rinated monofluorobenzene. Although significant amounts of meta isomer were found in experiments with fluorine to fluorobenzene ratios up through 2, it is interesting to note that no meta isomer was found when the fluorine to fluorobenzene ratios were 3 or greater. The fact that no polymers were found indicates that the technique used was successful in eliminating polymer formation.

Desirable characteristics inherent to the molecular sieve technique are: (1) substrate molecules are separated and localized, which ensures dimolecular reactions; (2) adsorptive properties of the molecular sieves permit loading and unloading a substance in a completely reversible fashion; (3) molecular sieves function as a third body to dissipate the heat of reaction; (4) heat of reaction is generated over a greater area; and (5) adsorbed substrate is not free to participate in polymer formation.

As may be seen from the procedure described earlier in this work, a complete fluorination can be carried out with minimal effort in a matter of hours. Although in a typical reaction the amount of products obtained are within the limits of experimental error, the molecular sieves were found to have lost approximately one-half of their active loading sites with each successive fluorination. Efforts to determine the cause of active site loss resulted in experiments which showed the endogenous hydrofluoric acid reacting with the silicates of the molecular sieves and reducing the number of loading sites. After several unsuccessful attempts to use the molecular sieves repeatedly, it was found that the gradual degradation of the molecular sieves represented an uncontrollable reaction parameter. In order to ensure reproducible results, each experiment in this study was begun with fresh unused molecular sieves, thereby overcoming the aforementioned difficulty.

Conclusion

Conditions have been optimized to form the greatest amount of difluorobenze product. Under the following conditions: temperature, −78 °C; fluorination schedule, 10/20/30; and fluorine to substrate ratio, 3; a maximum yield of 19.7% monofluorinated product was obtained. Despite the relatively high yield of desired products, there was no meta isomer found; however, measurable amounts of the meta isomer were observed in the experiments conducted at the lower ratios. The usual polymer formation, which is expected when elemental fluorine is allowed to react with organic substrates, was not observed due to aforementioned factors. Although this technique is easily accomplished, there is one drawback. The major difficulty lies in the fact that a completely inert molecular sieve has not been found; therefore, this work is being discontinued.

Registry No.—Fluorine, 7782-41-4; fluorobenzene, 462-06-6; *o*-difluorobenzene, 367-11-3; *m*-difluorobenzene, 372-18-9; *p*-difluorobenzene, 540-36-3.

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Notes

Reactions of α-Alkoxy-α,β-unsaturated Carbonyl Compounds[1]

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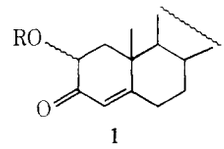
Received December 5, 1977

α-Alkoxy-α,β-unsaturated carbonyl compounds have attracted our attention because of their potential as addends in annulation and addition reactions. The products of these reactions, α-alkoxycarbonyl compounds (e.g., 1), would be useful intermediates in the synthesis of natural products, e.g., cerin or β-ecdysone. It was uncertain, however, whether the unsaturated carbonyl of the addend would be sufficiently reactive to participate in the required reactions. Mesomeric electron donation from the alkoxy group[2] might make the system less susceptible to nucleophilic attack even as the carbonyl group is activating the alkene. As model compounds for study, we have chosen methyl α-methoxyacrylate (**2**) and 2-ethoxy-1-buten-3-one (**3**). We have investigated reactions of these compounds with nucleophiles (as a prelude to studies of the Robinson annulation), with lithium dialkylcuprates, and with dienes.

Compound **2** was prepared from methyl 2,3-dibromopropionate by the method of Ogata et al.[3] The enone **3**, originally obtained by Harris as an unidentified side product in the preparation of 3,3-diethoxy-2-butanone (**4**),[4] was prepared



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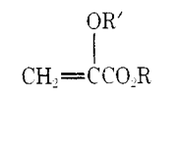
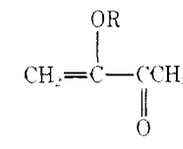
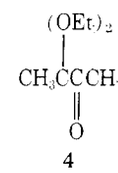


2, R = R′ = Me
6, R = Et; R′ = Me
7, R = R′ = Et



3, R = Et
5, R = Me



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in our work by distilling ketal **4** from $KHSO_4$[5] (cf. the preparation of the methyl analogue, **5**[6]).

Although reactions of nucleophiles with **6**[7] and **7**[8] have been reported, no successful conjugate addition to any of these compounds has yet been described. Attempts to induce the addition of the sodium enolates of cyclohexanone, methylcyclohexanone, dimedone, or 2-carbethoxycyclohexanone to **2** or **3** were unsuccessful. Dimethyl sodiomalonate, however, was an effective nucleophile toward both **3** and **2**, giving **8** and **9**, respectively. The best yields (60%) of **8** were obtained by refluxing an ether–methanol solution of **3**, dimethyl malonate, and sodium methoxide for 24 h. By comparison, the analogous reaction with methyl vinyl ketone occurs within 2 h at room

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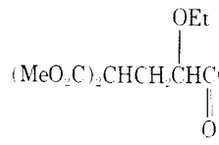

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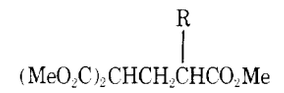
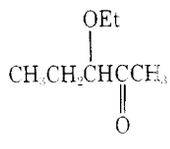


9, R = OMe
10, R = H
11, R = Me

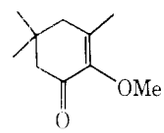
temperature.[9] The acrylate **2** was even more sluggish. When a solution of dimethyl malonate and **2** in ether–methanol was heated with sodium methoxide for 4 days, a 59% yield of **9** was obtained. In comparison, a 79% yield of **10**[10] was obtained from methyl acrylate after only 4 h under the same conditions.

Since Michael additions are, in general, only moderately susceptible to steric influence at the α carbon,[11] and since the α-substituted methyl methacrylate readily adds nucleophiles under the above conditions (60% yield of **11**[10] after 5 h), the steric bulk of the alkoxy group probably has only a slight role in decreasing the reactivity of **2** and **3.** The electronic factors which are probably responsible for most of this decrease may be of two types. The alkoxy group may act to stabilize the carbon–carbon double bond[2b] of the enone, thus retarding reactions in which that bond is affected. Or, the enolate intermediate in the Michael addition[12] may be destabilized by mesomeric electron donation from oxygen.[2a] The available data indicate that this destabilization may compete with stabilization by inductive electron withdrawal in the case of α-alkoxy, sp^2-hybridized carbanions.[2a,13] Sufficient evidence is not available to indicate which of these two electronic effects is primarily responsible for the deactivation of **2** and **3.**

Another conjugate addition to **3,** that of lithium dimethylcuprate, has also been investigated. Relatively vigorous conditions (3 h at room temperature) are required in order to obtain an 85% yield of **12.** House and Umen found that alkoxyenone **13** also reacted more sluggishly than expected under these conditions.[14] The effect of the alkoxy group in



12



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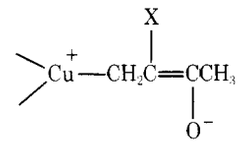
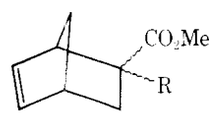


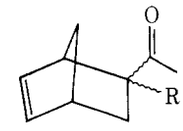
14

these cases is probably to slow the formation of the enolate-like intermediate, **14,** so that that step becomes rate determining.[15]

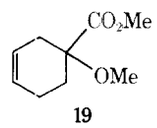
We have also investigated the reactivity of **2** and **3** toward dienes. The unsubstituted enones, methyl acrylate and methyl vinyl ketone, form adducts **15**[16] and **16**[17] respectively when treated with cyclopentadiene at room temperature. However, neither **2** nor **3** formed an adduct, detectible by GLC or TLC,



15, R = H
17a, R = OMe; *endo*-CO_2Me
b, R = OMe; *exo*-CO_2Me



16, R = H
18, R = OEt
21, R = OMe



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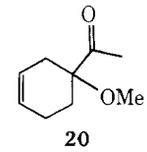

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in methylene chloride or ether at room temperature, or in refluxing benzene or toluene. Acid catalysis (aluminum chloride or acetic acid) was likewise ineffective, The addition could be effected by heating the dienophile in a large excess of diene at 160–190 °C. Thus, **2** afforded a 54% yield of **17** and **3** afforded a 61% yield of **18** upon treatment with cyclopentadiene. Treatment of **2** and **3** with butadiene in a similar manner afforded cyclohexenes **19** (49% yield) and **20** (40% yield), respectively. Reactions of analogues **5**,[6] **6**,[7] and **7**[18] have with dienes also been reported to occur at high temperatures.

The exo and endo diastereomers of **17** were readily separated by preparative GLC. The structural assignments were made on the basis of the relative positions of the NMR signals of protons on the substituents at C-2 (signals due to endo-substituent protons are upfield from those due to the exo).[19] The ratio of substituent protons are upfield from those due to the exo).[19] The ratio of endo ester **17a** to exo ester **17b** was 38:62 as determined by GLC. Thus, **2** shows selectivity opposite to that shown by methyl acrylate (70:30) but very similar to that shown by methyl methacrylate (32:68).[20] The similarity in the endo:exo ratios obtained from **2** and methyl methacrylate indicates the presence of similar steric interactions[21] in the transition states. Thus, the decrease in dienophile reactivity must be caused by the electronic effects of the alkoxy group.

Despite the success of the separation of the diastereomers of **16**[7] and **21**,[6] we have been unable to separate the diastereomers of **18** by GLC or TLC. However, the ratio of *endo*-acetyl to *exo*-acetyl may be estimated from NMR signals at δ 2.20 and 2.30, respectively. The observed ratio of 1:2 is very much different from the 63:37 ratio found for the diastereomers of **21.**[6] The endo:exo ratio of the norbornenes obtained from methyl vinyl ketone is 83:17, while that from methyl isopropenyl ketone is 42:58.[22] Thus, the endo:exo ratio for **18** is that to be expected from steric interactions while that for **21** is surprisingly high. The reasons for this difference are not obvious.

Although these α-alkoxy-α,β-unsaturated carbonyl compounds are less reactive toward nucleophiles and dienes than the unsubstituted analogues, they will undergo conjugate additions and Diels–Alder reactions. Synthetically useful intermediates may be prepared if these reactions can be extended. We are attempting to apply the Michael additions of enone **3** in a Robinson annulation sequence.

Experimental Section

General. NMR spectra were recorded with a Varian T-60 spectrometer and are reported in ppm downfield from tetramethylsilane. Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer using a thin film of the oil between sodium chloride plates. The UV spectra were recorded on a Beckmann DB-G spectrophotometer. Melting points were obtained with a Thomas-Hoover melting point apparatus and are uncorrected. The elemental analyses were performed by Galbraith Laboratories, Inc. An Aldrich Kugelrohr apparatus was utilized for bulb-to-bulb distillation. GLC was accomplished using: (A) a 2 ft × 0.25 in. 10% SE-30 column, (B) a 6 ft × 0.50 in. 20% SE-30 column, or (C) a 6 ft × 0.25 in. 20-M Carbowax column.

2-Ethoxy-1-buten-3-one (3). To a flask containing 5.53 g (34.5 mmol) of **4**[4] and 268 mg (2 mmol) of $KHSO_4$ was attached a short-path distillation head with a receiving flask containing 2 mL of saturated aqueous $NaHCO_3$. A 180 °C sand bath was used to quickly warm the contents of the flask. After completion of the distillation, the $NaHCO_3$ solution was extracted with 30 mL of ether. The ether solution was dried (Na_2CO_3) and concentrated in vacuo. The residue was distilled under vacuum (10 Torr), the fraction distilling between 40 and 50 °C being collected. Thus, 2.158 g of a 85:15 mixture of **3** and **4** was obtained. Further purification was accomplished by preparative GLC (column A). **3:** IR 1710, 1610 cm^{-1}; NMR ($CDCl_3$) δ 1.37 (t, J = 7 Hz, 3 H), 2.28 (s, 3 H), 3.80 (q, J = 7 Hz, 2 H), 4.42 (d, J = 2 Hz, 1 H), 5.18 (d, J = 2 Hz, 1 H); mass spectrum (70 eV) m/e 114 (P), 99, 70 (base),

44, 43; UV (95% C_2H_5OH) λ_{max} 250 nm (ϵ 4.2 × 10^3).

Methyl 2-Carbomethoxy-4-ethoxy-5-oxohexanoate (8). To a solution of 23 mg (1 mmol) of sodium in 3 mL of methanol and 15 mL of ether was added dropwise 789 mg (6.0 mmol) of dimethyl malonate. This was followed by dropwise addition of 838 mg of a mixture of **3** and **4** (4.2 mmol of **3**). The solution was then refluxed for 24 h. After cooling, it was acidified with 1 N HCl, washed twice with 10 mL of water, once with saturated aqueous $NaHCO_3$, and again with water. After drying ($MgSO_4$) and concentration in vacuo 1.12 g of a crude product was obtained. This crude product was found by GLC analysis using tetradecane as an internal standard to contain 620 mg of **8** (59% yield). Preparative GLC (Column B) was used to further purify **8:** IR 1750, 1735, 1715 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 2.20 (s, ≈3 H), 2.1–2.4 (m, ≈2 H), 3.2–3.7 (m, 3 H), 3.77 (s, 6 H); mass spectrum (70 eV) *m/e* 203, 187, 143 (base), 115. Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.37; H, 7.34.

Dimethyl 2-Carbomethoxy-4-methoxyglutarate (9). When 1.311 g (11 mole) of **2**,[3] 1.744 g (13 mmol) of dimethyl malonate, and 2.1 mmol of sodium methoxide in an ether–methanol solution were refluxed for 4 days and the product isolated as above, the yield of **9** was estimated by GLC (column A) to be 58%. The crude product was subjected to bulb-to-bulb distillation followed by preparative GLC. **9:** IR 1745 (very broad) cm^{-1}; NMR ($CDCl_3$) δ 2.47 (m, 2 H), 3.47 (s, 3 H), 3.68 (s, 3 H), 3.74 (s, 6 H), 3.7 (m, ≈2 H); mass spectrum (70 eV) *m/e* 217, 189, 130 (base). Anal. Calcd for $C_{10}H_{16}O_7$: C, 48.39; H, 6.50. Found: C, 48.60; H, 6.32.

3-Ethoxy-2-pentanone (12). To a solution of lithium dimethylcuprate, prepared from 1.457 g (7.6 mmol) of cuprous iodide and 9 mL of 1.6 M methyllithium at 0 °C, was added a solution containing 2.75 mmol of **3** in 2 mL of ether. The mixture was stirred at room temperature for 3 h after which time it was diluted with 50 mL of ether and washed with dilute ammonium hydroxide until the aqueous layer was colorless. The ether layer was dried (Na_2SO_4) and concentrated by distillation. One half of the crude material was subjected to preparative GLC (column B) from which was obtained **12:** IR 2980, 1717 cm^{-1}; NMR ($CDCl_3$) δ 0.93 (t, J = 7 Hz, 3 H), 1.23 (t, J = 7 Hz, 3 H), 1.67 (q, J = 7 Hz, 2 H), 2.13 (s, 3 H), 3.47 (q, J = 7 Hz, ≈2 H), 3.57 (t, J = 7 Hz, ≈1 H).

From the other half of the crude material was obtained 204 mg of a semicarbazone: mp 109–11 °C (lit.[23] mp 93–5 °C); NMR ($CDCl_3$) δ 0.90 (t, J = 7 Hz, 3 H), 1.2 (t, J = 7 Hz, 3 h), 1.5 (m, ≈2 H), 1.83 (s, ≈3 H), 3.37 (q, J = 7 Hz, 2 H), 3.67 (t, J = 7 H_z, 1 H), 5.83 (broad s, 2 H). Anal. Calcd for $C_8H_{17}O_2N_3$: C, 51.32; H, 9.15; N, 22.44. Found: C, 51.29; H, 8.90; N, 22.34.

***endo*- and *exo*-2-Carbomethoxy-2-methoxy-5-norbornene (17a and 17b).** A stainless steel bomb containing 1.005 g (8.7 mmol) of **2** and 5.04 g (77 mmol) of cyclopentadiene was heated at 165 °C for 12 h. The reaction mixture was chromatographed on silica gel. The portion eluting with chloroform yielded 850 mg of **17** (53% yield). The endo and exo isomers were separated by preparative GLC (column C). The reaction mixtures before column chromatography had been found by GLC to contain a 38:62 ratio of the isomers. They were identified as below.

Shorter retention time isomer (**17a**): IR 2950, 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.5–2.1 (m, 4 H), 2.9 (m, ≈1 H), 3.1 (m, ≈1 H), 3.23 (s, 3 H), 3.71 (s, 3 H), 5.88 (d of d, J_1 = 3 Hz, J_2 = 6 Hz, 1 H), 6.28 (d of d, J_1 = 3 Hz, J_2 = 6 Hz, 1 H); mass spectrum (70 eV) *m/e* 182 (P), 117 (base). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.93; H, 7.68.

Longer retention time isomer (**17b**): IR 2950, 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.2–1.8 (m, 3 H), 2.27 (d of d, J_1 = 3 Hz, J_2 = 12 Hz, 1 H), 2.9 (m, 1 H), 3.13 (s, 3 H), 3.3 (m, 1 *H*), 3.80 (s, 3 H), 6.07 (d of d, J_1 = 3 Hz, J_2 = 6 Hz, 1 H), 6.40 (d of d, J_1 = 3 H_2, J_2 = 6 Hz, 1 H); mass spectrum (70 eV) *m/e* 182 (P), 117 (base).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 66.01; H, 7.73.

2-Ethoxy-2-acetyl-5-norbornene (18). In a stainless-steel bomb were placed 0.64 g of a mixture of **3** and **4** (4.2 mmol of **3**) and 3.7 g (55 mmol) of freshly distilled cyclopentadiene. The sealed bomb was kept in a sand bath at 160 °C for 40 h. Silica gel column chromatography of the reaction products afforded 464 mg (61% yield) of the Diels–Alder adduct, **18**, upon elution with benzene–chloroform (1:1). Preparative GLC (column C) afforded an analytical sample of the mixture of endo and exo isomers of **18:** IR 3050, 2970, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.17 (t, J = 7 Hz, *endo*-OCH_2CH_3), 1.22 (t, J = 7 Hz, *exo*-$O\text{-}CH_2CH_3$), 1.3–2.0 (m, 4 H), 2.20 (s, *endo*-$COCH_3$), 2.30 (s, *exo*-$COCH_3$), 2.7–3.4 (m, 4 H), 5.8–6.4 (m, 2 H).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.42; H, 8.84.

4-Carbomethoxy-4-methoxycyclohexene (19). A sealed bomb containing 2.03 g (17.4 mmol) of **2**, approximately 5 g (90 mmol) of butadiene, and 10 mg of hydroquinone was heated at 190 °C for 56 h. The reaction mixture was extracted with 100 mL of hot acetonitrile and the residue from the concentration of that solution was chromatographed on a silica gel column. The fraction eluted with benzene–chloroform (1:1) contained 1.45 g of **19** (49% yield). This material was further purified by bulb-to-bulb distillation. **19:** IR 1735, 1655 cm^{-1} NMR ($CDCl_3$) δ 2.0 (m, 4 H), 2.4 (m, 2 H), 3.24 (s, 3 H), 3.74 (s, 3 H), 5.64 (bs, 2 H); mass spectrum (70 eV) *m/e* 139, 112 (base). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.56; H, 8.40.

4-Ethoxy-4-acetylcyclohexene (20). A solution of 978 mg of a mixture of **3** and **4** (4.3 mmol of **3**), 4 g (74 mmol) of butadiene, and 10 mg of hydroquinone in 5 mL of benzene was placed in a stainless-steel bomb and heated at 190 °C for 70 h. The reaction mixture was treated as above to give 290 mg (40% yield) of **20.** A bulb-to-bulb distillation afforded a sample of **20** for analysis: IR 3030, 1710, 1652 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 1.7–2.4 (m, 6 H), 2.20 (s, 3 H), 3.30 (q, J = 7 Hz, 2 H), 5.65 (br s, 2 H); mass spectrum (70 eV) *m/e* 125, 97, 80. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.54; H, 9.73.

Registry No.—**2,** 7001-18-5; **3,** 65915-73-3; **4,** 51933-13-2; **8,** 65915-74-4; **9,** 65942-40-7; **12,** 65915-75-5; **12** semicarbazone, 65915-76-6; **17a,** 65915-77-7; **17b,** 65915-78-8; *exo*-**18,** 65915-79-9; *endo*-**18,** 65915-80-2; **19,** 65915-81-3; **20,** 65915-82-4; dimethyl malonate, 108-59-8; cyclopentadiene, 542-92-7; butadiene, 106-99-0.

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Synthesis of 8-Methoxy- and 11-Methoxybenz[*a*]anthraquinones via Diels–Alder Reaction of 1,4-Phenanthraquinone

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Received December 5, 1977

We have been interested in the synthesis of oxygenated derivatives of 7,12-dimethylbenz[*a*]anthracene (one of the most potent carcinogenic polycyclic aromatic hydrocarbons).[1,2] Since excellent methods[3,4] exist to convert 7,12-

0022-3263/78/1943-2277$01.00/0