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Oxygen Promoted Addition of 1,3-Dioxolane to Electron-deficient Alkenes

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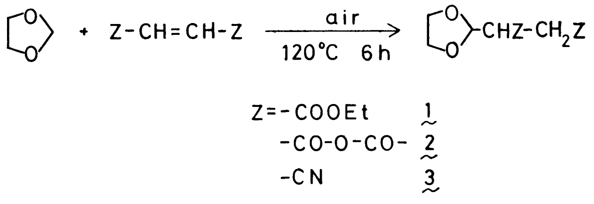
1,3-Dioxolane reacted with electron-deficient alkenes, such as diethyl maleate, maleic anhydride, diethyl fumarate and fumaronitrile, under an oxygen atmosphere or in air to give 1:1 adducts in good to excellent yields. The presence of oxygen promoted the reaction. The reaction appears to be characteristic of 1,3-dioxolane. Methylal and ethylal did not react with diethyl maleate under the same conditions.

Recently, great attention has been paid to C_1 chemistry, in which carbon monoxide and methanol are key materials as starting C_1 compounds.[1] However, only a little attention has been paid to the chemistry of other C_1 compounds, such as formic acid and formaldehyde. We have recently shown that formic acid, a C_1 derivative from carbon monoxide, could be used as a hydrogen source for catalytic reduction of ketones and aldehydes.[2]

On the other hand, 1,3-dioxolane, formaldehyde ethylene acetal, is known to react with several alkenes by UV irradiation, or in the presence of radical initiators.[3] The reactions have been considered to proceed in radical mechanisms. The present work describes the reaction of 1,3-dioxolane with electron-deficient alkenes under an air or an oxygen atmosphere to give 1:1 adducts. The reaction is simple and convenient, since the reaction is carried out without irradiation or radical initiators.

Results and Discussion

1,3-Dioxolane reacted with such electron-deficient alkenes as diethyl maleate, maleic anhydride, diethyl fumarate, and fumaronitrile in air at 120 °C for 6 h to give 1:1 adducts (Scheme 1). The results are listed in Table 1. These alkenes reacted with 1,3-dioxolane only at the 2-position. On the other hand, simple alkenes such as 1-octene reacted at the 4-position as well as at the 2-position of 1,3-dioxolane to give 1:1 adducts in low yields by initiators.[4] In the present study, diethyl maleate reacted with 1,3-dioxolane in air or under oxygen atmosphere to give 1:1 adducts in 73 and 83% yields, respectively (Runs 1 and 2).



Scheme 1.

The higher yield under the latter conditions suggests that the oxygen atmosphere may be more favorable than air for the formation of the 1:1 adducts. No 1:1 adduct was obtained under an argon atmosphere. These results showed that the presence of oxygen was essential for the reaction. Conversion of diethyl maleate and yield of the 1:1 adduct decreased at a lower reaction temperature (80 °C) and a shorter reaction time (3 h) (Runs 3 and 4). Radical initiators such as di-*t*-butyl peroxide (DTBP) or azobisisobutyronitrile (AIBN) could also initiate the reaction under an inert atmosphere (Runs 5 and 6). As a radical initiator, DTBP was more effective than AIBN. The decomposition of DTBP has a half-life of about 20 h at 120 °C and of about 1 h at 150 °C, whereas AIBN decomposes into 1-cyano-1-methylethyl radicals under mild conditions (40 °C). AIBN is useful as a initiator in the range from 40 °C to 80 °C.[5] The radical species from AIBN would not work efficiently at such a high reaction temperature (120 °C). Oxygen atmosphere appears to be more favorable to the reaction than the addition of initiators.

The effect of molar ratio, 1,3-dioxolane/alkene, on the product yield was examined in detail by employing diethyl maleate. The results are shown in Table 2.

TABLE 1. THE 1:1 ADDITION OF 1,3-DIOXOLANE TO ALKENES[a)]

Run	Alkene	Conversion[b)] / %	Atmosphere	Product	Yield[b)] / %
1	Diethyl maleate	93	Air	**1**	73
2	Diethyl maleate	100	Oxygen	**1**	83
3[c)]	Diethyl maleate	39	Air	**1**	16
4[d)]	Diethyl maleate	50	Air	**1**	24
5[e)]	Diethyl maleate	100	Argon	**1**	69
6[f)]	Diethyl maleate	40	Argon	**1**	18
7	Maleic anhydride	98	Air	**2**	89
8	Diethyl fumarate	100	Air	**1**	38
9	Fumaronitrile	54	Air	**3**	23

a) A mixture of 1,3-dioxolane (60 mmol) and alkene (6.0 mmol) was stirred at 120 °C for 6 h. b) Determined by GLC based on the amount of alkene used. c) Reaction temperature: 80 °C for 6 h. d) Reaction time: 3 h at 120 °C. e) DTBP was used as a radical initiator. f) AIBN was used as a radical initiator.

TABLE 2. THE 1:1 ADDITION OF 1,3-DIOXOLANE TO DIETHYL MALEATE: EFFECT OF MOLAR RATIO

Run	Molar ratio[b)]	Conversion/%[c)]	Product yield/%[c)]
10	1:1	57	4
11	5:1	85	52
12	10:1	93	73
13	20:1	100	88

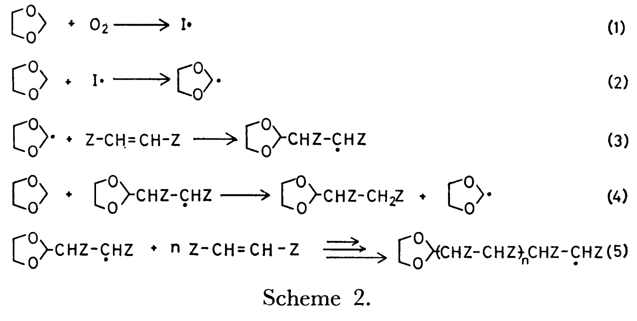
a) At 120 °C, for 6 h, under air. b) 1,3-Dioxolane/Maleate. c) Product **1**: Determined by GLC based on the amount of diethyl maleate.

The yield of 1:1 adduct decreased dramatically with a decrease in the molar ratio. In runs 10 and 11, the product mixture contained a considerable amount of oligomers, whose molecular weights were less than 800 according to gel-permeation chromatography.

With maleic anhydride, the 1:1 adduct was obtained in excellent yield (Run 7). However, the alkenes with (*E*)-configuration gave the product in poor yields. Diethyl fumarate and fumaronitrile gave the 1:1 adducts in 38 and 23% yields respectively (Runs 8 and 9).

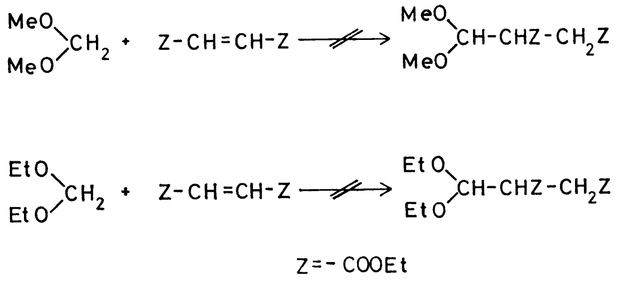
For this reaction, only the alkene having two electron-withdrawing groups appears to react with 1,3-dioxolane under the conditions used. Methyl acrylate and acrylonitrile gave no 1:1 adducts even at a more elevated temperature, 180 °C. 1-Hexene was also inactive for the present reaction.

The reactions is considered to proceed in radical mechanisms (Scheme 2), since the 1:1 adduct was obtained with radical initiators (Runs 5 and 6) and the reaction was inhibited completely with a radical scavenger such as 2,6-di-*t*-butyl-4-methylphenol. A peroxide species is generated by the reaction of 1,3-dioxolane with oxygen (Step 1), and this presumably initiates the chain reaction leading to the 1:1 adducts (Step 2—4). In the reaction between 2-phenyl-1,3-dioxolane and oxygen, a peroxide species has been isolated.[6)] In runs 10 and 11, the yields of 1:1 adduct drastically decreased. In these runs, step 5 would predominate and many oligomers of the alkene were produced.



Scheme 2.

The present reaction is characteristic of 1,3-dioxolane. Methylal and ethylal, formaldehyde dimethyl acetal and diethyl acetal, did not react with diethyl maleate under the same reaction coditions as run 1 (Scheme 3). This difference occurs because peroxide species are liable to be generated with the more strained cyclic ether.[7)]



Scheme 3.

The present reaction is considered to be a modified hydroformylation reaction since the ethylene acetal moiety is easily hydrolyzed into carbonyl groups. Hydroformylation of internal conjugated alkenes such as diethyl maleate and maleic anhydride is known to be rather difficult and requires severe conditions.[8)] Therefore, the present reaction offers an alternative route to the hydroformylation of these alkenes with a simple precedure under rather mild conditions.

Experimental

1,3-Dixolane and other reagents were carefully purified by distillation over suitable drying reagents before use. The boiling points are uncorrected. IR spectra were measured on a Hitachi model 215 grating spectrophotometer. ^{1}H-NMR spectra (300 MHz) were recorded on a Nicolet NTC-300 spectrometer equipped with 1180E computer system. ^{13}C-NMR spectra (25.05 MHz) were obtained using a JEOL JNM FX-100 pulsed Fourier Transform spectrometer. The chemical shift values were expressed in ppm relative to $\mathrm{Me_4Si}$ as an internal standard. Gel-permeation chromatograms were recorded on a Waters ALC/GPC 244 equipped with four columns ($10^5+10^4+10^3+500$ Å). The molecular weight was estimated according to calibration curves obtained with standard polystyrenes.

General Reaction Procedure. A 50 ml stainless steel autoclave equipped with a glass liner was charged with an alkene (6 mmol, 1.0 ml) and 1,3-dioxolane (60 mmol, 4.2 ml) under an air or an oxygen atmosphere. The autoclave was set in an oil bath and the temperature was raised to 120 °C in 20 min. The mixture was stirred magnetically at 120 °C for 6 h. The products were isolated by distillation under reduced pressures and submitted to analysis (IR, NMR, and MS). The GLC analysis of the reaction products was made using a column (3 mm$\phi \times$3 m) packed with Silicone OV-17 on Uniport HP 60—80 mesh. The yields of products were determined by GLC.

*The Reaction of Diethyl Maleate or Fumarate with 1,3-Dioxolane gave **1**.* **1**: Colorless oil, bp 116—119 °C/0.9 Torr (1 Torr≈133.322 Pa). ^{13}C-NMR ($\mathrm{CDCl_3}$): $\delta=14.1$ (q, $-\mathrm{COOCH_2\underline{C}H_3}$), 30.4(t, $-\mathrm{CH{-}\underline{C}H_2{-}}$), 45.9 (d, $-\mathrm{\underline{C}H{-}CH_2{-}}$), 60.7(t, $-\mathrm{COO\underline{C}H_2CH_3}$), 61.6(t, $-\mathrm{COO\underline{C}H_2CH_3}$), 65.3(t, $-\mathrm{\underline{C}H_2CH_2{-}}$), 102.9 (d, $-\mathrm{O{-}\underline{C}H{-}O{-}}$), 170.8 (s, C=O), and 171.8 (s, C=O). ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta=1.25$ (3H, t, $J=6.9$ Hz, $-\mathrm{COOCH_2C\underline{H}_3}$), 1.27 (3H, t, $J=6.9$ Hz $-\mathrm{COOCH_2C\underline{H}_3}$), 2.59(1H, d of d, $J=16.8$, 4.6 Hz, $-\mathrm{CH{-}CH_2{-}}$), 2.76(1H, d of d, $J=16.8$, 9.2 Hz, $-\mathrm{CH{-}C\underline{H}_2{-}}$), 3.20(1H, d of d of d, $J=9.2$, 4.6, 4.6 Hz, $-\mathrm{C\underline{H}{-}CH_2{-}}$), 3.84—4.01(4H, m, $-\mathrm{O{-}C\underline{H}_2{-}C\underline{H}_2{-}O{-}}$), 4.13(2H, q, $J=6.9$ Hz, $-\mathrm{COOC\underline{H}_2CH_3}$), 4.19(2H, q, $J=6.9$ Hz, $-\mathrm{COOC\underline{H}_2{-}CH_3}$), and 4.19 (1H, d, $J=4.6$ Hz, $-\mathrm{O{-}C\underline{H}{-}O{-}}$). IR (neat): 1735 cm^{-1} (ν C=O) and 1030 cm^{-1} (ν C–O–C). MS(*m*/*e*): 246(M$^+$), and 201 (M$^+-$OEt). Found: C, 53.95;

H, 7.60; O 38.74%. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37; O, 38.98%.

The Reaction of Maleic Anhydride with 1,3-Dioxolane Gave ***2.*** **2**: Colorless oil, bp 128—138 °C/1.2 Torr. ^{13}C-NMR ($CDCl_3$): $\delta=28.5$ (t, $-CH-\underline{C}H_2-$), 44.8(d, $-\underline{C}H-CH_2-$), 65.7(t, $-O-\underline{C}H_2-\underline{C}H_2-O-$), 100.7(d, $-O-\underline{C}H-O-$), and 169.6 (s, C=O). ^{1}H-NMR ($CDCl_3$): $\delta=2.958$ (1H, d, $J=8.4$ Hz, $-CH-C\underline{H}_2-$), 2.961(1H, d, $J=6.6$ Hz, $-CH-C\underline{H}_2-$), 3.54(1H, d of d of d, $J=8.4$, 6.6, 2.4 Hz, $-C\underline{H}-CH_2-$), 3.84—4.17(4H, m, $-C\underline{H}_2-C\underline{H}_2-$), and 5.29 (1H, d, $J=2.4$ Hz, $-O-C\underline{H}-O-$). IR (neat): 1785 cm^{-1} (ν C=O), and 1860 cm^{-1} (ν C=O).

The Reaction of Fumaronitrile with 1,3-Dioxolane Gave ***3.*** **3**: Colorless oil, bp 111—114 °C/4 Torr. The ^{13}C-NMR spectra of the isolated product gave a similar pattern to those of **1** and **2**. ^{13}C-NMR ($CDCl_3$): $\delta=16.3$ (t, $-CH-C\underline{H}_2-$), 33.9 (d, $-\underline{C}H-CH_2-$), 66.1 (t, $-O-\underline{C}H_2-\underline{C}H_2-O-$), 100.6 (d, $-O-\underline{C}H-O-$), 115.5 (s, $-CN$), and 119.1 (s, $-CN$).

The 1:1 Addition in the Presence of Radical Initiator. The 50 ml autoclave was charged with diethyl maleate (6.0 mmol, 1.0 ml), 1,3-dioxolane (60 mmol, 4.2 ml), and a radical initiator, DTBP (0.6 mmol, 87.7 mg) or AIBN (0.6 mmol, 81.7 mg), and then the mixture was stirred at 120 °C for 6 h under an argon atmosphere.

The Reaction in the Presence of Radical Scavenger. The 50 ml autoclave was charged with diethyl maleate (6.0 mmol, 1.0 ml), 1,3-dioxolane (60 mmol, 4.2 ml), and 2,6-di-*t*-butyl-4-methylphenol (15 mmol, 3.31 g) under air. The mixture was stirred at 120 °C for 6 h.

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