν_{max} (Nujol) 3080, 1730, 1640, 1235, 1020 cm^{-1}; nmr (CCl_4) δ 4.89 (1 H, m, HCOCO), 4.68 (2 H, s, $C{=}CH_2$), 1.92 (3 H, s, CH_3COO), and 1.71 (3 H, s, $CH_3C{=}C$) superimposed on 1.0–2.3 (13 H, complex, methylene envelope); *m/e* 162 (M^+ − AcOH).

***exo*-7-Acetyl-*endo*-3-hydroxybicyclo[3.3.1]nonane (7) and Its Acetate (8).** The ketol **3** (100 mg, 0.55 mmol) was added under nitrogen to a stirred solution of sodium methoxide in dry methanol (15 ml) (from 2 g of sodium) and stirring was continued for 16 hr at 18°. The reaction mixture was poured into water (40 ml) and extracted with ether (3 × 15 ml). The combined ethereal extracts were dried (Na_2SO_4) and evaporated to give a colorless oil. The crude material was purified by preparative tlc plate (20% ether–chloroform). Starting material (49 mg, 55%) was recovered and the ketol **7** (lower R_f) was isolated (40 mg, 45%): mp 69–71°; ν_{max} (Nujol) 3420, 1690, 1060, 1020 cm^{-1}; nmr (CCl_4) δ 4.05 (1 H, m, HCOH), 3.28 (1 H, br, exchangeable, OH), 2.14 (3 H, s, CH_3CO) superimposed on 1.0–2.5 (13 H, complex, methylene envelope); *m/e* 164 ($M^+ - H_2O$). *Anal.* Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.94. Found: C, 72.29; H, 9.90.

Acetylation of the product with acetic anhydride in pyridine for 15 hr at 20° gave compound **8** (82%): mp 36–37°; ν_{max} (Nujol) 1730, 1700, 1230, 1010 cm^{-1}; nmr (CCl_4) δ 5.05 (1 H, m, CHOCO), 2.12 (3 H, s, CH_3COO), and 2.04 (3 H, s, CH_3CO) superimposed on 1.1–2.2 (13 H, complex, methylene envelope); *m/e* 164 (M^+ − AcOH). *Anal.* Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 70.03; H, 9.22.

Ozonolysis of the Olefin 9. The vinyl acetate **9** (40 mg, 0.18 mmol) in methanol (2 ml) was cooled to −78° (Dry Ice–acetone bath) and treated with ozone (*ca.* 3%, 600 ml/min) for 30 min. The reaction mixture was then poured with stirring into a solution (cooled in a Dry Ice–acetone bath) of methanol (10 ml), acetic acid (3 ml), and sodium iodide (4.8 g). The solution was extracted with ether (2 × 10 ml) and the combined ethereal extracts were washed with 10% sodium thiosulfate solution (2 × 10 ml), saturated sodium bicarbonate (2 × 10 ml), and water (2 × 10 ml). The ether extract was dried (Na_2SO_4) and evaporated to give a colorless oil which crystallized on trituration with ether. Recrystallization from ether–petroleum ether gave a white, crystalline product (33 mg, 82%), mp 37–39°. The mixture melting point with compound **8** was 36–37°.

Registry No.—**2,** 21898-84-0; **3,** 51911-60-5; **5,** 51911-61-6; **6,** 51911-62-7; **7,** 51922-41-9; **8,** 51911-63-8; **9,** 51911-64-9.

References and Notes

(1) A. C. Udding, H. Wynberg, and J. Strating, *Tetrahedron Lett.*, 5719 (1968).

(2) For a precedent of a Wittig reaction on a hemiacetal, see, for example, E. J. Corey, N. M. Weinshenker, T. K. Schaaf, and W. Huber, *J. Amer. Chem. Soc.*, **91**, 5675 (1969).

(3) Compound **7** on treatment with sodium methoxide in methanol gave the same approximate ratio of products. This product ratio thus represents the end point of a complex series of equilibria in which presumably the hemiacetal **4** plays an important role. It should be noted that, in the diagrams of the bicyclic structures above, no conformational preference is implied.

Condensation of Cyclic Nitrones with 3,5-Dicarbomethoxypyridinium Tosylate

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While a wide variety of nucleophiles will condense with pyridinium salts,[1] there are relatively few reported examples of condensations involving carbon nucleophiles which form stable dihydropyridines.[1,2] Since nucleophilic attack by carbon nucleophiles leads to the formation of new carbon–carbon bonds, these reactions are of potential synthetic utility. We would like to report an unusually facile condensation between the pyridinium nucleus and cyclic nitrones.

A single product **5** was formed when the pyridinium salt **1** was allowed to stand for 2 days at room temperature in an excess of the nitrone **2** (Scheme I). Spectroscopic data indicated that **5** was a 1,4-dihydropyridine formed through the condensation between **1** and **2** with the loss of toluenesulfonic acid: mass spectrum *m/e* 438 (M^+); nmr δ 4.20 ppm (1 H, doublet, J = 3 Hz, proton at C_4 in the dihydropyridine nucleus); λ_{max} (MeOH) 220 nm (ϵ 30,900), 265 (15,100), and 353 (8750).[1,3] These data, when interpreted within the framework of known nitrone chemistry,[4] suggest that the position of attachment to the nitrone ring is at the 3′-carbon atom rather than the 5′-carbon atom, which cannot be excluded on the basis of the spectroscopic data alone.

Support for this structure assignment was provided by the condensation between 5,5-dimethyl-Δ^1-pyrroline 1-oxide (**3**) and **1**. This reaction afforded a mixture of dihydropyridine isomers. The major isomer was the crystalline 1,4-dihydropyridine **6** which was analogous to **5**. **6** had mass spectrum *m/e* 466 (M^+); nmr δ 4.20 ppm (1 H, doublet, J = 3 Hz); λ_{max} (MeOH) 223 nm (ϵ 32,300), 250 sh (14,300), and 358 (7430). The minor component was an oil that appeared to be a mixture of the 1,2-dihydropyridine diastereomers **7** which could not be resolved even after extensive chromatography.

The condensation of **1** with nitrone **4** also yielded both the 1,4- (**8**) and the 1,2-dihydropyridines (**9**). In this case