oil. The oil was taken up in ether, filtered, and concentrated; removal of the ether yielded a yellow powder: 1.5 g (46%); mp 99–100 °C. Heating this solid to 100 °C in vacuo (a vacuum sublimation apparatus serves the purpose) removed volatile impurities; the recovered solid had a melting point of 106–107 °C and was pure: IR ($CHCl_3$) 2061, 1985 (C≡O), 1720 (C=O), 1610, 1490, 1290 cm^{-1}; NMR ($CDCl_3$) δ 7.90–6.75 [q, 4, ArH, consisting of 7.90–7.65 (d, 2, J = 7 Hz) and 7.00–6.75 (d, 2, J = 7 Hz)], 5.80–5.20 (m, 2, H_2 and H_3 complexed vinyl protons), 4.10–3.90 (d, 1, J = 8 Hz, H_1 complexed vinyl proton), 3.85 (s, 3, OCH_3), 2.15–1.93 (m, 1, H_5 complexed vinyl proton), 0.93–0.70 (dd, 1, J = 2, 5 Hz, H_4 complexed vinyl proton). Anal. Calcd for $C_{15}H_{12}O_5Fe$: C, 54.91; H, 3.66. Found: C, 54.85; H, 3.69.

p-(1,3-Butadienyl)benzoic Acid (1c). Compound 5 (2.0 g, 0.011 mol) and 25 mL of 20% NaOH were placed in a 100-mL round-bottomed flask. The mixture was refluxed for 12 h. Upon cooling, the mixture was gravity filtered, and the filtrate was acidified with dilute sulfuric acid; fluffy white crystals precipitated. These crystals were collected by suction filtration and recrystallized from ethanol-water: 1.15 g (60%); mp 126–127 °C; IR (KBr) 1750 (C=O), 1600, 1420, 1390 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.83; H, 5.79. Found: C, 75.67; H, 5.51.

p-[(π-1,3-Butadiene)tricarbonyliron]benzoic Acid (2c). Compound 6 (2.0 g, 6.1 mmol) and 25 mL of 20% NaOH were added to a 100-mL round-bottomed flask, and the mixture was heated at reflux for 12 h. Upon cooling, the solution was gravity filtered, and the yellow filtrate was acidified with dilute sulfuric acid. The yellow-green crystals which precipitated were collected by suction filtration. Recrystallization from ethanol-water produced 2c: 1.13 g (59%); mp 170–175 °C dec; IR (KBr) 2990, 2040, 1950 (C≡O), 1750 (C=O), 1600, 1420, 1390 cm^{-1}. Anal. Calcd for $C_{14}H_{10}O_5Fe$: C, 53.52; H, 3.21. Found: C, 53.93; H, 2.98.

pK_a Measurements.[17] All pK_a measurements were carried out in 80% ethanol-water (80/20 by volume) by titrimetric methods at 25 ± 1 °C. Solvents were degassed before titration and stirred with a stream of nitrogen during titration. A Corning Model 12 pH meter was used equipped with a Beckman glass electrode. Standardization was carried out by using an aqueous ethanol buffer.[16]

Aqueous ethanol solutions of acids 1c and 2c and benzoic acid were prepared; concentrations were standardized to 0.1 N. These solutions were titrated with standardized 0.1 N NaOH. During the titration, for each increment of base added sufficient ethanol was added to maintain the 80% composition, and pH values were obtained. Calculations were carried out as exemplified by Albert and Serjeant[5] except no activity corrections were made. The average deviation within any titration varied from 0.03 to 0.09 pH units; two titrations were done for each of the acids.

Registry No. 1c, 79201-19-7; 2c, 79215-47-7; 3, 619-66-9; 4, 1571-08-0; 5, 79201-20-0; 6, 79201-10-8; $Fe_3(CO)_{12}$, 17685-52-8.

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Regioselective γ-Elimination of Sulfones under Michael Reaction Conditions

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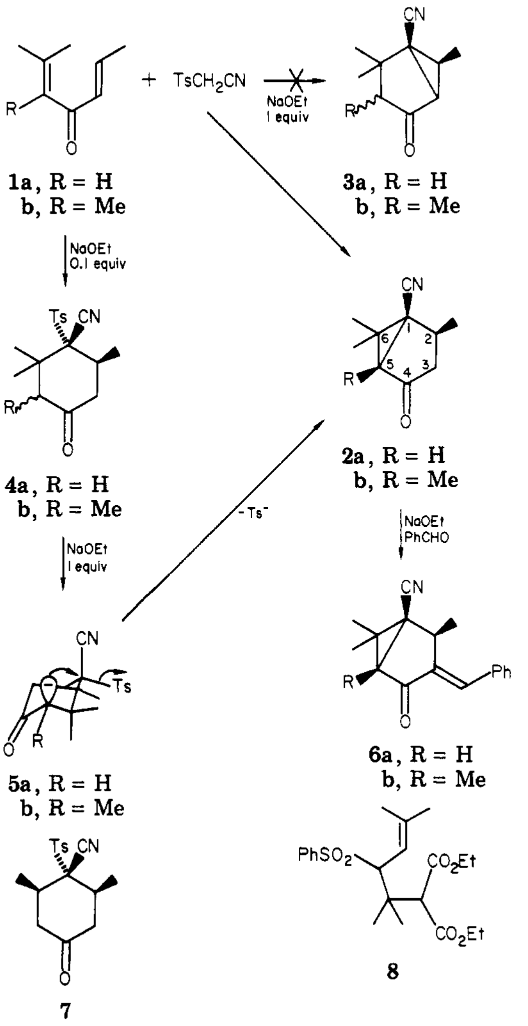
Received June 2, 1981

The double Michael reaction of [(4-methylbenzene)-sulfonyl)]acetonitrile with 2-methyl-2,5-heptadien-4-one (1a) gives[1] a bicyclic nitrile. Of the alternative structures 2a and 3a, we originally[1] favored 3a. In fact, the correct structure is 2a as shown in Scheme I.

Scheme I



The Michael reaction product 4a is obtained when 0.1 molar equiv of sodium ethoxide is employed and is probably an intermediate in the formation of 2a. Treatment of 4a with 1 equiv of base leads to the same nitrile 2a as is obtained by the one-step procedure.

The original assignment of structure 3a was motivated by two kinetic considerations: either (i) the protons at C_3 are more accessible for enolization or (ii) the transition state leading to 3a is less crowded. Evidently i is not a significant factor, since the methyl substituted homologue 1b cyclizes equally regioselectively, to provide bicyclic nitrile 2b. Regarding ii, it is now clear that in this instance the well-documented[2] "*gem*-dimethyl effect" has a decisive influence on the course of the reaction.

The structure of the bicyclic nitriles (2a,b) was established by preparation of the benzylidene derivatives (6a,b) and by 360-MHz NMR spectroscopy. The cis stereochemistry at C_2 is assigned in view of the substantial deshielding of the methine proton at that position (3a, δ 2.50; 3b, δ 2.44). This is attributed to either steric crowding[3] or cyclopropane anisotropy.[4-6] Mechanistic considerations

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also support this assignment. It has been shown[7] that Michael-type ring closures may lead initially to the kinetically favored product, but that under the reaction conditions equilibration occurs, leading to the irreversible formation of the thermodynamically more stable product. In this case the more stable ring-closure product is the 2-cis isomer **4a**; and its more stable conformation, as in **5a**, places the sulfone group in the equatorial position necessary for γ-elimination,[8] which leads to **2a** with 2-cis stereochemistry.

The symmetrical compound **7**, which lacks a *gem*-dimethyl group, does not undergo this elimination reaction under the relatively mild conditions employed (sodium ethoxide, 25 °C). This result is consistent with Woodward's observation[8] that γ-elimination of sulfones requires more drastic conditions. On the other hand, in Martel's synthesis of chrysanthemic acid[9] via the diester **8**, γ-elimination of the sulfone occurred readily under the conditions of the Michael reaction. This supports our conclusion that the elimination is both accelerated and directed by the influence of the *gem*-dimethyl group at C_6.

Experimental Section

Melting points were determined with a Kofler hot-stage apparatus, IR spectra with Perkin-Elmer 137B and 281 spectrometers, and ^{1}H NMR spectra (Me_4Si as internal standard) with a Varian T60A or a Bruker WM 360 instrument. Gas chromatography/mass spectrometry was performed on a Hewlett-Packard 5985 instrument.

***c*-2,6,6-Trimethyl-4-oxobicyclo[3.1.0]hexane-*r*-1-carbonitrile (2a).**[10] A suspension of [(4-methylbenzene)sulfonyl]acetonitrile (40 g) in 2-methyl-2,5-heptadien-4-one (25 g) and ethanol (200 mL) was treated with a 20-mL aliquot of a sodium ethoxide solution [sodium (5 g) in ethanol (200 mL)] and stirred until the suspended material dissolved. The remainder of the sodium ethoxide solution was added, and the mixture was allowed to stand overnight. Dilution with water (1 L) and extraction with dichloromethane (2 × 150 mL), followed by distillation, gave 19.25 g (58.5%) of **2a**: bp 95–100 °C (0.3 mmHg); GLC showed two main components (91 + 5%); GLC/mass spectra (CI) indicated *m/e* 164 (M + 1) for both components; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 3 H), 1.44 (s, 3 H), 1.44 (d, 3 H, J = 7 Hz), 2.08 (br d, 1 H, J = 18 Hz), 2.30 (s, 1 H), 2.44 (dd, 1 H, J = 18, 9 Hz), 2.50 (m, 1 H); other spectroscopic data and elemental analyses previously reported.[1]

***c*-2,5,6,6-Tetramethyl-4-oxobicyclo[3.1.0]hexane-*r*-1-carbonitrile (2b).** The title compound was prepared by a method similar to that employed for **2a**. The crude product was crystallized from petroleum ether (bp 65–90 °C) in 52% yield: mp 83–84 °C; GLC/mass spectra (CI) as before showed one main component, *m/e* 178 (M + 1); ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.35 (s, 3 H), 1.37 (s, 3 H), 1.40 (d, 3 H, J = 7 Hz), 2.06 (dd, 1 H, J = 18, 3 Hz), 2.50 (m, 1 H), 2.52 (dd, 1 H, J = 18, 8 Hz); IR (Nujol mull) 2220, 1720, 1470, 1380, 1300, 1110, 850 cm^{-1}.

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.61; H, 8.51; N, 8.20.

2,6,6-Trimethyl-4-oxo-3-(phenylmethylene)bicyclo[3.1.0]hexane-1-carbonitrile (6a). A mixture of the nitrile **2a** (1.63 g) and benzaldehyde (1.1 g) was treated with 10% sodium ethoxide in ethanol (1 mL). An immediate exotherm was observed, and the mixture solidified. Recrystallization from ethanol gave 1.61 g (64%) of **6a**: mp 159–161 °C; mass spectrum, *m/e* 251 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.42 (d, 3 H, J = 7 Hz), 1.43 (s, 3 H), 2.42 (s, 1 H), 3.63 (dq, 1 H, J_q = 7, J_d = 2 Hz), 7.28 (d, 1 H, J = 2 Hz), 7.45 (br s, 5 H); spin-decoupling irradiation at δ 1.42 collapses the signal at δ 3.63 to a doublet, irradiation at δ 7.28 collapses the signal at δ 3.63 to a quartet, and irradiation at δ 3.63 collapses the signals at δ 1.42 and 7.28 to singlets; IR (Nujol mull) 2210, 1705, 1615, 940 cm^{-1}.

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.40; H, 7.02; N, 5.53.

2,5,6,6-Tetramethyl-4-oxo-3-(phenylmethylene)bicyclo[3.1.0]hexane-1-carbonitrile (6b) was prepared from the nitrile **2b** by a similar procedure to that employed for **6a**. The product was recrystallized from ethanol to give 69% **6b**: mp 119–121 °C; ^{1}H NMR δ 1.17 (s, 3 H), 1.39 (s, 3 H), 1.39 (d, 3 H, J = 7 Hz), 1.50 (s, 3 H), 3.72 (q, 1 H, J = 7 Hz), 7.5 (complex, 6 H); IR (Nujol mull) 2220, 1705, 1610, 1040, 940 cm^{-1}.

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.48; H, 7.30; N, 5.47.

Acknowledgment. We thank Mr. N. Secord and his colleagues for recording GC/mass spectra and Dr. W. Bremser of BASF, Ludwigshafen, for the 360-MHz ^{1}H NMR spectra.

Registry No. 1a, 66031-92-3; **1b**, 79255-57-5; **2a**, 79255-58-6; **2b**, 79255-59-7; **4a**, 73583-67-2; **6a**, 79255-60-0; **6b**, 79255-61-1; [(4-methylbenzene)sulfonyl]acetonitrile, 5697-44-9.

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Ozonolysis of Tetraphenylcyclopentadienone

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Received April 17, 1981

At the present time the only established examples of the 1,4 addition of ozone to conjugated diene systems are with aromatic compounds of the anthracene type, such as anthracene itself, various 9,10-disubstituted anthracenes, and certain benzoanthracenes.[1,2] No similar additions to aliphatic systems have been reported. In the hope of discovering such, we investigated the ozonation of tetraphenylcyclopentadienone (**1**). Although our anticipation was not fulfilled, the results of the ozonation were unusual enough to be of interest.

Ozonation of **1** in dichloromethane at −78 °C with 1 mol equiv of ozone resulted in two products: 5-(benzoyloxy)-3,4,5-triphenyl-1-oxacyclopent-3-en-2-one (**12**, 56% yield) and the known 1,2,3-triphenylpropane-1,3-dione (**14**, 32% yield).

The stucture of **12** was established through elemental analysis, NMR, IR, and mass spectra, a positive hydroxamic acid[3] test for an ester function, and hydrolysis to benzoic acid and known lactol **13**. The NMR spectrum of **12** revealed only aromatic protons centered at δ 8.0 (2 H) and 7.3 (18 H); the IR spectrum showed two carbonyl stretching bands at 1767 and 1745 cm^{-1}; and the mass spectrum contained a parent peak at *m/e* 432 and fragmentation peaks at *m/e* 404, 327, 311, 282, 265, 253, 207, 178, 121, 105, 77, and 51. The compound gave negative peroxide tests with KI and HI and no molecular oxygen was evolved during the ozonolysis. The structure assignment was confirmed by X-ray crystallography.[4]

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