Table II. Reductive Dehalogenation by Polymer-Supported $FeH(CO)_4^-$ Anion

Alkyl halide	Registry no.	Product[b]	Registry no.	Yield,[c] %
$C_6H_5COCH_2Br$	70-11-1	$C_6H_5COCH_3$	98-86-2	90
	822-85-5		108-94-1	92
$CH_3(CH_2)_3CH(Br)COOCH_3$		$CH_3(CH_2)_4COOCH_3$	106-70-7	81
$C_6H_5CH(Br)C_6H_5$	776-74-9	$C_6H_5CH_2C_6H_5$	101-81-5	85
$C_6H_5CH(Br)CH(Br)C_6H_5$	5789-30-0	*trans*-$C_6H_5CH{=}CHC_6H_5$	103-30-0	85

[a] The reaction were performed in THF at room temperature for 5 h. [b] Products were identified by comparison with authentic samples. [c] Yields were determined by GLC internal standard method. [d] At reflux.

We have also found that the reaction of polymer-supported $HFe(CO)_4^-$ anion **3** with certain types of halides gives the dehalogenated product in good to excellent yields (Table II): α-bromo ketones, esters, and aromatic bromide functionalities are employed as substrates.[7]

The reaction is performed in THF at room temperature for 5 h and once more the product is easily recovered from the mixture by simple filtration.

We can conclude that ease of workup and greater effectiveness are the general features of the reactions described above, which were developed as part of a program carried out in our laboratory with the trend to demonstrate the usefulness of polymer-supported anions in organic synthesis.

Experimental Section

General. ^1H NMR spectra were measured in $CDCl_3$ solution by a Perkin-Elmer R1 2B instrument with tetramethylsilane as internal standard. Infrared spectra were recorded on a Perkin-Elmer Model 7108 infrared spectrophotometer and the mass spectra (MS) were taken on a Varian Mat III (70 eV). Vapor-phase chromatography was performed on a Hewlett-Packard 5750 instrument equipped with 5% SE 30 stainless steel column (10 ft × 0.25 in.). Anhydrous diethyl ether and tetrahydrofuran (THF) were obtained by distillation from sodium wires and then from $LiAlH_4$.

Preparation of the Polymer-Supported $HFe(CO)_4^-$ Reagent. To a stirred solution of KOH (5.6 g, 100 mmol) in water–ethanol 50:50 (100 mL) pentacarbonyliron (4.5 mL, 33 mmol) was added under argon. The mixture was stirred for 2 h under reflux. To this red-brown solution 24 g of Amberlyst A-26 (chloride form ion-exchange resin, Rohm and Haas, as purchased) was added.

After stirring for 15 min the exchange was complete and the tetracarbonylhydridoferrate anion was bound on the polymer support and the liquid phase appeared colorless: we can hence assume for our resin a capacity of about 1.5 mmol/g. After rinsing with deaerated water to neutrality and then with dry methanol and dry ether, the resin was dried by blowing with argon and then was directly used for the reaction in order to avoid traces of iron complexes in the solution.

Efforts to regenerate the resin, at the moment, failed to give useful, reproducible results.

Pelargonaldehyde from *n*-Octyl Bromide (General Procedure). The polymer-supported tetracarbonylhydridoferrate anion (**3**; 33 mmol), obtained as previously described, was transferred into a reaction flask equipped with a mechanical stirrer, reflux condenser, and argon inlet. *n*-Octyl bromide (11 mmol) was added along with THF (50 mL) and the mixture was refluxed for 4 h, following the starting material conversion by GLC. As soon as the reaction was complete, the resin was filtered off and the filtrate slowly distilled under reduced pressure to remove the solvent. Bulb-to-bulb distillation of the residue affords 1.40 g of pelargonaldehyde (90%): IR (neat) 1720 (C=O); NMR ($CDCl_3$) δ 0.9 (m, CH_3), 1.2–1.9 (m, $(CH_2)_6$), 2.1–2.5 (m, CH_2CHO), 9.8 (CHO); MS *m/e* 142 (M^+).

Acetophenone from ω-Bromoacetophenone (General Procedure). The polymer-supported tetracarbonylhydridoferrate anion (**3**; 33 mmol) was added to ω-bromoacetophenone (11 mmol) in THF (50 mL). After stirring for a 4 h at room temperature, the resin was filtered off and the solvent carefully removed by distillation under reduced pressure. Bulb-to-bulb distillation of the residue affords 1.2 g of acetophenone (90%) identified by comparison with an authentic sample.

Registry No.—Iron carbonyl complex, 18716-80-8.

References and Notes

(1) J. P. Collman, *Acc. Chem. Res.*, **8**, 342 (1975); G. P. Boldrini, M. Panunzio, and A. Umani-Ronchi, *J. Chem. Soc., Chem. Commun.*, 359 (1974); *Synthesis*, 733 (1974); Y. Watanabe, M. Yamashita, M. Igami, T. Mitsudo, and Y. Takegami, *Bull. Chem. Soc. Jpn.*, **49**, 2824 (1976).
(2) G. Cainelli, M. Panunzio, and A. Umani-Ronchi, *J. Chem. Soc., Perkin Trans. 1*, 1273 (1975).
(3) J. P. Collman, S. R. Winter, and D. R. Clark, *J. Am. Chem. Soc.*, **94**, 1788 (1972).
(4) M. P. Cooke, Jr., *J. Am. Chem. Soc.*, **92**, 6080 (1970).
(5) P. Krumholz and H. M. A. Stettiner, *J. Am. Chem. Soc.*, **71**, 3035 (1949).
(6) G. Cainelli, F. Manescalchi, and M. Panunzio, *Synthesis*, 472 (1976).
(7) H. Alper, *Tetrahedron Lett.*, 2257 (1975).
(8) H. C. Brown and R. A. Coleman, *J. Am. Chem. Soc.*, **91**, 4606 (1969).

m-Chloroperbenzoic Acid Oxidation of 2-Trimethylsilyloxy-1,3-dienes. Synthesis of α-Hydroxy and α-Acetoxy Enones

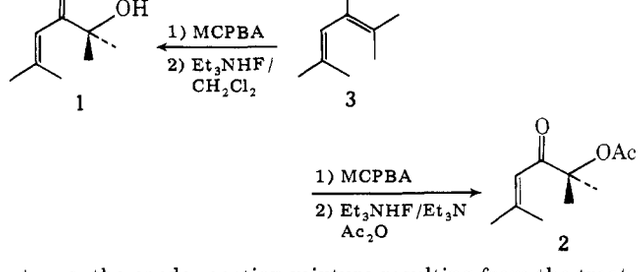
G. M. Rubottom* and J. M. Gruber

Department of Chemistry, University of Idaho, Moscow, Idaho 83843

Received August 16, 1977

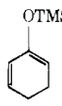
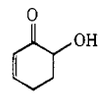
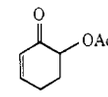
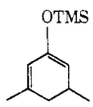
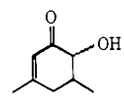
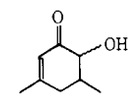
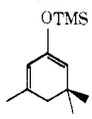
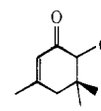
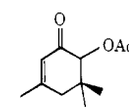
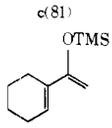
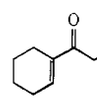
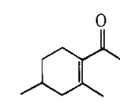
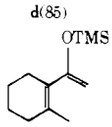
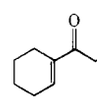
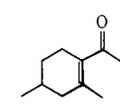
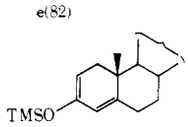
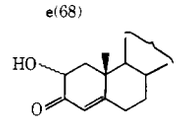
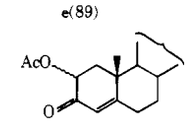
Synthetic methods for the introduction of oxygen functionality to the α-carbon of enone systems have relied almost exclusively upon treatment of the appropriate enone with lead(IV) acetate (LTA).[1] However, erratic yields as well as high reaction temperatures mitigate against the general use of this procedure. Since α-oxygenated enones continue to serve as important synthetic intermediates, as evidenced by recent syntheses of acorenone-B,[2] pyroangolensolide,[3] and prostaglandin anologues,[4] improved methods for the production of these useful compounds should be welcomed.

We report an efficient and extremely mild method for the preparation of both α-hydroxy enones (**1**) and α-acetoxy enones (**2**). Treatment of 2-trimethylsilyloxy-1,3-dienes (**3**) with *m*-chloroperbenzoic acid (MCPBA), followed by hydrolysis or acetylation, affords **1** or **2**, respectively. In the former instance, the crude reaction mixture resulting from the treatment of **3** with MCPBA is separated from the *m*-chlorobenzoic acid and the solvent (hexane) removed in vacuo. Treatment of the crude residue with a a methylene chloride solution of triethylammonium fluoride,[5] followed by aqueous workup,



0022-3263/78/1943-1599$01.00/0 © 1978 American Chemical Society

Table I. MCPBA Oxidation of 2-Trimethylsilyloxy-1,3-dienes 3

Isolated 3 from corresponding enone (% yield)	Registry no.	Isolated 1 (% yield)	Registry no.	Isolated 2 (% yield)	Registry no.
 a(80)	54781-19-0	 a(70)	65311-22-0	 a(60)	55444-14-9
 b(86)	65311-20-8	 b/b′[a](87)		 b/b′[a](80)	
 c(81)	54781-28-1	 c(82)	61592-66-3	 c(98)	19019-49-9
 d(85)	54781-35-0	 d(83)	65311-19-5	 d(74)	65311-23-1
 e(82)	65311-21-9	 e(68)	65311-18-4	 e(89)	65311-14-0
 f[b]	62017-99-60	 f(2α)/f(2β)′[a](80)[c]		 f(2β); f′(2α) (44);[c] (29)[c]	

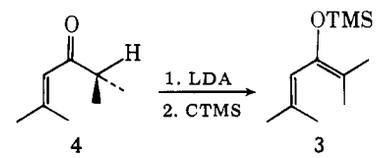
[a] Mixture of cis/trans isomers; registry no.: **1b,** 65311-16-2; **1b′,** 65311-17-3, **1f**(2α)571-15-3; **1f**(2β)′, 65375-81-7; **2b,** 55519-03-4; **2b′,** 55444-10-5. [b] Not isolated; see Experimental Section. [c] Yield based on cholest-4-en-3-one; registry no.: **2f,** 65311-15-1; **2f′** 2066-08-2.

affords **1** in excellent yields (see Table I). If, on the other hand, the crude reaction mixture, free of *m*-chlorobenzoic acid and hexane, is allowed to react with a solution of triethylammonium fluoride and triethylamine in acetic anhydride, excellent yields of **2** result (see Table I).

In all examples, oxidation occurred only at the 1,2-double bond in **3.** This phenomenon is general for these systems, as evidenced by the reaction of **3** with Simmons–Smith reagent[6] and halogen.[7] It should be noted that lead(IV) benzoate, in certain cases, adds to **3** in a 1,4 manner.[8] Further, in the present work, no evidence of products arising from the oxidation of both double bonds in **3** was obtained.

Yields of **2f** and **2f′** represent a substantial increase over those reported for the LTA reaction with Δ^4-cholestenone,[9] and the mildness of the procedures outlined allows isolation of labile compounds such as **1a,b,b′,** and **2a,b,b′,** again in high yield. Although the regiospecificity of the transformation is excellent, **3b** and **3f** gave cis–trans mixtures of both the α-hydroxy enones as well as the α-acetoxy enones (see Experimental Section). With **3f,** the less stable 2β-acetoxy-Δ^4-cholestenone (**2f**) predominated (44%), while the more stable 2α-isomer **2f′** was obtained in 29% yield. The isolation of **2** represents the highest reported yield for the transformation of a steroidal enone into its 2β-acetoxy derivative.[10]

Starting materials **3** were conveniently prepared by a modification of the method used by Ainsworth for the production of alkyl trimethylsilyl ketene ketals[11] (eq 1). Kinetically controlled proton removal from **4** was effected with strong base (LDA) and the resulting carbanions were quenched with chlorotrimethylsilane (CTMS). Nonaqueous



4 3 (1)

workup affords **3** in excellent yields (see Experimental Section).

The lability of **3f** led us to conduct the oxidation reactions on the crude diene. Yields of **1f/1f′** and **2f/2f′** indicate that isolation of **3** is not necessary in the work reported.

Although no mechanstic studies were attempted, the MCPBA reactions of **3** most likely follow a pathway previously noted for the reaction of trialkylsilyl enol ethers with MCPBA.[12]

Experimental Section

General. Melting points were determined with a Thomas-Hoover capillary melting-point apparatus and are uncorrected. Proton magnetic resonance (NMR) spectra were recorded at 60 MHz on a Varian Anaspect EM 360 spectrometer using tetramethylsilane as an internal standard. Infrared spectra (IR) were obtained on a Perkin-Elmer 621 grating infrared spectrometer. Low-resolution mass spectral data (MS) were obtained with a Perkin-Elmer RMU 6E instrument at 15 eV and are recorded as *m/e* with the relative abundance in parentheses. Elemental microanalysis were determined with a Perkin-Elmer 240 elemental analyzer. For column chromatography, silica gel Woelm, 0.032–0.063 mm (ICN Pharmaceuticals GmbH & Co.), was used. The MCPBA (tech, 85%) was purchased from Aldrich Chemical Co., Inc. The triethylammonium fluoride was obtained as a white solid (very hygroscopic) by the procedure of Hunig.[13] Anhydrous magnesium sulfate was employed as a drying agent.

Preparation of 2-Trimethylsilyloxy-1,3-dienes (3).[11] General Procedure. To a solution of 5.10 g (50.5 mmol) of diisopropylamine in 100 mL of dry DME under an atmosphere of nitrogen was added, at −15 °C (ice–methanol bath), 20.6 mL (49.5 mmol) of *n*-butyllithium (2.4 M in hexane). Then, 45.4 mmol of enone **4** was added dropwise over 5 min. After 10 min of stirring at −15 °C, 11 mL (87 mmol) of CTMS was added rapidly. After stirring for 2 h at room temperature, the solvent was removed in vacuo (rotoevaporation), followed by the addition of 75 mL of pentane. Filtration and removal of the pentane in vacuo yielded crude **3**. Reduced pressure distillation afforded pure **3**.

4,6-Dimethyl-2-trimethylsilyloxycyclohexa-1,3-diene (3b): 86%; bp 81.5–85.0 °C (9.5 mm); IR (neat) 1660, 1605 cm^{-1}; NMR (CCl_4) δ 0.18 (s, 9 H), 1.00 (d, 3 H, J = 7 Hz), 1.80 (s, 3 H), 2.00 (br d, 2 H, J = 7 Hz), 2.25 (m, 1 H), 4.40 (m, 1 H(: MS *m/e* 197 (15), 196 (M^+, 88), 182 (17), 181 (100), 165 (23), 82 (14), 75 (10), 73 (21), metastables 167.5, 151.

Anal. Calcd for $C_{11}H_{20}OSi$: C, 67.28; H, 10.27. Found: C, 67.11; H, 10.56.

4,6,6-Trimethyl-2-trimethylsilyloxycyclohexa-1,3-diene (3c): 81%; bp 54–57 °C (1.5 mm); lit.[7] bp 45–47 °C (0.05 mm).

1-(α-Trimethylsilyloxyvinyl)cyclohexene (3d): 85%; bp 85–89 °C (4.8 mm) lit.[14] bp 111–115 °C (18 mm).

1-(α-Trimethylsilyloxyvinyl)-2-methylcyclohexene (3e): 82%; bp 67–70 °C (1.6 mm); IR (neat) 1620 (sh), 1610 cm^{-1}; NMR (CCl_4) δ 0.19 (s, 9 H), 1.4–2.3 (m, 11 H), 4.00 (s, 1 H), 4.23 (s, 1 H); MS *m/e* 211 (18), 210 (M^+, 100), 196 (18), 195 (84), metastable 181.5.

Anal. Calcd for $C_{12}H_{22}OSi$: C, 68.50; H, 10.54. Found: C, 68.62; H, 10.71.

2-Trimethylsilyloxcyclohexa-1,3-diene (3a). Prepared by the method outlined by Conia.[6] A detailed procedure is given in reference 8: 80%; bp 56–58 °C (6.0 mm); lit.[9a] bp 33–37 °C (0.01 mm).

The MCPBA Oxidation–Hydrolysis of 2-Trimethylsilyloxy-1,3-dienes (3). General Procedure. To a prestirred solution (20 min at room temperature) of 450 mg (2.2 mmol) of MCPBA in 30 mL of hexane at −15 °C (ice–methanol bath) was added 2.0 mmol of **3** in 1 mL of hexane. After stirring for 1 h at room temperature, the reaction mixture was filtered and the hexane removed in vacuo. The residual MCPBA precipitated and was removed by filtration with the aid of 3–5 mL of pentane. Then, 75 mL of methylene chloride and 725 mg (6.0 mmol) of triethylammonium fluoride were added. After 5–10 h at room temperature, the reaction mixture was extracted sucessively with 15 mL of aqueous sodium bicarbonate, 15 mL of 1.5 N hydrochloride acid, and 15 mL of aqueous sodium bicarbonate. Drying, filtration, and removal of solvent in vacuo afforded crude **1**. Pure **1** was obtained via the methods noted for the specific cases below.

6-Hydroxy-2-cyclohexen-1-one (1a). Molecular distillation of crude **1a** at 100 °C (20 mm) gave 158 mg (70%) of **1a:** IR (neat) 3485, 1685, 1615 cm^{-1}; NMR (CCl_4) δ 1.5–2.8 (m, 4 H), 3.66 (s, 1 H–OH), 4.04 (AB q, 1 H, J = 6, 15 Hz), 5.98 (br d, 1 H, J = 10 Hz), 6.73–7.10 (m, 1 H); MS *m/e* 112 (M^+, 28), 84 (29), 68 (10), 67 (100), metastable 63.

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.51; H, 7.13.

***cis/trans*-3,5-Dimethyl-6-hydroxy-2-cyclohexen-1-one (1b/1b').** Molecular distillation of crude **1b/1b'** at 130 °C (15 mm) yielded 244 mg (87%) of a 60:40 mixture of *cis*-**1b**/*trans*-**1b** (NMR analysis): IR (neat) 3470, 1670, 1630 cm^{-1}; NMR (CCl_4) δ 0.87 (d, J = Hz, cis 3 H), 1.19 (d, J = 7 Hz, trans 3 H), 1.7–3.0 (m, 3 H), 1.99 (s, 3 H), 3.56 (br s, 1 H, –OH), 3.60 (d, J = 5 Hz, cis 1 H), 5.85 (br s, 1 H); MS *m/e* 140 (M^+, 15), 83 (10), 82 (100).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.62, H, 8.83.

6-Hydroxy-3,5,5-trimethyl-2-cyclohexen-1-one (1c). Molecular distillation of crude **1c** at 100 °C (5 mm) gave 248 mg (82%) of **1c:** mp 43–44 °C (hexane); lit.[15] mp 45–46 °C.

1-(α-Hydroxyacetyl)cyclohexene (1d). Molecular distillation of crude **1d** at 140 °C (15 mm) yielded 231 mg (83%) of **1d:** IR (neat) 3480, 1670, 1628 cm^{-1}; NMR (CCl_4) δ 1.4–2.5 (m, 8 H), 3.2 (s, 1 H, –OH), 4.37 (s, 2 H), 6.80 (m, 1 H); MS *m/e* 140 (M^+, 12), 110 (10), 109 (100), 81 (25), metastable 60.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.64; H, 8.75.

1-(α-Hydroxyacetyl)-2-methylcyclohexene (1e). Column chromatography (silica gel; hexane/ethyl acetate, 7:1) yielded 210 mg (68%) of **1e.** An analytical sample was obtained by molecular distillation of 150 °C (15 mm): IR (neat) 3440, 1676, 1607 cm^{-1}; NMR (CCl_4) δ 1.43–1.80 (m, 4 H), 1.98 (s, 3 H), 2.0–2.4 (m, 4 H), 3.3 (br s, 1 H, –OH), 4.19 (s, 2 H); MS *m/e* 154 (M^+, 8), 124 (10), 123 (100), 111 (8), 95 (32), 67 (8), metastable 73.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.08; H, 9.39.

2α/2β-Hydroxycholest-4-en-3-one (1f/1f').[16] The general procedure cited for the synthesis of **3** was applied using 1.15 g (2.97 mmol) of cholest-4-en-3-one (mp 80.5–81.5 °C) to prepare a pentane solution of **3f** (10 mL) which was used directly in the MCPBA reaction. Crystallization from hexane yielded 950 mg (80%) of **1f/1f',** mp 124–130 °C. Recrystallization from methanol furnished an analytical sample of the 2α/2β mixture: mp 139.0–139.5 °C; IR (KBr) 3400, 1675, 1610 cm^{-1}; NMR ($CDCl_3$) δ 0.72 (s), 0.80 (s), 0.98 (s), 1.30 (s), 4.0–4.6 (m, 8 lines, 1 H), 5.79 (s, 1 H), 3.55 (br s, 1 H, –OH); MS *m/e* 401 (31), 400 (M^+, 100), 357 (28), 356 (93).

Anal. Calcd for $C_{27}H_{44}O_2$: C, 80.69; H, 11.02.

The MCPBA Oxidation–Acetylation of 2-Trimethylsilyloxy-1,3-dienes (3). General Procedure. To a prestirred solution (20 min at room temperature) of 450 mg (2.2 mmol) of MCPBA in 30 mL of hexane at −15 °C (ice–methanol bath) was added 2.0 mmol of **3** in 1 mL of hexane. After stirring for 1 h at room temperature, the reaction mixture was diluted with 50 mL of hexane and extracted with aqueous sodium bicarbonate (2×, 20 mL). After drying, filtration, and removal of solvent in vacuo, 8 mL of acetic anhydride, 725 mg (6.0 mmol) of triethylammonium fluoride, and 1 mL of triethylamine were added. This solution was stirred for 12 h and then partitioned between 50 mL of aqueous sodium bicarbonate and 75 mL of ether. Additional solid sodium bicarbonate was added as required to complete the hydrolysis of the acetic anhydride. The ethereal solution was washed with 20 mL of water, 20 mL of 1.5 N hydrochloric acid, and 20 mL of aqueous sodium bicarbonate. The aqueous washes were extracted with an additional 30 mL of ether. The ether extracts were combined, dried, filtered, and concentrated in vacuo to afford crude **2.** Pure **2** was obtained as noted below.

6-Acetoxy-2-cyclohexen-1-one (2a). Molecular distillation of crude **2a** at 100 °C (10 mm) yielded 185 mg (60%) of **2a:** NMR (CCl_4) δ 5.20 (AB q, 1 H, J = 7, 12 Hz), lit.[1b] 5.20 (AB q, 1 H, J = 6.6, 12.0 Hz).

***cis/trans*-6-Acetoxy-3,5-dimethyl-2-cyclohexen-1-one (2b/2b').** Molecular distillation of crude **2b/2b'** at 150 °C (5 mm) afforded 291 mg (80%) of **2b/2b'** as a 60:40 mixture: NMR (CCl_4) δ 5.07 (2d, 1 H, J = 5, 13 Hz), lit.[17] 5.07 (2d, 1 H, J = 4.7, 12.5 Hz).

6-Acetoxy-3,5,5-trimethyl-2-cyclohexen-1-one (2c). With the acetylation reaction time extended to 48 h, removal of solvent yielded 385 mg (98%) of crystalline **2c:** mp 76.5–77.5 °C (hexene); lit.[15] mp 76–78 °C.

1-(α-Acetoxyacetyl)cyclohexene (2d). Molecular distillation of crude **2d** at 160 °C (5 mm) yielded 270 mg (74%) of **2d:** IR (neat) 1750, 1685, 1635 cm^{-1}; NMR ($CDCl_3$) δ 1.5–1.8 (m, 4 H), 2.0–2.45 (m, 4 H), 2.20 (s, 3 H), 5.03 (s, 2 H), 6.85 (m, 1 H); MS *m/e* 182 (M^+, 3), 140 (18), 109 (100), 81 (33), 43 (26).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.75; H, 7.93.

1-(α-Acetoxyacetyl)-2-methylcyclohexene (2e). Molecular distillation of crude **2e** at 160 °C (1 mm) afforded 347 mg (89%) of **2e:** IR (neat) 1750, 1695, 1610 cm^{-1}; NMR (CCl_4) δ 1.5–1.75 (m, 4 H), 1.84 (br s, 3 H), 2.0–2.2 (m, 4 H), 2.10 (s, 3 H), 4.62 (s, 2 H); MS *m/e* 196 (M^+, 5), 136 (7), 123 (100), 95 (26), metastable 73.5.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.33; H, 8.25.

2β-Acetoxycholest-4-en-3-one (2f) and 2α-Acetoxycholest-4-en-3-one (2f'). The procedure cited for the preparation of **1f/1f'** was followed. Methylene chloride was used as a solvent (enough to produce a homogeneous solution) in the acetylation procedure (48 h). Column chromatography of 24% of the crude material (silica gel; hexane/ethyl acetate, 9:1) afforded 136 mg (44%) of **2f** and 89 mg (29%) of **2f'.**

Compound 2f: mp 104.5–105.5 °C (petroleum ether); IR (KBr) 1748, 1680, 1620 cm^{-1}; NMR ($CDCl_3$) δ 0.70 (s), 0.08 (s) 1.18 (s), 2.12 (s, 3 H), 5.30 (AB q, 1 H, J = 12, 6 Hz), 5.76 (s, 1 H); MS *m/e* 442 (M^+, 16), 383 (27), 382 (87) 356 (26), 270 (13), 123 (10), 122 (100), metastable 331.

Anal. Calcd for $C_{29}H_{46}O_3$: C, 78.68; H, 10.47. Found: C, 78.85; H, 10.62.

Compound 2f': mp 137–138 °C (lit.[18] 140.5–141.5 °C); NMR ($CDCl_3$) δ 5.45 (AB q, 1 H, J = 14, 6 Hz), lit.[18] 5.44 (AB q, 1 H, J = 14, 6 Hz).

Acknowledgment. The authors thank the Research Council of the University of Idaho for financial support of this work.

Registry No.—**4a,** 930-68-7; **4b,** 1123-09-7; **4c,** 78-59-1; **4d,** 932-66-1; **4e,** 2047-97-4; **4f,** 601-57-0; CTMS, 75-77-4; MCPBA, 937-14-4.

References and Notes

(1) (a) W. Oppolzer, T. Sarkar, and K. K. Mahalanabis, *Helv. Chim. Acta*, **59**, 2012 (1976); (b) G. A. Russel, R. L. Blankespoor, K. D. Trakanovsky, C. S. C. Chung, P. R. Whittle, J. Mattox, C. L. Myers, R. Penny, T. Ku, Y. Kosugi, and R. S. Givens, *J. Am. Chem. Soc.*, **97**, 1906 (1975); (c) D. J. Rawlinson and G. Sosnovsky, *Synthesis*, 567 (1973); (d) R. Criegee in "Oxidation in Organic Chemistry", Part A, K. B. Wiberg, Ed., Academic Press, New York, N.Y., 1965, p 277.
(2) W. Oppolzer and K. K. Mahalanabis, *Tetrahedron Lett.*, 3411 (1974).
(3) Y. Fukuyama and T. Tokoroyama, *Tetrahedron Lett.*, 4869 (1973).
(4) A. Barco, S. Benetti, G. P. Pollini, P. G. Baraldi, M. Guarneri, and C. B. Vincentini, *Synth. Commun.*, **7**, 13 (1977).
(5) S. Hunig and G. Wehner, *Synthesis*, 391 (1975).
(6) C. Girard and J. M. Conia, *Tetrahedron Lett.*, 3327 (1973).
(7) L. Blanco, P. Amice, and J. M. Conia, *Synthesis*, 194 (1976).
(8) G. M. Rubottom and J. M. Gruber, *J. Org. Chem.*, **42**, 1051 (1977).
(9) (a) F. Seebeck and T. Reichstein, *Helv. Chim. Acta*, **27**, 948 (1944); (b) L. F. Fieser and M. A. Romero, *J. Am. Chem. Soc.*, **75**, 4716 (1953).
(10) (a) R. D. Burnett and D. N. Kirk, *J. Chem. Soc., Perkin Trans. 1*, 284 (1974); (b) R. D. Burnett and D. N. Kirk, *ibid.*, 1830 (1973).
(11) C. Ainsworth, F. Chen, and Y. N. Kuo, *J. Organomet. Chem.*, **46**, 59 (1972).
(12) (a) G. M. Rubottom, M. A. Vazquez, and D. R. Pelegrina, *Tetrahedron Lett.*, 4319 (1974); (b) A. G. Brook and D. M. Macrae, *J. Organomet. Chem.*, **77**, 619 (1974); (c) A. Hassner, R. H. Reuss, and H. W. Pinnick, *J. Org. Chem.*, **40**, 3427 (1975); (d) G. M. Rubottom and R. Marrero, *ibid.*, **40**, 3783 (1975); (e) R. K. Boeckman, Jr., and M. Ramaiah, *ibid.*, **42**, 1581 (1977); (f) R. A. Amos and J. A. Katzenellenbogen, *ibid.*, **42**, 2537 (1977).
(13) S. Hunig and G. Wehner, *Synthesis*, 180 (1975).
(14) C. Symmes, Jr., and L. B. Quinn, *J. Org. Chem.*, **41**, 238 (1976).
(15) A. W. Fort, *J. Org. Chem.*, **26**, 332 (1961).
(16) M. Tomoeda, M. Ishizaki, H. Kubayashi, S. Kanatomo, T. Koga, M. Inuzuka, and T. Furuta, *Tetrahedron*, **21**, 733 (1965).
(17) J. W. Ellis, *J. Org. Chem.*, **34**, 1154 (1969).
(18) T. Koga and M. Tomoeda, *J. Chem. Soc., Perkin Trans 1*, 1848 (1973).

Reactions of 2-Methyl-2*H*-cyclopenta[*d*]pyridazines with Nitration Reagents, Mercuric Acetate, and Tetracyanoethene[1,2]

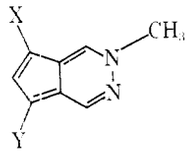
Arthur G. Anderson, Jr.,* David M. Forkey,[3] and Larry D. Grina[4]

Department of Chemistry, University of Washington, Seattle, Washington 98195

Received September 14, 1977

Azulene readily underwent mononitration on reaction with cupric nitrate and acetic anhydride,[5] tetranitromethane,[6] or nitric acid and acetic anhydride[6] with the last reagent also effecting dinitration. Mononitration of cyclopenta[*c*]thiapyran was accomplished with tetranitromethane.[7] Studies on the reactions of 2*H*-cyclopenta[*d*]pyridazines have shown that this system is also very reactive to electrophilic acylation,[8] halogenation,[9] and diazonium coupling,[10] so it was anticipated that direct nitration would occur with difficulty.

Treatment of 2-methyl-2*H*-cyclopenta[*d*]pyridazine (1) with tetranitromethane in methanol and pyridine gave extensive decomposition, Me_2SO alone gave > 90% recovery of unchanged 1, and Me_2SO plus triethylamine gave 10% recovered 1 and 7% of a mixture. The NMR spectrum showed the major components to be the 5- and 7-nitro derivatives (2 and 3) in a ratio of 1:3. Attempts to separate pure 2 and 3 failed. Attempts to introduce the nitro group with a mixture of nitric, acetic, and sulfuric acids gave unchanged 1 at room temperature and complete decomposition when warmed. Reaction with cupric nitrate and acetic anhydride at −78 °C gave a very low yield of an impure mixture of 2 and 3 and longer periods formed a tar, as did treatment of 1 with nitronium tetrafluoroborate in acetonitrile.



1, X = Y = H
2, X = H; Y = NO_2
3, X = NO_2; Y = H
4, X = Br; Y = NO_2
5, X = NO_2; Y = Br
6, X = NO_2; Y = I
7, X = I; Y = NO_2
8, X = Y = HgOAc
9, X = C(CN)=C(CN)$_2$; Y = H
10, X = H; Y = C(CN)=C(CN)$_2$

The sole route to a pure nitro derivative of 1 found was the reaction of the 7-bromo compound with silver nitrite, a method which had been discovered with 1,3-dibromoazulene and 5,7-dichlorocyclopenta[*c*]thiapyran in earlier work.[7] In the present case a 75% yield of 3 was obtained. Attempts to achieve dinitration of 3 led to decomposition. As was found for the dibromoazulene and dichlorocyclopenta[*c*]thiapyran compounds, treatment of the 5,7-dibromo derivative of 1 with excess silver nitrite effected the substitution of only one bromine per molecule and a mixture of the 5-nitro-7-bromo (4) and 5-bromo-7-nitro (5) products (79%) was obtained. That the presence of the strongly electron-withdrawing group in 5 and 6 was responsible for the inertness of the second bromine[7] was reaffirmed by the fact that the 5-trifluoroacetyl-7-bromo compound[9] gave no reaction with silver nitrite in 30 h. The 5,7-diiodo derivative of 1 also gave a mixture of the 5-nitro-7-iodo (7) and 5-iodo-7-nitro (6) products. Attempts to separate 4 from 5 and 6 from 7 were not successful.

The reaction of 1 with mercuric chloride gave a product which appeared to be a complex of the expected 5,7-bis(chloromercuri) derivative[11] with mercuric chloride. Reaction with 2 equiv of mercuric acetate, however, gave a 65% yield of the 5,7-diacetoxymercuri compound (8). The use of excess mercuric acetate resulted in no separation of 8 from the solution, and 8 was redissolved by the reagent, again indicating complexation. An attempt to convert 8 to the 5,7-dibromo derivative by reaction with NBS gave a small amount of impure material which contained (spectral identification) the expected product.

Azulene reacts with tetracyanoethene to give the substitution product, 1-azulyltricyanoethene.[12] This mode of reaction was also found for 1 and the 7-tricyanoethenyl compound (9) was isolated in 41% yield. Also obtained was a small amount (4%) of product spectrally (NMR, IR, mass spectrum) characterized as the isomeric 5-tricyanoethenyl derivative (10). The low solubility of 9 and 10 made their separation difficult. The immediate and pronounced darkening of the color observed upon contact of 1 with tetracyanoethene was consistent with the intermediacy of a charge transfer or π complex,[13] and it is suggested that the nonsubstitution reactions of 1 with the reagents for direct nitration wherein darkening also occurred might have involved an electron transfer from 1 to the electrophilic species.

Experimental Section[14]

7-Nitro-2-methyl-2*H*-cyclopenta[*d*]pyridazine (3). A mixture of 34.5 mg (0.164 mmol) of 7-bromo-2-methyl-2*H*-cyclopenta[*d*]-pyridazine[9] and 575.7 mg (3.74 mmol) of $AgNO_2$ in 14 mL of Me_2SO was heated (steam bath) for 16 h under a N_2 atmosphere and then shaken with 50 mL of H_2O and 50 mL of CH_2Cl_2. The resultant mixture was filtered and the filtrate phases were separated. The aqueous layer was extracted with CH_2Cl_2 and the solvent was removed from the combined, washed (H_2O), dried, and filtered organic solutions. Chromatography (silica gel plate, 4:1 $HCCl_3$–ether) separated two fractions, the first of which was unchanged starting material. The second yielded 21.7 mg (75%) of 3 as yellow needles: softening and sublimation at 164–169 °C; mp 170–171 °C; NMR (acetone) δ 9.72 (s, 1, H-4), 9.18 (s, 1, H-1), 7.9 (d, 1, H-6, J = 4 Hz), 6.77 (d, 1, H-5, J = 4 Hz), and 4.60 (s, 3, N–CH_3); UV (ether) ($\epsilon \times 10^{-3}$) 243 (24), 267 (12), 272 (sh, 11), 292 (5.3), 336 (8.3), 349 (sh, 6.4), and 416 nm (11). Anal. Calcd for $C_8H_7N_3O_2$: C, 54.24; H, 3.95. Found: C, 54.07; H, 4.12.

Reaction of 1 with Tetranitromethane. A solution of 3.0 mL (1.5 mmol) of 0.5 M tetranitromethane in methanol was added (30 min) to 109.3 mg (0.829 mmol) of 1 in 3 mL of Me_2SO and 0.5 mL of tri-

0022-3263/78/1943-1602$01.00/0 © 1978 American Chemical Society