$C_{10}H_{16}O_4N_2$: C, 52.62; H, 7.07; N, 12.27. Found: C, 52.89; H, 7.16; N, 12.25.

The procedure applied to crotonaldehyde and ethyl diazoacetate, followed by acetylation, produced 4.1 g of oil, the rapid filtration of whose 9:1 hexane–ethyl acetate solution through 200 g of neutral alumina (activity III) yielded 2.1 g of yellow, liquid ester **3:** IR 4.75 (s, N_2), 5.75, 5.88 (s, C=O) μm; ^{1}H NMR δ 1.26 (t, 3, J = 7 Hz, Me of Et), 1.30 (d, 3, J = 7 Hz, Me), 2.06 (s, 3, Me of Ac), 4.20 (q, 2, J = 7 Hz, CH_2), 5.33 (dd, 1, J = 14, 7 Hz, δ-H), 5.43 (s, 1, OCH), 6.00 (d, 1, J = 14 Hz, γ-H).

Use of the procedure on acrolein and ethyl diazoacetate afforded 4.5 g of oil whose alumina filtration as in the case of ester **3** above led to 1.2 g of yellow, liquid hydroxy ester **6a:** IR 3.00 (m, OH), 4.80 (s, N_2), 5.94 (s, C=O) μm; ^{1}H NMR δ 1.23 (t, 3, J = 7 Hz, Me), 4.20 (q, 2, J = 7 Hz, OCH_2), 5.20 (s, 1, OCH), 5.3–6.1 (m, 3, CH, CH_2).

When the procedure was applied to crotonaldehyde and ethyl diazoacetate, it yielded 3.7 g of an oil whose alumina chromatography, following the above route for ester **3**, gave 2.4 g of yellow, liquid hydroxy ester **6b:** IR 2.98 (m, OH), 4.80 (s, N_2), 5.93 (s, C=O) μm; ^{1}H NMR δ 1.26 (t, 3, J = 7 Hz, Me of Et), 1.73 (d, 3, J = 6 Hz, Me), 4.20 (q, 2, J = 7 Hz, CH_2), 5.23 (s, 1, OCH), 5.4–6.1 (m, 2, $(CH)_2$).

General Procedure for Pyrolysis. All pyrolyses were carried out by passage of neat diazo esters down a vertical, 25-cm long 2-cm i.d. glass tube, filled with glass helices and kept at 280 °C under 0.25 Torr pressure, and the products were trapped in a receiver cooled by dry ice. (Pyrolyses of cyclohexane solutions or pyrolyses of the neat diazo esters at atmospheric pressure yielded substances of different structures than those below.)

The thermolysis of crude diester **1** yielded an oil whose distillation [at 70–75 °C (0.25 Torr)] produced 1.06 g of liquid, air-sensitive ester **2** (27% overall yield for the two reactions): IR 5.68, 5.86 (s, C=O), 6.10 (s, C=C) μm; ^{1}H NMR δ 1.06 (d, 6, J = 7 Hz, Me_2), 1.23 (t, 3, J = 7 Hz, Me of Et), 2.20 (s, 3, Me of Ac), 2.43 (pentet, 1, J = 7 Hz, CH), 4.06 (q, 2, J = 7 Hz, CH_2), 5.53 (s, 1, olefinic H). Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 60.05; H, 8.14.

After pyrolysis of pure diester **3** the heating chamber was washed with ethyl acetate and the washings were evaporated. Chromatography of the residue, 1.68 g, on 100 g of neutral alumina (activity III) and elution with 9:1 hexane–ethyl acetate yielded 0.31 g of unidentified material and then 1.05 g of viscous liquid pyrazole **4** (23% overall yield): IR 2.89 (w, NH), 5.82, 5.89 (s, C=O), 6.31 (m, C=C) μm; ^{1}H NMR δ 1.33 (t, 3, J = 7 Hz, Me of Et), 1.60 (d, 3, J = 6 Hz, Me), 2.06 (s, 3, Me of Ac), 4.33 (q, 2, J = 7 Hz, CH_2), 5.96 (q, 1, J = 6 Hz, OCH), 6.76 (s, 1, CH).

Pyrolysis of pure hydroxy ester **6a** yielded 0.55 g of keto ester **7a** (20% overall yield); IR and ^{1}H NMR spectra were identical with those reported earlier.[3c]

Pyrolysis of pure hydroxy ester **6b** and subsequent heating of the pyrolysate at 60 °C (30 Torr) for the removal of volatile, unidentified material gave 1.6 g of liquid keto ester **7b** (53% overall yield); IR and ^{1}H NMR spectra were identical with those quoted earlier.[3c]

Acknowledgment. The authors express their gratitude to the Squibb Institute for Medical Research for support of this work.

Registry No.—**1,** 67272-01-9; **2,** 67272-02-0; **3,** 67272-03-1; **4,** 67272-04-2; **6a,** 67272-05-3; **6b,** 67272-06-4; **7a,** 22418-80-0; **7b,** 17544-47-7; isobutyraldehyde, 78-84-2; ethyl diazoacetate, 623-73-4; crotonaldehyde, 4170-30-3; acrolein, 107-02-8.

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(5) **Note Added in Proof:** An alternate short synthesis of esters of type **7** is described by P. Pollet and S. Gelin, *Synthesis*, 142 (1978).

Oxidation of Substituted Hydroquinone Monoalkyl Ethers to *p*-Benzoquinone Monoketals

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Blocked benzoquinones are potentially attractive intermediates in synthesis, but until recently no widely applicable methods were known for their preparation. Cyanotrimethylsilyloxycyclohexadienones[2,3,4] and *p*-benzoquinone ketals have received most of the attention. Olefination of the latter class of compounds produced protected quinone methides,[5] and other transformations led to polycyclic biaryls.[6] Carbonium ions derived from *p*-quinone monoketals by carbon–oxygen heterolysis were found to undergo [2 + 4] cycloadditions with olefins.[7] The resulting adducts were easily transformed to neolignans[8] of the bicyclo[3.2.1]octane, hydrobenzofuran, and spiro[5.5]undecane types.

In the past, quinone ketals were prepared sporadically, usually in low yields, by the oxidation of 4-alkoxy- or 4-aryloxyphenols in alcohol with copper(II) species, ceric salts, silver oxide, manganese dioxide, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[9] Consequently, these reagents were used only rarely until McKillop and Taylor described their preparation using thallium(III) nitrate as the oxidant.[10]

We have prepared a number of *p*-quinone ketals by this procedure (see Table I) and noticed that the yield of the acid-sensitive products could be increased by performing the oxidations in the presence of suspended potassium bicarbonate (see Experimental Section). To replace the toxic thallium salt and also because ketals **9** and **15** were not available by this method, other oxidants were examined. Of those tried, DDQ and ferric chloride proved to be most satisfactory. To suppress acid-catalyzed transformations of the resulting ketals, it is advisable to perform the oxidations with ferric chloride in the presence of potassium carbonate. Some of the more highly oxygenated ketals display significant water solubility, and the yields given in Table I could undoubtedly be improved if continuous extraction was used in the workup procedure.

Experimental Section

Melting points were determined on a Reichert hot-stage microscope and are corrected. Proton magnetic resonance (^{1}H NMR) spectra (90 MHz) were recorded on a Perkin-Elmer R-22 spectrometer and are reported in parts per million (δ) downfield from tetramethylsilane as an internal standard. Mass spectra were determined on a Varian MAT 44 instrument. Ultraviolet (UV) spectra were obtained on a Perkin-Elmer 202 spectrometer. Infrared (IR) spectra were taken with a Perkin-Elmer 247 or 237B grating spectrometer. Elemental analyses were performed by Robertson Laboratory, Florham Park, N.J.

Physical Properties of the New *p*-Quinone Ketals. 2-Allyl-4-methoxy-4,5-methylenedioxycyclohexa-2,5-dienone (4): mp 49–50 °C (ether–pentane); IR ($CHCl_3$) 1690, 1655, 1630 cm^{-1}; NMR (CCl_4) δ 3.09 (br d, 2, J = 7 Hz, C=CCH$_2$), 3.26 (s, 3, –OCH$_3$), 4.98–5.26 (m, 2, CH$_2$=C), 5.49 (s, 1, –OCH$_2$O–), 5.55 (s, 1, –OCH$_2$O–), 5.60 (s, 1, CO—CH=C), 5.70–6.10 (m, 1, C=CH), 6.53 (t, 1, J = 1 Hz, C=CH); UV (95% EtOH) 237 nm (ε 9350), 295 (3200); mass spectrum (70 eV), *m/e* (relative intensity) 208 (M$^+$, 13), 69 (100); ^{13}C NMR ($CDCl_3$) δ 32.6 (t of m), 51.2 (q), 97.6 (br), 98.9 (d), 98.9 (t), 117.9 (t of m), 127.8 (d of t), 134.4 (d of m), 142.8 (br), 168.3 (s), 186.8 (s). Exact mass calcd for $C_{11}H_{12}O_4$: 208.07356. Found: 208.07275.

2-Allyl-4-(2-chloroethoxy)-4,5-methylenedioxycyclohexa-2,5-dienone (5): mp 105–106 °C (ether–pentane); IR ($CHCl_3$) 1690, 1655, 1630 cm^{-1}; NMR ($CDCl_3$) δ 3.15 (br d, 2, J = 7 Hz, C=CCH$_2$), 3.53–3.92 (m, 4, –OCH$_2$CH$_2$Cl), 5.04–5.32 (m, 2, CH$_2$=C), 5.66 (s, 1, –OCH$_2$O–), 5.68 (s, 1, –OCH$_2$O–), 5.82 (s, 1, CO—CH=), 5.73–6.13

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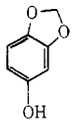
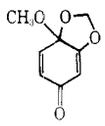
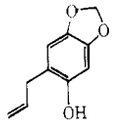
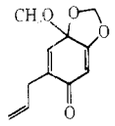
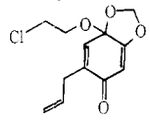
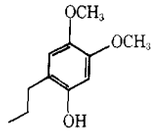
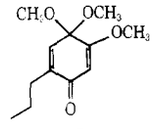
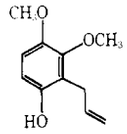
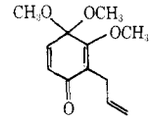
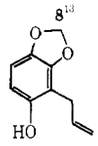
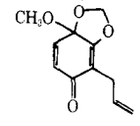
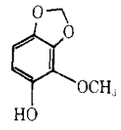
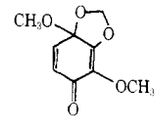
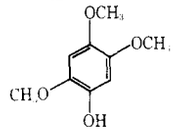
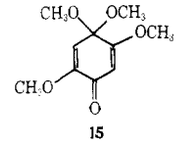
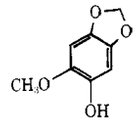
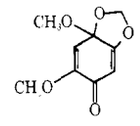
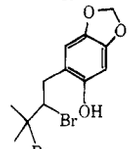
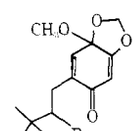
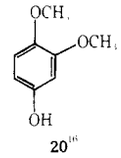
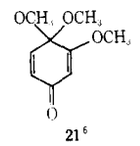
Table I

phenol	quinone ketal	yield, % DDQ	$FeCl_3$	$Tl(NO_3)_3$
 1	 2	<5	<5	83[a]
 3[7]	 4	88	84	78
	 5[7]	63		
 6[12]	 7	85	88	80
 8[13]	 9	75	0	0
 10[14]	 11	31	0	21
 12[15]	 13	57	0	68
 14[16]	 15	<5	78	0
 16[17]	 17	50	50	70
 18[18]	 19	97		
 20[16]	 21[6]	<5	<5	66

[a] Reference 10, 45%.

(m, 1, C=CH), 6.72 (t, 1, J = 7 Hz, C=CH); UV (95% EtOH) 239 nm (ϵ 9400), 296 (3000); mass spectrum (70 eV), m/e (relative intensity) 256 (M^+, 3), 228 (5), 226 (15), 191 (100), 69 (82). Anal. ($C_{12}H_{13}ClO_4$) C, H.

2-Propyl-4,4,5-trimethoxycyclohexa-2,5-dienone (7): mp 57–58 °C (ether–pentane); IR ($CHCl_3$) 1675, 1645, 1625 cm^{-1}; NMR (CCl_4) δ 0.95 (br t, 3, J = 7 Hz, CH_3C), 1.49 (m, 2, $-CH_2-$), 2.23 (br d, 2, J = 7 Hz, CH_2C=), 3.24 (s, 6, geminal OCH_3), 3.73 (s, 3, =C—OCH_3), 5.38 (s, 1, CO—CH=), 6.11 (br s, 1, C=CH); UV (95% EtOH) 235 nm (ϵ 12 300), 293 (3400); mass spectrum (70 eV), m/e (relative intensity) 226 (M^+, 6), 211 (32), 195 (73), 69 (100). Anal. ($C_{12}H_{18}O_4$) C, H.

2-Allyl-3,4,4-trimethoxycyclohexa-2,5-dienone (9): oil; IR (CCl_4) 1675, 1640, 1610 cm^{-1}; NMR (CCl_4) δ 3.03 (br d, 2, J = 6 Hz, C=CCH_2), 3.35 (s, 6, geminal OCH_3), 4.15 (s, 3, =C—OCH_3), 4.75–5.22 (m, 2, CH_2=C), 5.45–6.05 (m, 1, CH=C), 6.25 (d, 1, J = 10 Hz, CO—CH=), 6.47 (d, 1, J = 10 Hz, C=CH); UV (95% EtOH) 227 nm (ϵ 9100), 315 (3900); mass spectrum (70 eV), m/e (relative intensity) 224 (M^+, 11), 193 (57), 53 (100). Exact mass calcd for $C_{12}H_{16}O_4$: 224.10486. Found: 224.10649.

2-Allyl-4-methoxy-3,4-methylenedioxycyclohexa-2,5-dienone (11): oil; IR (CCl_4) 1700, 1660, 1615 cm^{-1}; NMR (CCl_4) δ 2.95 (br d, 2, J = 6 Hz, C=CCH_2), 3.25 (s, 3, $-OCH_3$), 4.73–5.17 (m, 2, CH_2=C), 5.53 (s, 1, $-OCH_2O-$), 5.58 (s, 1, $-OCH_2-$), 5.63–6.10 (m, 1, CH=C), 6.15 (d, 1, J = 10 Hz, CO—CH=), 6.70 (d, 1, J = 10 Hz, C=CH); UV (95% EtOH) 225 nm (ϵ 7200), 305 (3800); mass spectrum (70 eV), m/e (relative intensity) 208 (M^+, 6), 178 (100), 177 (59), 163 (52), 135 (66). Exact mass calcd for $C_{11}H_{12}O_4$: 208.07356. Found: 208.07298.

2,4-Dimethoxy-3,4-methylenedioxycyclohexa-2,5-dienone (13): mp 71–72 °C; IR (CCl_4) 1700, 1670, 1620 cm^{-1}; NMR (CCl_4) δ 3.28 (s, 3, C–OCH_3), 3.78 (s, 3, =C—OCH_3), 5.58 (s, 2, $-OCH_2O-$), 6.05 (d, 1, J = 10 Hz, CO—CH=), 6.78 (d, 1, J = 10 Hz, C=CH); UV (95% EtOH) 230 sh nm (ϵ 6200), 321 (3200); mass spectrum (70 eV), m/e (relative intensity) 198 (M^+, 5), 168 (100), 167 (72), 153 (57), 69 (94). Exact mass calcd for $C_9H_{10}O_5$: 198.05282. Found: 198.05355.

2,4,4,5-Tetramethoxycyclohexa-2,5-dienone (15): mp 158–159 °C (ethyl acetate); IR ($CHCl_3$) 1660, 1640, 1620 cm^{-1}; NMR ($CDCl_3$) δ 3.40 (s, 6, geminal OCH_3), 3.83 (s, 3, =C—OCH_3), 3.92 (s, 3, =C—OCH_3), 5.57 (s, 1, CO—CH=), 5.80 (s, 1, C=CH); UV (95% EtOH) 249 nm (ϵ 16 400), 304 (1800); mass spectrum (70 eV), m/e (relative intensity) 214 (M^+, 8), 199 (28), 183 (100), 171 (15), 155 (57), 140 (32), 125 (37), 69 (85). Anal. ($C_{10}H_{14}O_5$) C, H.

2,4-Dimethoxy-4,5-methylenedioxycyclohexa-2,5-dienone (17): mp 113–114 °C (chloroform–hexane); IR ($CHCl_3$) 1660, 1620 cm^{-1}; NMR ($CDCl_3$) δ 3.44 (s, 3, C–OCH_3), 3.82 (s, 3, =C—OCH_3), 5.71, 5.74, 5.77, and 5.82 (four sets of s, 4, vinyl protons and $-OCH_2O-$); UV (95% EtOH) 252 nm (ϵ 17 600), 306 (1600); mass spectrum (70 eV), m/e (relative intensity) 198 (M^+, 4), 167 (50), 125 (41), 109 (54), 69 (100). Anal. ($C_9H_{10}O_5$) C, H.

2-(2,3-Dibromo-3-methylbutyl)-4-methoxy-4,5-methylenedioxycyclohexa-2,5-dienone (19): mp 112–113 °C (ether–hexane); one diastereoisomer; IR (CCl_4) 1690, 1660, 1630 cm^{-1}; NMR ($CDCl_3$) δ 1.96 (s, 3, CH_3), 2.08 (s, 3, CH_3), 2.66 (d of d, 1, J = 15 and 10 Hz, CH_AH_BC=), 3.46 (s, 3, $-OCH_3$), 3.65 (d of t, 1, J = 15, 2, and 2 Hz, CH_AH_BC=), 4.54 (d of d, 1, J = 10 and 2 Hz, CHBr), 6.63, 6.67 and 6.72 (three sets of s, 3, vinyl proton and $-OCH_2O-$), 6.91 (m, 1, vinyl proton); UV (95% EtOH) 238 nm (ϵ 9200), 297 (3800); mass spectrum (70 eV), m/e (relative intensity) 396 (M^+, absent), 287 (33), 285 (34), 259 (4), 257 (4), 205 (14), 151 (26), 69 (79), 53 (100). Anal. ($C_{13}H_{16}Br_2O_6$) C, H.

3,4,4-Trimethoxycyclohexa-2,5-dienone (21): mp 61 °C (ether–hexane); IR ($CHCl_3$)·1670, 1635, 1610 cm^{-1}; NMR ($CDCl_3$) δ 3.35 (s, 6, geminal OCH_3), 3.81 (s, 3, =C—OCH_3), 5.66 (d, 1, J = 2 Hz, CH=C—O), 6.32 (d of d, 1, J = 10 and 2 Hz, CO—CH=), 6.59 (d, 1, J = 10 Hz, C=CHC(OCH_3)$_2$); UV (95% EtOH) 224 nm (ϵ 10 700), 290 (4700); mass spectrum (70 eV), m/e (relative intensity) 184 (M^+, 5), 169 (69), 153 (100), 125 (74), 110 (51), 95 (46), 69 (82). Anal. ($C_9H_{12}O_4$) C, H.

Thallium(III) Nitrate Oxidation. 2,4-Dimethoxy-4,5-methylenedioxycyclohexa-2,5-dienone (17). A *vigorously* stirred solution of 2-methoxy-4,5-methylenedioxyphenol (**16**) (5.7 g) in methanol (350 mL) containing finely powdered potassium bicarbonate (13.0 g) at 0 °C was treated with thallium trinitrate trihydrate (13.5 g) in approximately 2-g aliquots over 5 min. The mixture was stirred for 1 min at 0 °C and treated with sodium bicarbonate solution (300 mL, saturated) and then with ether (300 mL). The mixture was extracted with ether (4 × 200 mL), and the combined organic layers were washed with sodium chloride solution (3 × 100 mL, saturated). The combined aqueous layers were further extracted with ether (2 × 50 mL); the total organic extracts were dried (K_2CO_3) and evaporated in vacuo. Crystallization of the resulting solid from chloroform–hexane gave the pure dienone **17**, 4.7 g (70%).

Ferric Chloride Oxidation. 2-Propyl-4,4,5-trimethoxycyclohexa-2,5-dienone (7). To a *vigorously* stirred solution of 3,4-dimethoxy-6-propylphenol (6) (2.28 g, 11.6 mmol) in methanol (70 mL) containing finely ground potassium carbonate (8.15 g, 58 mmol) was added ferric chloride (15.7 g, 58 mmol) in one portion. The resulting mixture was kept at room temperature with continuous stirring for 30 min, and it was then poured into a saturated sodium bicarbonate solution. The aqueous solution was extracted thoroughly with ether; the combined organic extracts were washed once with brine and dried ($MgSO_4$). Evaporation of the solvent in vacuo gave 2.3 g (88%) of a pale yellow solid which appeared to be pure dienone 7 on the basis of spectroscopic evidence. Recrystallization from ether–pentane gave analytically pure dienone as white rods.

DDQ Oxidation. 2-Allyl-4-methoxy-4,5-methylenedioxycyclohexa-2,5-dienone (4). To a stirred solution of 2-allyl-4,5-methylenedioxyphenol (3) (1.78 g, 10 mmol) in methanol (100 mL) was added 2.5 g (11 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone followed by 100 mg of *p*-nitrophenol. The mixture was stirred at room temperature for 1 h, and the solvent was removed in vacuo. After the residue was taken up in ether, it was washed twice with saturated sodium bicarbonate and once with brine and dried ($MgSO_4$). The ether was then evaporated in vacuo to give an oil which was quickly filtered through a short column of silica gel with 40% ethyl acetate in hexane as solvent. Pure dienone 4 was obtained (1.84 g, 88%) as an oily solid which on recrystallization from ether–pentane gave white rods.

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Registry No.—**1**, 533-31-3; **2**, 57197-23-6; **3**, 19202-23-4; **4**, 64949-70-8; **5**, 67271-92-5; **6**, 6906-69-0; **7**, 67271-93-6; **8**, 66967-26-8; **9**, 66967-27-9; **10**, 67271-94-7; **11**, 67271-95-8; **12**, 23504-78-1; **13**, 67271-96-9; **14**, 20491-91-2; **15**, 67271-97-0; **16**, 21505-18-0; **17**, 67271-98-1; **18**, 67271-99-2; **19**, 67272-00-8; **20**, 2033-89-8; **21**, 64701-03-7.

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Palladium-Catalyzed Reductions of α,β-Unsaturated Carbonyl Compounds, Conjugated Dienes, and Acetylenes with Trialkylammonium Formates

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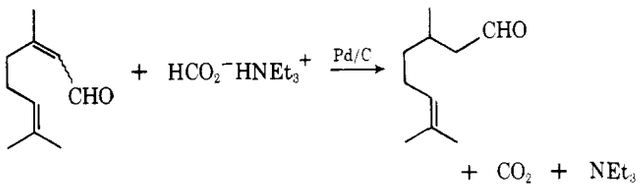
We have reported the convenient reduction of halo- and nitroaromatic compounds with triethylammonium formate and a palladium catalyst.[1] The reaction is quite selective and provides two advantages over catalytic hydrogenation: it can be done in an open flask and it is very simple to measure the exact amount of reducing agent (formic acid) required. We have now found that the trialkylammonium formate–palladium system also is very effective and convenient for reducing α,β-unsaturated carbonyl compounds to saturated carbonyl compounds, and in some instances conjugated dienes and acetylenes to monoenes.

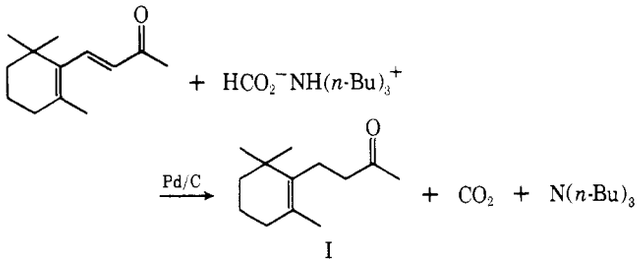
Results and Discussion

α,β-Unsaturated Carbonyl Compounds. A variety of α,β-unsaturated aldehydes, ketones, and esters were reduced at 100 °C with 10% excess formic acid, 30% excess triethyl- or tri-*n*-butylamine, and 1 mol % of palladium in the form of 10% palladium on carbon. The progress of the reductions could easily be monitored by measuring the amount of CO_2 evolved. We did this with several examples by carrying out the reactions in capped, thick-walled Pyrex bottles with a pressure gauge attached to a syringe needle inserted through the rubber liner of the bottle cap. Completion of the reaction was confirmed by GLC analysis. Products were isolated by filtering the solution from the catalyst and distilling the filtrate, or by first washing with aqueous acid and then distilling. The trialkylammonium formates generally form a second liquid phase in the reduction reaction, but dissociate and distill when heated. The compounds reduced by these procedures are listed in Table I.

Citral reduced rather slowly under our usual conditions (44 h) but very cleanly to citronellal in 91% (isolated) yield. Crotonaldehyde reduced more rapidly (8 h). Mesityl oxide, 2-

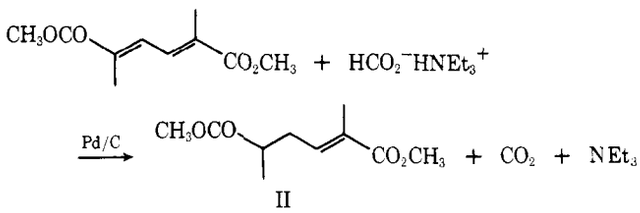


cyclopentenone, 3-methyl-2-cyclopentenone, and benzalacetone all reduced in high yields to the expected saturated ketones. The conjugated dienone, β-ionone, with 1.1 equiv of formic acid produced mainly (69%) the α,β-saturated enone, I. Only 2% of the α,β-unsaturated enone was formed. The remaining product was polymer.



I

Methyl crotonate, methyl cinnamate, and diethyl fumarate reduced to the saturated esters in high yield. Dimethyl (*E,E*)-2,5-dimethyl-2,4-hexadienedioate gave 96% of the monoene, II, under the usual conditions with only 4% completely saturated ester formed. Methyl sorbate gave a mixture of monoenes with methyl 2-hexenoate predominating (65%).



II

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