

δ 5.75 (br, 1, C-4), 4.11 (t, 2, $J = 7$ cps, C-21a), 2.29 (t, 2, $J = 7$ cps, C-21), 2.05 (acetates), 1.19 (C-19), and 0.72 (C-18).

Anal. Calcd for $C_{26}H_{38}O_5$: C, 72.53; H, 8.90. Found: C, 72.65; H, 9.09.

Tritylation of 20 β ,21a-dihydroxy-21-methyl-5-pregnen-3-one 3-Ethylene Ketal (10a).—A solution of 4.22 g (10.8 mmol) of diol ketal 10a in 75 ml of dry pyridine was partially distilled *in vacuo* and replenished with pyridine to a volume of 100 ml. To this was added 3.47 g of freshly crystallized trityl chloride and the solution was allowed to stand for 40 hr. Another 0.5 g of trityl chloride was added and 24 hr later no starting material remained according to tlc [acetone–benzene (1:4)]. The pyridine was removed *in vacuo* and the addition and distillation of benzene *in vacuo* was repeated three times. The residue was taken up in 150 ml of methylene chloride, washed with 5% NaHCO_3 solution and water, dried (MgSO_4), and concentrated to dryness. After crystallizing from acetone, 4.82 g of 11a was obtained in two crops, mp 187–191°. The total yield of 6.0 g (88.3%) included a third crop of crystals, mp 179–183°. A sample was recrystallized from acetone for analysis: mp 188–191°; ir (CS_2) 2.86 (OH), 3.30, 3.33, 13.48, and 14.23 μ (aryl); nmr δ 7.23–7.53 (trityl), 5.4 (broad, 1, C-6), 3.95 (ketal), 3.35 (t, 2, $J = 6$ cps, C-21a), 1.05 (C-19), and 0.78 (C-18).

Anal. Calcd for $C_{43}H_{58}O_4$: C, 81.61; H, 8.28. Found: C, 81.63; H, 8.18.

The acetate 11b was prepared from 11a in quantitative yield and crystallized from acetone as colorless needles: mp 193–194°; ir (CS_2) 3.30, 3.34, 13.47, and 14.23 (aryl), 5.76 (ester C=O), and 8.10 μ (ester COC); nmr δ 7.2–7.5 (trityl), 5.36 (broad, 1, C-6), 4.95 (broad, 1, C-20), 3.93 (ketal), 3.12 (t, 2, C-21a), 1.84 (acetate),¹³ 1.01 (C-19), and 0.64 (C-18).

Anal. Calcd for $C_{45}H_{54}O_5$: C, 80.08; H, 8.06. Found: C, 80.09; H, 8.12.

Chromium Trioxide Oxidation of 11a.—A solution of 2.26 g (3.58 mmol) of hydroxy trityl ketal 11a in 40 ml of dry pyridine was added dropwise to a solution of 1.41 g (14.1 mmol) of chromium trioxide in 30 ml of dry pyridine and allowed to stand overnight at room temperature. After 300 ml of ether and 10 ml of methanol were added, the precipitate formed was filtered and

(13) The acetate protons shifted upfield by 0.20 ppm in the presence of a trityl group. See, e.g., D. Horton, J. B. Hughes, J. S. Jewell, K. D. Philips, and W. N. Turner, *J. Org. Chem.*, **32**, 1073 (1967).

washed with ether. The combined ether solution was washed with water and dried, and the solvent was removed *in vacuo*. The product solidified when treated with acetone–cold methanol and weighed 2.06 g (91%). This was sufficiently pure for the next step. Various attempts to prepare an analytical sample failed. From silica gel chromatography a homogeneous substance 12 was obtained from the benzene fraction: mp 78.5–81.5°; ir (CS_2) 3.29, 3.32, 13.47, and 14.22 (aryl), and 5.86 μ (20 C=O); nmr δ 7.2–7.6 (trityl), 5.4 (br, 1, C-6), 3.96 (ketal), 3.44 (t, 2, $J = 6$ cps, C-21a), 2.62 (t, 2, $J = 6$ cps, C-21), 1.03 (C-19), and 0.63 (C-18).

21-Hydroxymethylprogesterone (7a).—Hydrolysis of 1.72 g (2.73 mmol) of 21-trityloxymethylprogesterone 3-ethylene ketal (12) in 100 ml of 80% acetic acid was complete after the solution had been shaken for 17 hr at room temperature. After 100 ml of water was added, the solution was extracted with ether and the organic extract was washed with dilute Na_2CO_3 and water, dried (MgSO_4), and concentrated *in vacuo* to a yellowish gum. The residue was chromatographed on silica gel, and the fraction eluted with acetone–benzene (1:4) yielded 726 mg (78%) of 7a, which was crystallized from acetone: mp 140.5–141.5°; uv max (MeOH) 241 $m\mu$ (ϵ 17,800); ir (CS_2) 2.82 (OH), 5.90 (20 C=O), and 5.96 μ (3 C=O); nmr δ 5.74 (br, 1, C-4), 3.85 (t, 2, $J = 5$ cps, C-21a), 2.62 (t, 2, $J = 5$ cps, C-21), 1.19 (C-19), and 0.69 (C-18); ORD (c 0.0527) $[\Phi]_{550}^{25} + 550^\circ$, $[\Phi]_{365}^{25} + 1540^\circ$, $[\Phi]_{358}^{25} + 2000^\circ$, $[\Phi]_{351}^{25} + 1870^\circ$, $[\Phi]_{312}^{25} + 15,200^\circ$, $[\Phi]_{273}^{25} + 780^\circ$.

Anal. Calcd for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 76.54; H, 9.57.

Acetylation of 7a resulted in a quantitative yield of the acetate 7b, which crystallized from acetone in orthorhombic prisms: mp 129–129.5°; ir (CS_2) 5.73 (ester C=O) and 8.14 (ester COC), 5.86 (20 C=O), and 5.96 μ (3 C=O); nmr δ 5.78 (br, 1, C-4), 4.38 (t, 2, $J = 6$ cps, C-21a), 2.72 (t, 2, $J = 6$ cps, C-21), 2.04 (acetate), 1.20 (C-19), and 0.71 (C-18).

Anal. Calcd for $C_{24}H_{34}O_4$: C, 74.58; H, 8.87. Found: C, 74.39; H, 8.75.

Registry No.—2a, 22486-07-3; 2b, 22528-31-0; 3a, 22486-08-4; 3b, 22486-09-5; 4, 22486-10-8; 5a, 22486-11-9; 5b, 22486-12-0; 7a, 22486-13-1; 7b, 22486-15-3; 10a, 22486-16-4; 10b, 22485-90-1; 11a, 22485-91-2; 11b, 22485-92-3; 12, 22528-29-6.

Photochemistry of 5-Norbornenylacetone and 5-Norbornenylacetaldehyde

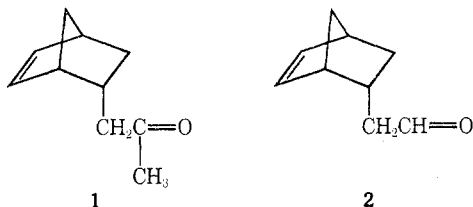
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Irradiation of the δ,ϵ -unsaturated carbonyl compounds **1** and **2** led to mixtures of oxetanes as the major photo-products.

As part of a broad study of the photochemical behavior of unsaturated polycyclic ketones,¹ it was of interest to examine the two norbornene systems **1** and **2**. It was hoped that studies of these systems would be informative as to the intramolecular modes of interaction of the excited carbonyl groups with the double bond. More specifically, for example, one has the possibility



(1) R. R. Sauer, W. Schinski, and M. M. Mason, *Tetrahedron Lett.*, 79 (1969).

of intramolecular energy transfer² from the triplet state of the carbonyl group of **1** ($E_T = 80\text{--}82$ kcal/mol³) to the norbornene double bond ($E_T \cong 72$ kcal/mol⁴). On the other hand, triplet transfer from the aldehyde function of **2** ($E_T \cong 69$ kcal/mol⁵) would be expected to be considerably less efficient. Substantive product differences in the two cases would serve as a basis for interpretations as to the nature of the transfer process. Lastly, our interest in these systems was enhanced by the intriguing chemical possibilities, e.g., Norrish Type II cleavage or cyclobutanol formation, which might

(2) H. Morrison, *J. Amer. Chem. Soc.*, **87**, 932 (1965); P. A. Leermakers, J.-P. Montillier, and R. D. Rauh, *Mol. Photochem.*, **1**, 57 (1969); D. O. Cowan and A. A. Baum, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. P 117.

(3) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

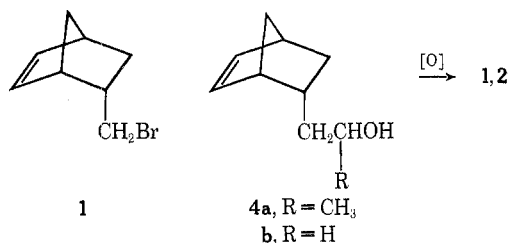
(4) See D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

(5) J. D. Borman, J. H. Stanley, W. V. Sherman, and S. G. Cohen, *J. Amer. Chem. Soc.*, **85**, 4010 (1963).

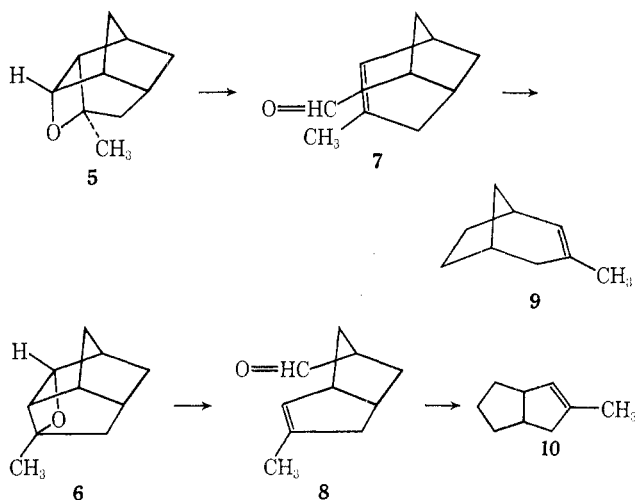
follow intramolecular abstractions of the γ hydrogen at the bridgeheads.

Results and Discussion

Ketone **1** was prepared by chromic acid oxidation of the alcohols (**4a**) obtained from the reaction of the Grignard reagent of bromomethylnorbornene (**3**) with acetaldehyde. Aldehyde **2** was obtained by mild oxidation of 5-norbornenylethanol (**4b**).⁶ Preparative



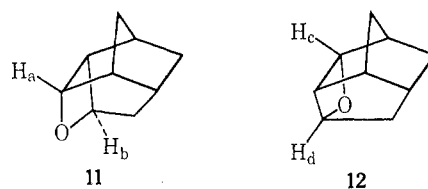
photolyses were carried out on nitrogen-purged solutions of **1** or **2** in benzene or ether with Corex-filtered light. Under these conditions, **1** was consumed with the concurrent production of a 2:1 mixture of products. A careful search revealed only trace amounts of acetone and norbornadiene, the expected products of a Norrish Type II cleavage. That the two major products were isomeric with **1** was demonstrated by elemental analyses on samples obtained by fractional distillation of the product. From a consideration of infrared and nmr spectral data, it was clear that these isomers were oxetanes. Since the problem of differentiating between the two possible oxetanes **5** and **6** could not be unambiguously resolved by analysis of the spectral data, a chemical means was devised. The key reaction involved acid-catalyzed cleavage of the oxetane ring,⁷ a process which would be expected to lead to the isomeric aldehydes **7** and **8**. Since the parent hydrocarbons



3-methylbicyclo[3.2.1]oct-2-ene (**9**) and 3-methylbicyclo[3.3.0]oct-2-ene (**10**) are both known compounds,⁸ the desired correlations could be achieved by decar-

bonylation reactions. Experimentally, it was found that the major oxetane gave **9** after rearrangement and decarbonylation, a fact which verifies the assignment of **5** to this isomer. Similarly, the minor isomer must be **6**, since olefin **10** was produced on rearrangement and decarbonylation.

Finally, irradiation of the aldehyde **2** led to two isomeric oxetanes in a ratio of 22:78. Analysis of the nmr spectral parameters in the low-field region suggested that the major isomer corresponded to structure **11**, since the observed broad doublet at δ 4.50 ($J = 6$ cps) assigned to H_a and H_b bore resemblance to the gross structure of the multiplet (doublet of triplets, $J = 7.5, 1.5,$ and 1.5 cps) for the analogous proton in **5**. Similarly, the low-field proton in **6** ($q, J = 7.5$ and 4.5 cps) had a counterpart, H_c , in the low-field region of **12** ($q, J = 8$ and 5 cps). The remaining proton, H_d ($t, J = 4$ cps), had no counterpart in the spectra of either **5** or **6**. This analysis, while self-consistent, is not regarded as definitive. The basic arguments would not be altered if the structural assignments for **11** and **12** were reversed, however.



Thus no significant differences in product type were observed for the two photolyses. Nevertheless, the results are of interest in that they extend the limits of the intramolecular Paterno-Büchi reaction in the sense that photocyclizations of δ, ϵ -unsaturated ketones have not previously been observed to lead to products of the types represented by **6** and **12**. Moreover, they represent relatively simple examples of carbonyl systems which possess γ -hydrogen atoms but which do not undergo appreciable Norrish Type II reactions.⁹ Owing to the wide variations in the efficiency of Type II eliminations in cyclic compounds, speculations as to the role of the double bond in the cases at hand would be premature.¹⁰

Experimental Section

Elemental analyses were done by Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were determined as films or as noted on a Perkin-Elmer Model 21 spectrophotometer. Nuclear magnetic resonance data were obtained from a Varian Model A-60 spectrometer in carbon tetrachloride with tetramethylsilane as internal standard. Gas chromatograms were determined on an Aerograph A-90 P instrument using 12 ft \times 0.25 in. columns of Carbowax 20 M on Chromosorb G or as noted. Melting points were determined on a Mel-Temp apparatus and are uncorrected.

exo,endo-5-Norbornenylacetaldehyde (**2**).—An ice-cold solution of 32.3 g (0.23 mol) of *exo,endo*-4b⁶ in 1.5 l. of acetone was treated with 60 ml of 8.0 N Jones reagent¹¹ over a period of 70 min. The resulting mixture was diluted with 4.5 l. of water and extracted with chloroform. The extracts were washed with

(9) For a discussion and other examples, see A. Padwa and D. Eastman, *ibid.*, **91**, 463 (1969).

(10) A quantitative study of this problem is in progress in these laboratories with A. Rousseau. For a recent discussion and references on the intermolecular mechanism of carbonyl-olefin energy transfer, see J. Satiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3659 (1969).

(11) C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

(6) R. R. Sauer, R. M. Hawthorne, and B. I. Dentz, *J. Org. Chem.*, **32**, 4071 (1967); E. Allred and J. Marichich, *Tetrahedron Lett.*, 949 (1963).

(7) G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, **76**, 4237 (1954). Traces of acid present in unpurified carbon tetrachloride smoothly catalyzed these rearrangements.

(8) For a reference to **9**, see W. Kraus and R. Dewald, *Justus Liebig's Ann. Chem.*, **689**, 21 (1965). H. C. Brown and W. J. Hammar [*J. Amer. Chem. Soc.*, **89**, 1524 (1967)] have reported the synthesis of **10**.

sodium bicarbonate solution and dried over MgSO_4 . Evaporation of the extracts gave 5.40 g (17%) of an oil: bp 57° (1.5 mm); nmr δ 9.71 (m, $\text{HC}=\text{O}$), 5.92 (m, $\text{HC}=\text{C}$), 2.82 (s), and 2.6–0.55 (m); ir 5.78 ($\text{C}=\text{O}$) and 13.92 ($\text{C}=\text{C}$) μ . Gc analysis (152°) showed an *exo/endo* ratio of 17:83.

Satisfactory elemental analysis of **2** could not be obtained owing to rapid air oxidation.

The 2,4-dinitrophenylhydrazone was prepared, mp $131\text{--}130^\circ$.

Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_4$: C, 56.96; H, 5.10; N, 17.71. Found: C, 57.14; H, 5.34; N, 17.47.

exo,endo-5-Norbornenylacetone (**1**). **A**.—A solution of 13.1 g (0.096 mol) of **2** in 20 ml of dry ether was added to the Grignard reagent prepared from 20.6 g (0.14 mol) of methyl iodide and 3.89 g (0.16 g-atom) of magnesium in 20 ml of ether. The resulting solution was heated at reflux for 1 hr, at which time it was poured onto a mixture of ice and hydrochloric acid. The crude alcohols (**4a**) were extracted into ether which was dried and evaporated.

A small sample of *exo,endo-1-(5-norbornenyl)propan-2-ol* (**4a**) was purified by gas chromatography: nmr δ 5.98 (m, $\text{HC}=\text{C}$), 3.70 (m, HCO), 2.75–0.6 (m), and 1.10 (d, $J = 7$ cps, CH_3); ir 2.92 (m, OH), 3.25 (w, $\text{HC}=\text{C}$), 8.90 (m, CO), and 13.98 μ (s, $\text{HC}=\text{CH}$).

Anal. Calcd for $\text{C}_{10}\text{H}_{16}\text{O}$: C, 78.89; H, 10.60. Found: C 78.51; H, 10.49.

The crude alcohol was dissolved in 200 ml of acetone and treated with 31 ml of Jones reagent¹¹ at $0\text{--}10^\circ$. After the mixture had been stirred for 10 min, enough isopropyl alcohol to destroy the excess reagent was added. The resulting mixture was poured into 1 l. of water followed by ether extraction. The dried extracts were evaporated and the residue was distilled to yield 7.42 g (51%) of **1**: bp $64\text{--}65^\circ$ (0.6–0.5 mm); nmr δ 6.03 (m, $\text{HC}=\text{C}$), 3.0–0.3 (m), and 2.09 (CH_3); ir 5.83 (s, $\text{C}=\text{O}$) and 13.98 (s, $\text{HC}=\text{CH}$) μ . Gc analysis (153°) showed a 15:85 ratio of *exo/endo* isomers.

Anal. Calcd for $\text{C}_{10}\text{H}_{16}\text{O}$: C, 79.95; H, 9.39. Found: C, 80.22; H, 9.53.

B.¹²—The Grignard reagent of 5-bromomethylnorbornene (15% *exo*)¹³ was prepared from 153 g (0.82 mol) and 21.9 g (0.90 g-atom) of magnesium in 500 ml of ether. A solution of 66 g (1.22 mol) of freshly distilled acetaldehyde in 70 ml of ether was added over a 20-min period to the cooled ($5\text{--}10^\circ$) Grignard solution. The resulting mixture was heated at reflux for 15 min and poured over a mixture of ice and hydrochloric acid. The product was extracted into ether which was washed with sodium bicarbonate solution and dried over MgSO_4 . The crude product obtained on evaporation showed four components on gc analysis (153°)—*exo* and *endo-1* and *exo* and *endo* alcohols **4a**.

The entire product was oxidized as above in 2 l. of acetone with 200 ml of Jones¹¹ reagent to yield 69.34 g (56%) of ketone **1**, bp $80\text{--}83^\circ$ (15 mm).

Photolyses.—Preparative-scale irradiations were carried out in cylindrical flasks equipped with nitrogen inlet tubes at the bottom. The lamps used were 450-W (type L) Hanovia medium-pressure mercury arcs which were housed in a water-cooled immersion cell equipped with a Corex 9700 filter sleeve. The compound to be irradiated was dissolved in dry benzene or ether and the solution was purged with dry, oxygen-free nitrogen for 15 min before irradiation was commenced.

Irradiation of 1.—A solution of 12.04 g of **1** in 1 l. of ether was irradiated for 20 hr. Gc analysis (150°) revealed only a trace of starting materials and two new peaks in the ratio 2:1. An nmr spectrum of the concentrated reaction mixture revealed two singlets at 1.37 and 1.22 ppm in the ratio of ca. 1:2. Distillation of the crude photosylate at 2 mm gave a 7.52-g (62%) fraction, bp $42\text{--}65^\circ$, which was essentially pure oxetanes. A nonvolatile residue of 4.32 g remained. The pure oxetanes could be obtained by fractional distillation on a spinning-band column (18 in. \times 6 mm).

3-Methyl-4-oxatetracyclo[5.2.1.0.^{3,6,9}]decane (**5**) gave the following data: bp $68\text{--}73^\circ$ (6 mm); nmr δ 4.41 (d, of t, $J = 7.5$, 1.5, and 1.5 cps, HCO), 1.22 (s, CH_3), and 2.6–1.0 (m); ir (film) 9.10 (m), 9.52 (s), 9.71 (s), 9.85 (m), 10.48 (m), 11.28 (m), and 12.18 μ (s).

Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{O}$: C, 79.95; H, 9.39. Found: C, 80.25; H, 9.44.

5-Methyl-6-oxatetracyclo[5.3.0.0.^{3,9,8}]decane (**6**) gave the following data: bp $63\text{--}64^\circ$ (6 mm); nmr δ 4.57 (q, $J = 7.5$ and 4.5 cps, HCO), 1.37 (s, CH_3), and 2.9–1.1 (m); ir (film) 8.74 (m), 9.56 (m), 10.03 (s), 10.13 (s), 10.78 (s), 11.06 (m), and 12.08 μ (s).

Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{O}$: C, 79.95; H, 9.39. Found: C, 79.83; H, 9.36.

Irradiation of *endo-1*.—A 30-mg sample of *endo-1* was collected by preparative gc, $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 279 nm (ϵ 27). A deoxygenated solution in 0.30 ml of benzene was prepared and irradiated in a Pyrex nmr tube with the 3000- \AA source of a Rayonet photochemical reactor¹⁴ for 22 hr. Gc analysis revealed that 80% of the ketone had been consumed but that only trace amounts ($<0.1\%$) of acetone and norbornadiene could be detected.

Irradiation of 2.—Irradiation of 5.40 g of **2** in 1 l. of benzene for 3 hr gave 2.41 g (45%) of a solid which contained a trace of starting material. A pentane solution of the product was washed with dilute potassium permanganate until the color persisted. The acidic materials were removed by washing with aqueous sodium carbonate and the extracts were dried and evaporated to give 1.45 g of a mixture of **11** and **12**. An analytical sample was prepared by sublimation at 55° (1.5 mm).

Anal. Calcd for $\text{C}_9\text{H}_{12}\text{O}$: C, 79.37; H, 8.88. Found: C, 79.38; H, 9.06.

Gc analysis (152°) indicated the presence of two components in a ratio of 22:78. Small samples of the two isomers were collected for spectral purposes. The minor isomer, mp $143\text{--}150^\circ$, was assigned structure **12** (6-oxatetracyclo[5.3.0.0.^{3,9,8}]decane): nmr δ 4.70 (q, $J = 8$ and 5 cps, HCO), 4.88 (t, $J = 4$ cps, HCO), and 3.5–1.4 (m); ir (Nujol) 8.50 (m), 8.98 (m), 9.68 (m), 10.18 (s), 11.43 (m), 11.91 (m), and 12.15 μ (m).

The major component, mp $153\text{--}164^\circ$, was assigned structure **11** (4-oxatetracyclo[5.2.1.0.^{3,9,8}]decane): nmr δ 4.50 (d, $J = 6$ cps, HCO) and 3.5–1.0 (m); ir (Nujol) 9.42 (w), 9.93 (m), 10.20 (m), 11.33 (m), 11.96 (m), and 12.58 μ (m).

3-Methyl-*cis*-bicyclo[3.3.0]oct-2-ene-7-carboxaldehyde (**8**).—A solution of **6** in carbon tetrachloride¹⁵ was allowed to stand at 25° for 42 hr. At the end of this period, rearrangement to **8** was complete as shown by gc: nmr δ 9.50 (d, $J = 2$ cps, $\text{HC}=\text{O}$), 5.10 (m, $\text{HC}=\text{C}$), and 3.5–1.0 (m); ir 3.69 (w) and 5.78 μ (s).

The 2,4-dinitrophenylhydrazone was prepared by addition of **6** directly to an acid solution of 2,4-DNPH in ethanol; after crystallization from ethanol the melting point was $176\text{--}177.5^\circ$.

Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.06; H, 5.35; N, 16.46.

3-Methylbicyclo[3.2.1]oct-2-ene-6-carboxaldehyde (**7**).—The aldehyde was prepared as above. Gc analysis indicated two peaks in a 3:1 ratio which are presumed to be epimers: nmr δ 9.63 (d, $J = 2$ cps, $\text{HC}=\text{O}$), 5.52 (d, $J = 7$ cps, $\text{HC}=\text{C}$), and 3.0–1.4 (m); ir 3.70 (w) and 5.80 μ (s).

The 2,4-dinitrophenylhydrazone was prepared as above, mp $153\text{--}155^\circ$.

Anal. Found: C, 58.03; H, 5.38; N, 17.17.

3-Methylbicyclo[3.3.0]oct-2-ene (**10**).—A mixture of 0.81 g of **8** and 0.20 g of 10% palladium on carbon was heated at 150° ¹⁶ in a short-path distillation apparatus. The bath temperature was gradually raised to 190° , at which time the evolution of gas appeared to cease. A vacuum was applied, whereupon 0.84 g of distillate was obtained. Preparative gc (Apiezon L, 125°) indicated one major product with a small shoulder. The ir spectrum of the collected material was virtually identical with that of an authentic sample of **10**;⁸ the nmr spectrum was identical with that of an authentic sample except for a small doublet at δ 0.95 in the decarbonylation product.

3-Methylbicyclo[3.2.1]oct-2-ene (**9**).—A 0.75-g sample of mixed aldehydes ($<10\%$ **8**) was heated at 138° for 4 hr with 0.35 ml of *t*-butyl peroxide.¹⁶ An additional 0.17 ml of peroxide was added followed by heating for 20 hr. Preparative gc (Apiezon L, 148°) revealed one major component, which was collected (0.105 g). The ir spectrum of this material was virtually identical with that of an authentic sample of **9**.⁸ About 10% **10** was present in this product, as determined by integration of the nmr spectrum in the δ 5.0 region.

(14) Obtained from the Southern New England Ultraviolet Co., Middletown, Conn.

(15) J. Wilt and V. P. Abegg, *J. Org. Chem.*, **33**, 925 (1968).

(16) J. A. Berson and C. J. Olsen, *J. Amer. Chem. Soc.*, **84**, 3178 (1962).

(12) This method proved to be the more convenient one owing to the availability of the starting materials.

(13) K. Alder and E. Windemuth, *Chem. Ber.*, **71**, 1939 (1938).

Registry No.—*endo*-1, 22842-22-4; *endo*-2, 15507-07-0; 2,4-dinitrophenylhydrazone of *endo*-2, 22842-24-6; 5, 22842-30-4; 6, 22842-31-5; 7, 22842-32-6; 2,4-dinitrophenylhydrazone of 7, 22842-33-7; 8, 22842-25-7; 2,4-dinitrophenylhydrazone of 8, 22842-26-8; 11, 22842-34-8; 12, 22842-35-9.

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Notes

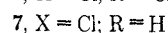
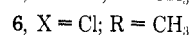
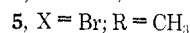
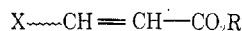
Pyrazole Product Ratio Analysis of the Reaction of Diazomethane with Methyl *cis*- and *trans*- β -Chloroacrylates

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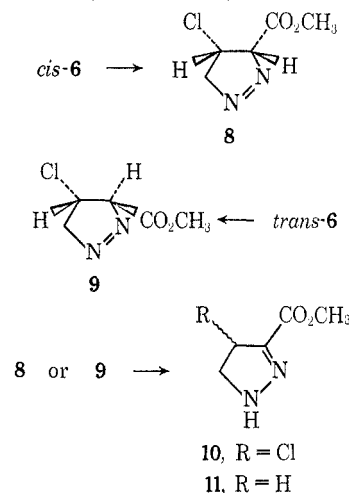
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Carbomethoxypyrazoles 1, 2, and 3 are obtained upon reaction of appropriately substituted methyl acrylates (*i.e.*, 4 and 5) with excess diazomethane in ether.^{1,2} However, the mechanism of pyrazole formation remains obscure. To probe into the nature of the intermediates in pyrazole formation, we studied the reaction of methyl *cis*- and *trans*- β -chloroacrylates 6 with diazomethane.



Concerted addition of diazomethane to *cis*- and *trans*-6 is expected to yield intermediate 1-pyrazolines 8 and 9, respectively. This conclusion is supported by the observation that activated olefins containing a β substituent which is not a leaving group react with diazomethane to yield 1-pyrazolines with retention of geometrical configuration.³ 1-Pyrazolines may readily isomerize to 2-pyrazolines.^{4,5} This isomerization, which is apparently very fast,⁶ would yield the 2-pyrazoline 10 as a common intermediate from either *cis*- or *trans*-6. Attempts, in our laboratories, to detect in-

termediate 1- or 2-pyrazolines spectrophotometrically failed. We therefore investigated the pyrazole product ratios, which we suspected would yield indirect evidence for the nature of the intermediates in pyrazole formation. If pyrazolines 8 and 9 are indeed formed during the reaction sequence, product analysis¹ should reflect the presence of these intermediates which are expected to eliminate HCl at different rates. Significant differences in pyrazole product ratio should only be observed if there are large differences in rates of elimination of HCl from intermediate stereoisomeric 1-pyrazolines and one of the elimination rates is faster than isomerization (8 or 9 \rightarrow 10).



Results and Discussion

Methyl *cis*- β -chloroacrylate (6) was prepared by cuprous chloride catalyzed addition of HCl to propiolic acid followed by esterification in methanol.⁷ The *trans* isomer 6 was prepared in a similar manner from *trans*- β -chloroacrylic acid (7) obtained by isomerization of *cis*-7 in 6 *N* HCl.⁷ A mixture of *cis* and *trans* isomers 6 could also be prepared by catalytic addition of HCl to methyl propiolate. Spinning-band distillation afforded pure *cis* and *trans* isomers in 60 and 5% yields, respectively. The purity of the geometrical β -chloro esters was confirmed by gas-liquid partition chromatography and by comparison with reported nmr spectra.⁷

Reaction of 10 mM *cis*-6 in 36–43 mM distilled diazomethane-ether in a Dry Ice-acetone bath for 4 hr,

(7) A. N. Kurtz, W. E. Billups, R. B. Greenlee, H. F. Hamil, and W. T. Pace, *J. Org. Chem.*, **30**, 3141 (1965).

(1) D. T. Witiak and M. C. Lu, *J. Org. Chem.*, **33**, 4451 (1968).

(2) H. von Pechman and E. Burkard, *Ber.*, **33**, 3594 (1900).

(3) T. V. VanAuken and R. L. Rinehart, Jr., *J. Amer. Chem. Soc.*, **84**, 3736 (1962).

(4) L. I. Smith and W. Pings, *J. Org. Chem.*, **2**, 23 (1937).

(5) L. I. Smith and K. L. Howard, *J. Amer. Chem. Soc.*, **65**, 159 (1943).

(6) L. I. Smith and K. L. Howard, *ibid.*, **65**, 165 (1943).