of methyl 3-(methylphenylamino)-2-propenoate as a light amber oil: NMR ($CDCl_3$) δ 3.21 (s, 3, NMe), 3.71 (s, 3, OMe), 4.92 (d, 1, J=13 Hz, C=CHCO), 6.91-7.58 (m, 5, aromatic), 7.92 (d, 1, J = 13 Hz, CH=CHCO); IR (film) 1675 (C=O), 1620, 1585, 1495, 1460 cm^{-1}. Anal. ($C_{11}H_{13}NO_2$) C, H, N.

Preparation of 4-(Methylphenylamino)-3-buten-2-one. Benzoquinone (108 mg, 1 mmol), $PdCl_2(CH_3CN)_2$ (26 mg, 0.1 mmol), LiCl (420 mg, 10 mmol), and methyl vinyl ketone (70 mg, 1 mmol, 81 μL) were mixed in THF (4 mL) as usual. Addition of N-methylaniline (107 mg, 1 mmol, 108 μL) and isolation after 24 h followed by medium-pressure liquid chromatography (5:1 hexane/ether) gave 111 mg (63%) of 4-(methylphenylamino)-3-buten-2-one as a light amber oil: NMR ($CDCl_3$) δ 2.19 (s, 3, $COCH_3$), 3.25 (s, 3, NMe), 5.41 (d, J = 13 Hz, C=CHCO), 6.99-7.59 (m, 5, aromatic), 7.90 (d, J = 13 Hz, CH=CHCO); IR (film) 1665 (s, C=O), 1610, 1590, 1550, 1500 cm^{-1}. Anal. ($C_{11}H_{13}NO$) C, H, N.

Preparation of 3-(Methylphenylamino)-2-propenonitrile. Benzoquinone (108 mg, 1 mmol), $PdCl_2(CH_3CN)_2$ (26 mg, 0.1 mmol), LiCl (420 mg, 10 mmol), and acrylonitrile (53 mg, 1 mmol, 66 μL) were mixed as usual. Addition of N-methylaniline (107 mg, 1 mmol, 108 μL) and isolation after 24 h followed by medium-pressure liquid chromatography (5:1 hexane/Et_2O, silica gel) gave 83 mg (53%) of 3-(methylphenylamino)-2-propenonitrile as a light amber oil: NMR ($CDCl_3$) δ 3.20 (s, 3, NMe), 4.15 (d, J = 15 Hz, C=CHCN), 6.90-7.58 (m, 6, aromatic and CH=CHCN); IR (film) 2200 (C≡N), 1620, 1590, 1500, 1460, 1430, 1360, 1345, 1325, 1310 cm^{-1}. Anal. ($C_{10}H_{10}N_2$) C, H, N.

Preparation of Methyl 3-[(2-Bromophenyl)amino]-2-propenoate. Benzoquinone (108 mg, 1 mmol), $PdCl_2(CH_3CN)_2$ (26 mg, 0.1 mmol), LiCl (420 mg, 10 mmol), and methyl acrylate (86 mg, 1 mmol, 90 μL) were combined in THF (4 mL) as usual. Addition of 2-bromoaniline (172 mg, 1 mmol), isolation after 24 h, and medium-pressure liquid chromatography (5:1 hexane/Et_2O) gave 194 mg (76%) of methyl-3-[(2-bromophenyl)amino]-2-propenoate as a light yellow oil: NMR ($CDCl_3$) δ 3.80 (s, 3, NMe), 4.92 (d, J = 8 Hz, C=CHCO), 6.18-7.63 (m, 5, aromatic and CH=CHCO), 10.30 (br s, 1, NH); IR (film) 3300 (m, NH), 1680 (C=O), 1630, 1600, 1580, 1520, 1460 cm^{-1}. Anal. ($C_{10}H_{10}NO_2$) C, H, N.

Preparation of Methyl 3-[(2-Nitro-4-methoxyphenyl)amino]-2-propenoate. Benzoquinone (108 mg, 1 mmol), $PdCl_2(CH_3CN)_2$ (26 mg, 0.1 mmol), LiCl (420 mg, 10 mmol), and methyl acrylate (860 mg, 10 mmol, 900 μL) were combined in THF (10 mL) as usual. Addition of 2-nitro-4-methoxyaniline (168 mg, 1 mmol), isolation after 24 h and medium-pressure liquid chromatography (5:1 hexane/Et_2O, silica gel) gave 87 mg (35%) of methyl-3-[(2-nitro-4-methoxyphenyl)amino]-2-propenoate as an orange solid, mp 100-104 °C. Running the reaction with an equimolar amount of methyl acrylate gave 47 mg (19%) of the product as a 2:1 mixture of cis and trans isomers: NMR ($CDCl_3$) δ 3.83 and 3.86 (s, 6, p-OMe and COOMe), 5.09 (d, J = 9 Hz, 1, C=CHCO), 6.10 (br s, 1, NH), 6.72-7.79 (m, 4, aromatic and CH=CHCO); IR (KBr) 1680 (C=O), 1635, 1600, 1570, 1530, 1515, 1460 cm^{-1}. Anal. ($C_{11}H_{12}N_2O_5$) C, H, N.

Preparation of Methyl 3-[(2-Nitrophenyl)amino]-2-propenoate. Benzoquinone (108 mg, 1 mmol), $PdCl_2(CH_3CN)_2$ (26 mg, 0.1 mmol), LiCl (420 mg, 10 mmol) and methyl acrylate (86 mg, 1 mmol, 90 μL) were combined in THF (4 mL) as usual. Addition of 2-nitroaniline (138 mg, 1 mmol), isolation after 24 h, and medium-pressure liquid chromatography (10:1 hexane/Et_2O, silica gel) gave 35 mg (16%) of methyl-3-[(2-nitrophenyl)amino]-2-propenoate as an orange solid: NMR ($CDCl_3$) δ 3.80 (s, 3, NMe), 5.10 (d, J = 8 Hz, C=CHCO), 6.69-7.77 (m, 4, aromatic), 8.20 (dd, J = 8 Hz, CH=CHCO); IR (KBr) 3220 (NH), 1675 (C=O), 1600, 1570,1505, 1445, 1380,1330,1315 cm^{-1}. Anal. ($C_{10}H_{10}N_2O_4$) C, H, N.

Preparation of Methyl 3-[(4-Methylphenyl)amino]-2-propenoate. Benzoquinone (108 mg, 1 mmol), $PdCl_2(CH_3CN)_2$ (26 mg, 0.1 mmol), LiCl (420 mg, 10 mmol), and methyl acrylate (860 mg, 10 mmol, 900 μL) were combined as usual. Addition of p-toluidine (107 mg, 1 mmol), isolation after 24 h, and medium-pressure liquid chromatography (5:1 hexane/ether) gave 31 mg (16%) of methyl 3-[(4-methylphenyl)amino]-2-propenoate as a white solid: mp 49-52 °C; NMR ($CDCl_3$) δ 2.55 (s, 3, p-Me), 4.00 (s, 3, OMe), 5.00 (d, J = 8 Hz, C=CHCO), 6.97-7.65 (m, 5, aromatic and CH=CHCO); IR (KBr) 3300 (m, NH), 1670 (C=O), 1620, 1580, 1520, 1500, 1480, 1460 cm^{-1}. Anal. ($C_{11}H_{13}NO_2$) C, H, N.

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Registry No. (*E*)-6 (R = Me; X = H; Z = COOMe), 7542-92-9; (*E*)-6 (R = Me; X = H; Z = COMe), 76946-78-6; (*E*)-6 (R = Me; X = H; Z = CN), 76946-79-7; (*Z*)-6 (R = H; X = o-Br; Z = COOMe), 76946-80-0; (*Z*)-6 (R = H; X = o-NO_2; Z = COOMe), 76946-81-1; (*Z*)-6 (R = H; X = o-NO_2), 76946-82-2; (*E*)-6 (R = H; X = o-NO_2, p-OMe; Z = COOMe), 76946-83-3; (*Z*)-6 (R = H; X = p-Me; Z = COOMe), 7542-87-2; methyl acrylate, 96-33-3; methyl vinyl ketone, 78-94-4; N-methylaniline, 100-61-8; acrylonitrile, 107-13-1; 2-nitro-4-methoxyaniline, 96-96-8; 2-nitroaniline, 88-74-4; p-toluidine, 106-49-0; $PdCl_2(CH_3CN)_2$, 14592-56-4.

Dimethylaluminum Chloride Catalyzed Reactions of Methyl α-Cyanoacrylate with Alkenes

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The methyl α-cyanoacrylate–Me_2AlCl complex reacts with alkenes to give zwitterion **2**. Ring closure on carbon gives the cyclobutane **3** with ~90% retention of alkene stereochemistry, ring closure on oxygen gives dihydropyran **5**, and a 1,5-hydrogen shift gives the ene adduct **4**. Reaction of the zwitterion **2** with another molecule of methyl α-cyanoacrylate gives 2:1 adducts.

Introduction

We have found that methyl acrylate undergoes aluminum chloride catalyzed ene reactions at 25 °C with reactive alkenes.[2,3] Introduction of an electron-withdrawing group in the α-position of the acrylate ester should increase its reactivity and extend the reaction to less reactive alkenes. We have recently reported that methyl α-chloro- or -bromoacrylate is roughly an order of magnitude more reactive than methyl acrylate in Lewis acid catalyzed ene reactions.[4]

(1) Fellow of the Alfred P. Sloan Foundation, 1979-81.
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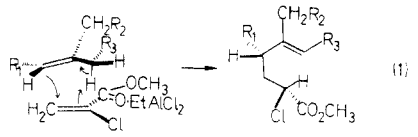
Table I. Reactions of Alkenes with Methyl α-Cyanoacrylate (1) and Me_2AlCl

alkene	equiv of 1 (Me_2AlCl)	temp, °C (time, h)	% yield 3	4	5	7	8
	0.9 (1.4)	0 → 25 (1.5)	2	26	4	4	8
	1.2 (0.9)	−78 → 25 (1)	**12a**, 3; **13a**, 6	4	5	5	25
	0.9 (0.8)	0 (3)	**12b**, 2.9; **12c**, 0.3; **13b**, 3.4; **13c**, 0.3	**10a**, 3.8; **11a**, 3.6	1	**10b**, 2; **11b**, 1	10
	0.9 (0.8)	0 → 25 (5.5)	**12b**, 0.3; **12c**, 2.4 **13b**, 0.4; **13c**, 5.07	**10a**, 10.0; **11a**, 1.5	6	**10b**, 8	7
	0.67 (0.61)	0 (1)	1	17	2	3	6

[a] 12% **9** was isolated.

Remarkably, these reactions are highly stereoselective and regioselective with trisubstituted alkenes, giving 90–100% of the ene adduct resulting from endo addition of the ester group and transfer of a hydrogen from the alkyl group syn to the vinylic hydrogen (eq 1). Since even more reactive acrylate ester derivatives are desired, we decided to explore the effect of stronger electron-withdrawing groups in the α-position.



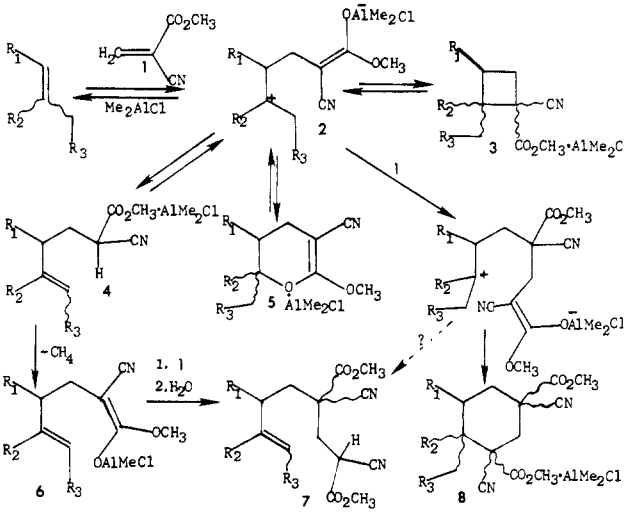
(1)

Results and Discussion

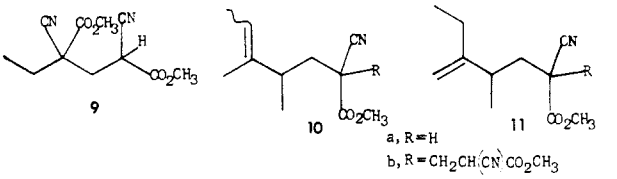
Methyl α-cyanoacrylate (1) reacts with alkenes in the presence of 1 equiv of the mild Lewis acid Me_2AlCl[3] at 0 °C in CH_2Cl_2 to give low to moderate yields of a complex mixture of 1:1 and 2:1 adducts (see Scheme I). The results are shown in Table I. Considerable amounts of polymer are also formed.

All products formed appear to arise from a common zwitterionic intermediate **2**, which is formed by conjugate addition of the alkene to the **1**·Me_2AlCl complex. Ring closure on carbon will give rise to cyclobutane **3** as a mixture of stereoisomers, ring closure on the enolate oxygen will give dihydropyran **5**, which is formally the adduct of an inverse electron demand Diels–Alder reaction, and a 1,5-proton shift will give the ene adduct **4**. The zwitterion can also undergo a 1,4-dipolar cycloaddition,[5] reacting with **1** to give cyclohexane **8**. Due to the unique ability of Me_2AlCl to function as a proton scavenger, as well as a Lewis acid,[3] the **4**·Me_2AlCl complex probably loses methane to give **6**, which adds to **1** to give **7** after workup. Conjugate addition of a methyl group to **1** followed by addition of the intermediate to a second molecule of **1** to give **9** occurs in the absence of alkene (64%) or when nonnucleophilic alkenes such as 1-hexene are used (12%).[6] Since several of the steps in Scheme I are reversible, the ratio of products will be very dependent on reaction conditions. For instance, the reaction with 2-methyl-2-butene

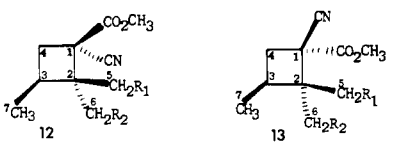
Scheme I



gives a higher percentage of 2:1 adducts since an excess of **1** was used.



a, R = H
b, R = $CH_2CH(CN)CO_2CH_3$



a, $R_1 = R_2 = H$
b, $R_1 = CH_3$, $R_2 = H$
c, $R_1 = H$, $R_2 = CH_3$

The reactions of (*E*)- and (*Z*)-3-methyl-2-pentene were examined to determine the regiochemistry of the ene adducts since methyl α-chloroacrylate shows a high selectivity for a hydrogen on the alkyl group syn to the vinylic hydrogen (eq 1).[4] Products obtained from **1** show a similar selectivity, but with a competing preference for the formation of the most stable double bond which is much less pronounced in the reactions of methyl α-chloroacrylate. (*E*)-3-methyl-2-pentene and **1** give a 7:1 mixture of ene

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(6) The formation of **7** and **9** and the apparent absence of adducts incorporating three molecules of **1** may be due to stabilization of the aluminum salts of **7** and **9** by binding of the aluminum to the second ester group.

Table II. NMR Spectral Data of 12 and 13

carbon no.	^{13}C NMR shift (^{1}H shift), δ					
	12a	12b	12c	13a	13b	13c
1	a	50.6	50.8	a	49.2	50
2	47.3	47.2	48.9	46.9	46.0	a
3	36.4	37.2	35.5	36.2	36.6	35.2
4	31.4	31.3	31.4	31.4	31.5	31.6
5	18.0 (0.97)	23.9 (1.50)	15.0 (0.96)	21.7 (1.34)	26.9 (1.77)	17.6 (1.33)
6	26.8 (1.36)	23.9 (1.39)	33.6 (1.81)	25.3 (1.04)	21.7 (1.06)	32.7 (1.39)
7	14.0 (0.92)	14.8 (0.98)	14.2 (0.90)	14.7 (0.98)	15.7 (1.12)	15.6 (1.00)
R_1		8.5 (0.79)			8.2 (0.98)	
R_2			7.9 (0.92)			7.9 (0.82)

[a] Not observed.

adducts **10a** and **11a**, while the *Z* isomer and **1** give a 1:1 mixture. Both **10a** and **11a** are formed as mixtures of diastereomers. This is not a reflection on the stereochemistry of the ene reaction since the α-proton is very acidic. We believe that **7** is formed from **4** since the ratio of **10b**:**11b** (type 7) is similar to **10a**:**11a** (type 4). Formation of **7** from the zwitterionic precursor to **8** is also possible.

The regiochemistry of the methyl α-chloroacrylate ene reaction, which proceeds in >80% yield in these cases, can be explained by minimization of steric hindrance between the exo substituent on the enophile and the substituents on the less substituted end of the double bond of the "ene" component in a concerted reaction (eq 1). The zwitterionic intermediate **2** should be preferentially formed with the same geometry as the transition state for the concerted reaction since this gauche conformation minimizes steric hindrance and maximizes electrostatic attraction. Bond rotation and other reactions compete with a 1,5-proton shift, allowing the formation of **10a** and **11a** as well as cyclobutanes and dihydropyrans. The preferential formation of **10a** is due to product development control of the 1,5-proton shift favoring the formation of the more stable double bond.

All four possible cyclobutanes, **12b**, **12c**, **13b**, and **13c**, are isolated from (*E*)- and (*Z*)-3-methyl-2-pentene, although the two cyclobutanes formed with retention of stereochemistry constitute ~90% of the cyclobutane fraction. The result is analogous to the cycloaddition of TCNE with enol ethers which gives 82–98% retention of stereochemistry.[7]

The stereochemistry of the cyclobutanes was proven by analysis of the ^{1}H and ^{13}C NMR spectra, using the cyclobutanes obtained from 2-methyl-2-butene as a model (see Table II). Cyclobutanes **12a** and **13a** are tentatively assigned from the proton spectra of the cyclobutane methylene group. In similar systems both the cyano and methyl groups shield a cis hydrogen relative to a trans hydrogen while the carbomethoxy group has the opposite effect.[8] Due to competing shielding effects all three cyclobutane hydrogens of **12a** absorb as a multiplet at δ 2.4. In **13a** the effects are reinforcing: the 4α-H absorbs at δ 2.79 (dd, J = 9, 11 Hz), the 3α-H absorbs at δ 2.45 (m), and the 4β-H absorbs at δ 1.94 (dd, J = 8, 11 Hz). The cyclobutanes derived from (*E*)- and (*Z*)-3-methyl-2-pentene have similar spectra.

Since the chemical shifts of the methyl protons could not be unambiguously assigned, ^{13}C NMR spectra were used to assign the stereochemistry of the methyl substituents of **12** and **13**. The ^{13}C NMR sppctra of **12a** and **13a** were assigned, using methyl cyclobutanecarboxylate,[9] cyclobutanecarbonitrile,[10] and 1,1,2-trimethylcyclohexane[11] as models. The γ-shielding by the C-7 methyl group allows unambiguous assignment of the resonance due to the C-5 and C-6 methyl groups. Replacement of a hydrogen of the 5-methyl group of **12a** with a methyl group leads to the expected downfield shift of the α-carbon C-5 (+5.9 ppm) and upfield shift of the γ-carbon C-6 (-2.9 ppm), allowing unambiguous assignment of the stereochemistry of **12b**. The other three isomers show similar shifts (see Table II).

Conclusion

Noncatalyzed addition reactions of electron-rich and electron-poor alkenes to form zwitterionic intermediates are well-known. The addition of enamines to methyl vinyl ketone gives products corresponding to **3**–**5**.[12] Tetracyanoethylene reacts with enol ethers and other electron-rich alkenes to give cyclobutanes.[7] Methylenemalononitrile reacts with styrene to give an adduct corresponding to **8** and an alternating copolymer.[13] Our study demonstrates that this reaction can be extended to simple alkenes as the nucleophilic component, if the electron-poor alkene is made more electrophilic by complexation to a Lewis acid.

This study also helps define the scope of Lewis acid catalyzed ene reactions. As compounds to be used as enophiles become more electron poor, the activation energy for the formation of a zwitterionic intermediate decreases faster than the activation energy for an apparently concerted ene reaction. Methyl α-chloroacrylate gives synthetically useful ene adducts in high yield while the more reactive methyl α-cyanoacrylate gives a complex mixture of products formed via **2**.

Experimental Section

Methylene chloride was dried by distillation from CaH_2. Methyl cyanoacrylate was purchased from Eastman Chemical Products, Inc., under the trade name Eastman Adhesive 910 and used as received. Me_2AlCl was purchased from Texas Alkyls as a 14.6% solution in heptane (0.724 g/mL, 1.14 M).

Reaction of 1 with (*Z*)-3-Methyl-2-pentene. Methyl α-cyanoacrylate (**1**) (0.55 g, 5.0 mmol) was added to a solution of 0.47 g (5.6 mmol) of (*Z*)-3-methyl-2-pentene in 15 mL of CH_2Cl_2 at 0 °C in a flame-dried 50-mL flask under nitrogen. Me_2AlCl solution (4 mL, 4.6 mmol) was slowly added and the solution was stirred for 3 h at 0 °C. The reaction was quenched by addition of 10 mL of ether followed by careful addition of a saturated solution of sodium dihydrogen phosphate. After gas evolution ceased, 1 M hydrochloric acid was added dropwise until the precipitated alumina had dissolved. The aqeueous layer was

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washed 3 times with 10 mL of ether. The combined organic layers were dried ($MgSO_4$) and evaporated to give 0.918 g of crude product. Purification of 0.519 g by medium-pressure chromatography on silica gel with 1:1 pentane–ether as eluent gave 83.5 mg (15%) of a mixture of cyclobutanes and ene adducts, 6.6 mg (1%) of dihydropyran **5** ($R_1 = R_2 = R_3 = CH_3$), 12.5 mg (2%) of **10b** and **11b**, and 59.0 mg (10%) of **8** ($R_1 = R_2 = R_3 = CH_3$).

The first fraction was purified by preparative GC on 0.25 in. × 9 ft, 10% DEGS on Chromosorb PNAW at 145 °C with a flow rate of 70 mL/min. All four cyclobutanes and two ene adducts were isolated. Yields shown in Table I are based on analysis of the chromatogram. ^{13}C NMR data are given in Table II.

The spectral data for **12c** follow: NMR ($CDCl_3$) δ 3.79 (s, 3), 2.4 (m, 3), 1.81 (q, 2, J = 7.5 Hz), 0.96 (s, 3), 0.90 (m, 3 virtually coupled), 0.92 (t, 3, J = 7.5 Hz); IR (CCl_4) 2970, 2235, 1747, 1255 cm^{-1}; GC t_R 51 min.

The spectral data for **13b** follow: NMR ($CDCl_3$) δ 3.79 (s, 3), 2.91 (dd, 1, J = 7, 11.7 Hz), 2.18 (m, 1), 1.89 (dd, 1, J = 11.7, 6.2 Hz), 1.77 (q, 2, J = 7 Hz), 1.12 (d, 3, J = 7 Hz), 1.06 (s, 3), 0.98 (t, 3, J = 7 Hz); IR (CCl_4) 2970, 2235, 1747, 1255 cm^{-1}; mass spectrum, m/e (relative intensity, %) 166 (M^+ - 31, 6), 155 (6), 154 (64), 122 (13), 110 (8), 94 (9), 85 (9), 84 (100), 80 (9), 70 (5), 69 (59), 67 (10), 56 (16), 55 (24), 41 (29); GC t_R 55.0 min.

The spectral data for **12b** follow: NMR ($CDCl_3$) δ 3.78 (s, 3), 2.39 (m, 3), 1.50 (q, 2, J = 7.2 Hz), 1.39 (s, 3), 0.98–1.05 (m, 3, virtually coupled), 0.79 (t, 3, J = 7 Hz); IR (CCl_4) 2985, 2235, 1745, 1255 cm^{-1}; mass spectrum, m/e (relative intensity, %) 166 (M^+ - 29, 1), 164 (M^+ - 31, 5), 163 (2), 155 (5), 154 (44), 120 (8), 95 (11), 85 (7), 84 (100), 80 (10), 69 (53), 56 (14), 55 (14), 42 (8), 41 (30); GC t_R 59.8 min.

The spectral data for **13c** follow: NMR ($CDCl_3$) δ 3.81 (s, 3), 2.75 (dd, 1, J = 8, 10 Hz), 2.1–2.6 (m, 1), 1.94 (dd, 1, J = 9, 10 Hz), 1.39 (q, 2, J = 7 Hz), 1.33 (s, 3), 1.00 (d, 3, J = 6.8 Hz), 0.82 (t, 3, J = 7 Hz); IR (CCl_4) 2970, 2235, 1740 cm^{-1}; GC t_R 62.5 min. Anal. Calcd. for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78. Found: C, 67.50; H, 9.07.

The spectral data for **11a** follow: NMR ($CDCl_3$) δ 4.83 (br s, 2), 3.78 (s, 3), 3.42 (m, 1), 2.4 (m, 1), 1.7–2.2 (m, 2), 1.58 (br, 2), 0.95–1.13 (m, 6); IR (CCl_4) 3095, 2970, 2250, 1755, 1644, 1260, 895 cm^{-1}; GC t_R 80.4 min.

The spectral data for **10a** follow: NMR ($CDCl_3$) δ 5.3 (m, 1), 3.78 (s, 3), 3.41 (m, 1), 2.0–2.5 (m, 1), 1.7–2.0 (m, 2), 1.4–1.7 (m, 6), 1.04 and 1.02 (2 d, 3, J = 7 Hz, CH_3 of two diastereomers); IR (CCl_4) 2960, 2250, 1755, 1260 cm^{-1}; GC t_R 85.2 min.

The spectral data for dihydropyran **5** ($R_1 = R_2 = R_3 = CH_3$) follow: NMR ($CDCl_3$) δ 3.76 (s, 3), 1.2–2.3 (m, 5), 1.32 (s, 3), 0.95 (d, 3, J = 6 Hz), 0.92 (t, 3, J = 6 Hz); IR (neat) 2975, 2200, 1760 (sh), 1640 cm^{-1}; UV max (ETOH) 298 nm (ε 195), 230 (2755).

The spectral data for **10b** (obtained pure from (*E*)-3-methyl-2-pentene) follow: NMR ($CDCl_3$) δ 5.30 (m, 1), 3.83–3.90 (several s, 3), 3.77 (t, 1 J = 7 Hz), 2.1–2.6 (m, 2), 1.8–2.1 (m, 3), 1.4–1.6 (m, 6), ~1.0 (2 d, 3, J = 7 Hz); IR (neat) 2960, 2200, 1750 cm^{-1}; mass spectrum, m/e (relative intensity, %) 307 (5), 306 (M^+, 25), 294 (2), 291 (7), 280 (2), 276 (2), 275 (12), 274 (3), 266 (2), 265 (11), 264 (29), 248 (9), 247 (18), 243 (8), 233 (6), 220 (6), 219 (5), 215 (8), 211 (33), 210 (33), 209 (8), 208 (46), 206 (11), 205 (8), 196 (10), 195 (46), 194 (16), 180 (24), 179 (29), 178 (14), 176 (43), 167 (11), 166 (74), 164 (23), 163 (13), 162 (11), 148 (26), 141 (10), 140 (14), 136 (30), 135 (12), 134 (20), 132 (11), 127 (25), 126 (24), 122 (14), 121 (25), 120 (22), 112 (95), 109 (24), 107 (24), 105 (24), 100 (41), 99 (39), 98 (57), 97 (79), 96 (79), 95 (29), 94 (22), 93 (33), 87 (72), 84 (83), 83 (95), 82 (36), 81 (95), 80 (95), 79 (60), 77 (43), 69 (97), 68 (89), 67 (95), 66 (47), 59 (98), 56 (66), 55 (100), 54 (63), 53 (97), 52 (97), 51 (51), 43 (97), 42 (60), 41 (97), 39 (97); mol wt calcd for $C_{16}H_{22}N_2O_4$ 306.1579, found 306.1572.

The spectral data for **11b** were estimated from the mixture of **10b** and **11b** obtained from (*Z*)-3-methyl-2-pentene: NMR ($CDCl_3$) δ 4.84 (br s, 2).

The spectral data for **8** ($R_1 = R_2 = R_3 = CH_3$) follow: NMR ($CDCl_3$) δ 3.80 (several s, 6), 2.4–2.8 (m, 2), 0.9–2.4 (m, 14); IR (neat) 2980, 2250, 1755 cm^{-1}; mol wt calcd for $C_{16}H_{22}N_2O_4$ 306.1579, found 306.1588.

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Registry No. 1, 137-05-3; (*E*)-**10a** (isomer 1), 77257-17-1; (*E*)-**10a** (isomer 2), 77257-18-2; (*Z*)-**10a** (isomer 1), 77257-19-3; (*Z*)-**10a** (isomer 2), 77257-20-6; **10b**, 77257-21-7; **11a** (isomer 1), 77270-01-0; **11a** (isomer 2), 77257-22-8; **11b**, 77257-23-9; **12a**, 77257-24-0; **12b**, 77257-25-1; **12c**, 77287-00-4; **13a**, 77257-26-2; **13b**, 77287-01-5; **13c**, 77287-02-6; methylenecyclohexane, 1192-37-6; 2-methyl-2-butene, 513-35-9; (*Z*)-3-methyl-2-pentene, 922-62-3; (*E*)-3-methyl-2-pentene, 616-12-6; 1-hexene, 592-41-6; Me_2AlCl, 1184-58-3.

Condensations at the 6 Position of the Methyl Ester and the Dimethylamide of 3,5-Dioxohexanoic Acid via 2,4,6-Trianions

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The trianions of methyl 3,5-dioxohexanoate and *N,N*-dimethyl-3,5-dioxohexanamide have been prepared by treatment of the compounds first with NaH to form the monoanions and then with 2 equiv of *sec*-butyllithium. The trianions are highly nucleophilic at the 6 position. Alkylation with benzyl chloride, aldol condensation with benzophenone, and acylation with methyl benzoate gave terminal condensation products but methyl acetate failed to condense with the trianions, proton transfer from the acetyl methyl group occurring instead. Both trianions underwent β-ketoacylation with methyl benzoylacetate but only the diketo ester trianion condensed with methyl acetoacetate. The resulting 1,3,5,7,9-pentacarbonyl compounds underwent cyclization reactions to give aromatic products. Complex aromatic products derived from 1,3,5,7,9,11-hexacarbonyl compounds were obtained from condensations of the diketo ester trianion with 4-methoxy-6-methyl-2-pyrone and of the diketo amide trianion with 4-methoxy-6-phenyl-2-pyrone.

Several classes of 1,3-dicarbonyl compounds have been converted to 2,4-dianions by treatment with 2 equiv of strong bases.[1] In all cases the resulting dianions have been highly nucleophilic and the initial reactions with electro-

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