105–106 °C; IR ($CHCl_3$) 1705 (C=O), 1635 (C=N) cm^{-1}; UV (ethanol) nm (log ϵ) 282 (4.13); ^1H NMR ($CDCl_3$) δ 2.01 (s, 3 H), 3.85 (s, 3 H), 6.9–7.2 (m, 2 H), 7.3–7.7 (m, 2 H), 12.0 (s, 1 H). Anal. ($C_{12}H_{11}NO_4$) C, H, N.

Preparation of 12a from 16. A mixture of **16** (1 g, 4.3 mmol) in anhydrous benzene (50 mL) and aluminium chloride (1.33 g, 10 mmol) was refluxed for 2 h. The reaction mixture was then poured into cold 10% hydrochloric acid (200 mL), the organic layer was separated, and the aqueous layer was extracted with benzene (50 mL). The combined extracts were dried (Na_2SO_4) and evaporated and the residue was recrystallized from ethanol to give **12a**: 0.23 g (27%); identical (melting point, IR, ^1H NMR) with the sample obtained from **9a**.

2-Methyl-4*H*-[1]benzopyrano[3,4-*d*]oxazol-4-one (17). A. From Beckmann Rearrangement of the Oxime 10a. In Thionyl Chloride. To a suspension of **10a** (2.19 g, 10 mmol) in anhydrous chloroform (100 mL) was added thionyl chloride (4.4 mL, 60 mmol). The mixture was refluxed for 4 h and then poured into cold water. The organic layer was washed with 5% $NaHCO_3$ and water, dried (Na_2SO_4), concentrated, and chromatographed over silica gel (methylene chloride as eluent) to give the oxazole **17**: 0.8 g (79%); mp 196–197 °C (ethanol) (lit.[32] mp 195–196 °C).

In Acetic Acid. A mixture of **10a** (2.19 g, 10 mmol) in acetic acid (100 mL) was refluxed for 4 h. After removal of acetic acid, the residue was dissolved in methylene chloride (50 mL), washed with 5% $NaHCO_3$ and water, dried (Na_2SO_4), concentrated, and chromatographed over silica gel (methylene chloride as eluent) to give first the isoxazole **7b** (0.25 g, 12%) and then the oxazole **17** (1 g, 50%): mp 194–195 °C (ethanol).

The spectral properties of **17** (IR, ^1H NMR) were the same as for an authentic sample prepared by the following procedure.

B. From 4-Hydroxy-3-nitrosocoumarin (18). A modification of the literature method[33] was used. A solution of **18**[28] (1.15 g, 6 mmol) in acetic anhydride (50 mL) was hydrogenated (ca. 1 atm) over 0.5 g of 10% Pd/C until 2 equiv of hydrogen have been taken up. The mixture was then refluxed for 30 min, filtered to remove the catalyst, and evaporated in vacuo. The residue was recrystallized from ethanol to give the oxazole **17**: 0.7 g (58%); mp 194–195 °C.

Registry No. 1a, 39079-62-4; **1b**, 51751-37-2; **2a**, 51085-94-0; **2b**, 74555-98-9; **2c**, 79388-03-7; **2d**, 77037-46-8; **2e**, 92397-11-0; **2f**, 92397-12-1; **3**, 68723-84-2; **4a**, 61348-47-8; **4b**, 51138-49-9; **5b**, 92397-13-2; **5c**, 92397-14-3; **5d**, 92397-15-4; **5e**, 92397-16-5; **5f**, 92397-17-6; **6b**, 92397-18-7; **6c**, 92397-19-8; **6d**, 92397-20-1; **6e**, 92397-21-2; **6f**, 92397-22-3; **7b**, 64547-88-2; **7c**, 64517-77-7; **7d**, 64517-78-8; **7e**, 92397-23-4; **7f**, 92397-24-5; **8**, 92397-25-6; **9a**, 2555-37-5; **10a**, 32321-82-7; **11a**, 92397-26-7; **12a**, 92397-27-8; $CH_3C(O)CH_2C(O)OEt$, 141-97-9; $EtC(O)CH_2C(O)OEt$, 4949-44-4; $PhC(O)CH_2C(O)OEt$, 94-02-0; $CH_3C(O)O$-*o*-$C_6H_4C(O)Cl$, 5538-51-2; $CH_3NHC(CH_3)=CHC(O)OEt$, 870-85-9; AcO-*o*-$C_6H_4C(O)C(C(O)OEt)=C(CH_3)NHCH_3$, 92397-28-9; NH_2OH, 7803-53-4; 2-acetoxy-5-chlorobenzoyl chloride, 5538-53-4; 2-acetoxy-4-methylbenzoyl chloride, 57148-35-3.

Supplementary Material Available: Analytical data for all new compounds **2e–f**, **7b–f**, **6b**, **8**, **11a–e**, **12a**, **14–16**; ^1H NMR for compounds **2e–f**, **7b–f**, **11a–e** (2 pages). Ordering information is given on any current masthead page.

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Condensation of Crotonic and Tiglic Acid Dianions with Aldehydes and Ketones

Paul R. Johnson and James D. White*

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

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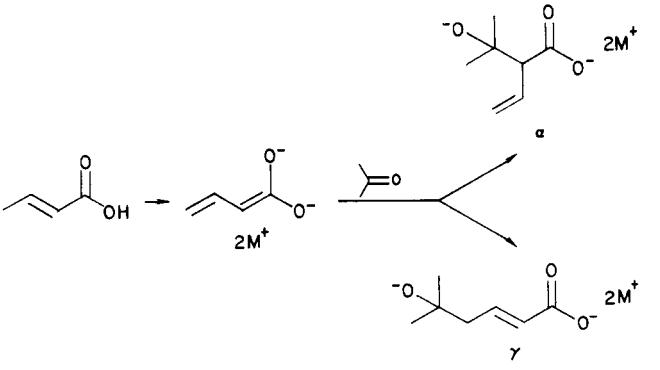
The lithium dianions of crotonic and tiglic acids reacted with *n*-heptanal, benzaldehyde, isobutyraldehyde, 2,2-dimethyl-3,3-dimethoxypropionaldehyde, acetone, and cyclopentanone at −78 °C, room temperature, and 65 °C to give α- and γ-condensation products. The kinetically controlled pathway gives largely or entirely the β-hydroxy acid from condensation at the α-carbon, but at higher temperature the reaction is reversible leading to the more stable δ-hydroxy α,β-unsaturated acid. In addition to the reaction temperature, steric effects associated with both the carbonyl electrophile and the acid dianion were found to influence the α:γ ratio of condensation products.

Deprotonation of the carboxylate salt of an α,β-unsaturated acid to give a dianion affords a practical means for introducing substitution at either the α- or γ-carbon of the acid. This chemistry, generalized in Scheme I, has been explored by Casinos and Mestres for the reaction of crotonate and senecioate (3,3-dimethylacrylate) dianions with aldehydes and ketones.[1] It was shown by these authors that the ratio of α- to γ-products was dependent on the structure of the acid, the structure of the carbonyl electrophile and, especially, on the temperature of the reaction.

The finding that both α- and γ-isomers can be obtained from the reaction of crotonate dianion with ketones supports the results of an earlier investigation of Pfeffer et al.[2] The latter attributed Watanabe's claim[3] of exclusive formation of the γ-product of crotonate dianion with cyclohexanone to the failure of the more hindered α-substituted acid to undergo esterification, which resulted in this isomer escaping detection. In their study of the reaction of senecioate dianion with benzaldehyde, Cardillo

Scheme I



(1) Casinos, I.; Mestres, R. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1651.
(2) Pfeffer, P.; Silbert, L.; Kensel, E. *Tetrahedron Lett.* **1973**, 1163.
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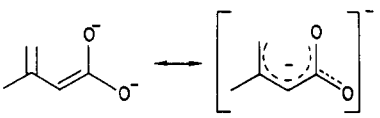
0022-3263/84/1949-4424$01.50/0

et al. likewise found that there was a temperature dependence of the α:γ ratio, with increased temperature favoring the γ-isomer.[4] It was further shown that the pair of metal counterions, as well as solvent polarity, exerted a major influence on the α:γ ratio. Increased ionic character of the organometallic bond (K^+–K^+ counterions, HMPA) enhanced the proportion of γ-product. A similar observation has been made by Vedejs et al., who found that addition of HMPA to the anion of the aldimine of tiglaldehyde greatly increased the yield of γ-product in its reaction with carbonyl electrophiles.[5]

Although the α:γ product ratio in the aldol reaction of α,β-unsaturated acid dianions is determined by several factors, the monoanion of an α,β-unsaturated ester affords an isomer distribution which is influenced primarily by the steric bulk of the substituent at the α-position. Thus, ethyl senecioate gave exclusively α-products with a series of carbonyl compounds, whereas ethyl tiglate and ethyl 2,3,3-trimethylacrylate gave only products of γ-condensation.[6] A further outcome of this study was the finding that the α:γ product ratio in the reaction of α,β-unsaturated ester enolates with alkyl halides bore little relationship to the isomer distribution observed with carbonyl electrophiles.

The ancillary question of double bond configuration in the γ-condensation product from crotonate dianion has been answered by the work of both Watanabe[3] and Pfeffer.[2] Only the γ-product of *E* configuration was obtained. However, with senecioate dianion, where proton removal at two alternative methyl sites is possible, there is a clear preference for syn deprotonation to generate the dianion A having s-cis or "U" geometry. Cardillo has made elegant

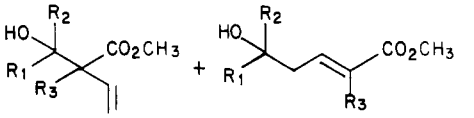


A

use of this specificity by employing A as an isoprene synthon in the preparation of a nerol derivative.[7] In the sole example involving γ-condensation of tiglate dianion, it was shown that this system is analogous to crotonate in giving exclusively the product of *E* configuration.[8]

In spite of the reasonably comprehensive study of Casinos and Mestres,[1] several significant issues were not addressed in their examination of dianion condensations of α,β-unsaturated acids. Foremost among these, from our perspective, were (a) the influence of an α-substituent in the acid on the α:γ product ratio and (b) the question of whether *E*/*Z* configuration could be preserved in the product. Since the γ-condensation of tiglate (or angelate) dianion with a malondialdehyde derivative was projected to play a key role in our plan for the synthesis of boromycin,[9] we chose to carry out a systematic investigation of this process. We report our results on the condensation of tiglate and crotonate dianions with certain aldehydes and ketones which extends earlier findings and defines more precisely the factors which control the α:γ isomer distribution.

Table I. Products of Condensation of Dianions of Crotonic and Tiglic Acids with Carbonyl Compounds[a]



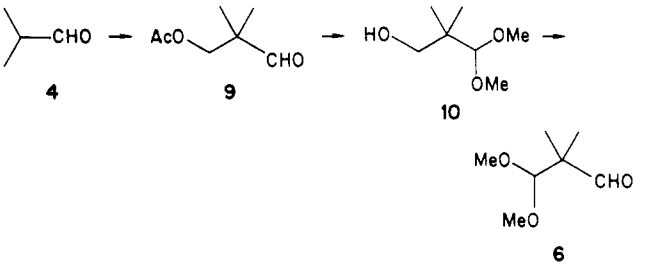
11 12

C=O compd	products 11 and 12			
		R_1	R_2	R_3
n-heptanal (3)	**a**	*n*-C_6H_{13}	H	H
	b	*n*-C_6H_{13}	H	CH_3
benzaldehyde (4)	**c**	C_6H_5	H	H
	d	C_6H_5	H	CH_3
isobutyraldehyde (5)	**e**	$(CH_3)_2CH$	H	H
	f	$(CH_3)_2CH$	H	CH_3
2,2-dimethyl-3,3-dimethoxy-propionaldehyde (6)	**g**	$(CH_3O)_2CHC(CH_3)_2$	H	H
	h	$(CH_3O)_2CHC(CH_3)_2$	H	CH_3
acetone (7)	**i**	CH_3	CH_3	H
	j	CH_3	CH_3	CH_3
cyclopentanone (8)	**k**	$-(CH_2)_4-$		H
	l	$-(CH_2)_4-$		CH_3

[a] After esterification with diazomethane.

Results and Discussion

Crotonic (1) and tiglic acids (2) were converted to their yellow dianions with 2 equiv of lithium diisopropylamide. These dianions in THF were reacted with *n*-heptanal (3), isobutyraldehyde (4), benzaldehyde (5), 3,3-dimethoxy-2,2-dimethylpropionaldehyde (6), acetone (7), and cyclopentanone (8) at −78 °C, room temperature, and at reflux. The aldehyde **6** was obtained by (i) condensation of **4** with aqueous formaldehyde in acetic acid containing a small quantity of sulfuric acid to give acetoxy aldehyde **9**,[10] (ii) saponification with 2 N sodium hydroxide[11] followed by treatment with trimethyl orthoformate in methanol containing *p*-toluenesulfonic acid to give **10**, and (iii) oxidation of this primary alcohol with pyridinium chlorochromate. The conversion of **4** to **6** proceeded in an overall 68% yield.



4 9 10 6

The crude product mixture from each reaction was quenched with NH_4Cl, then carefully acidified (3 N HCl), and treated with excess diazomethane. The resulting mixture of methyl esters (Table I) was conveniently assayed by ^1H NMR spectroscopy. The products (**11a–l**) of condensation at the α-carbon of **1** and **2** exhibit the typical ABX pattern of a vinyl group, the terminal methylene protons appearing as a multiplet at δ 5.0–5.2. The third vinylic proton in these structures was a multiplet in the crotonic acid series and a doublet of doublets in the tiglic acid series. In each case, this proton occurred at $\sim\delta$ 6.2. The distinguishing features of the products (**12a–l**) from condensation at the γ-carbon of **1** and **2** were the downfield β-vinylic proton (δ 6.85) and the pair of methylene protons at δ 2.3. Using these resonances, it was possible by careful integration to obtain two independent estimates of the

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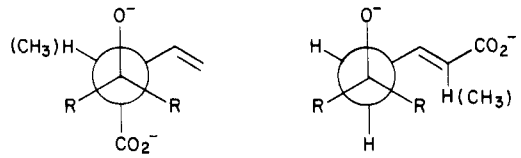
Table II. Ratio of α:γ Condensation Products (11:12) from Crotonic and Tiglic Acid Dianions with Carbonyl Compounds

products 11, 12	α:γ product ratio (yield, %)[a]		
	−78 °C	room temp	65 °C
a		100:0 (44)	1:1 (37)
b	20:1 (62)	15:1 (66)	1:5 (38)
c		100:0 (86)	1:1 (65)
d	100:1 (94)	15:1 (80)	0:100 (80)
e	20:1 (80)	4:1 (64)	1:4 (20)
f	3:1 (61)	1:3 (65)	0:100 (48)
g	3:1 (55)	3:2 (54)	1:20 (56)
h	1:1 (81)	2:5 (78)	0:100 (88)
i	20:1 (77)	2:1 (46)	1:2 (45)
j	10:1 (78)	1:2 (35)	1:11 (63)
k	6:1 (59)	5:2 (62)	0:100 (42)
l	100:0 (96)	1:1 (48)	0:100 (40)

[a] Measured on the methyl esters from treatment with CH_2N_2.

Chart I. Conformations of the α- and γ-Condensation Products from Crotonic and Tiglic Acid Dianions



proton count for each isomer. The α:γ product ratios calculated by this means are given in Table II.

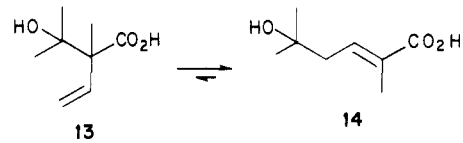
Separation of these isomeric methyl esters was readily achieved by medium-pressure liquid chromatography. However, no means could be found for clean separation of the mixture of erythro and threo stereoisomeric products which arise from the α-condensation mode with aldehydes. After purification, the β- and δ-hydroxy esters (**11** and **12**, respectively) were characterized as their 3,5-dinitrobenzoate derivatives. In all cases, the δ-hydroxy ester consisted of a single geometrical isomer, which was shown by ^1H NMR spectroscopy to have *E* configuration.

The data in Table II demonstrate that (i) the γ-condensation product is strongly favored for a given acid and carbonyl compound as the reaction temperature is raised from −78 to 65 °C, (ii) increased chain branching in the series of aldehydes **3**–**6** leads to an increased proportion of the γ-isomer, and (iii) tiglic acid gives a higher proportion of the γ-product than crotonic acid for a given carbonyl compound and reaction temperature. The latter two observations suggest that steric effects play a dominant role in this condensation, a result which can be easily rationalized by conformational analysis of the α- and γ-products (Chart I). Gauche interactions between the R groups and the vinyl and carboxylate substituents in the α-isomer should disfavor this compound relative to the γ-isomer, where the bulkier of the two R groups can be positioned between two hydrogen atoms. Conformational analysis also explains why tiglic acid, containing an α-methyl substituent, gives a higher proportion of γ-product than crotonic acid. This is most clearly seen in the condensation with the branched aldehydes **5** and **6** at room temperature, where the α:γ ratio is reversed in going from **1** to **2**. Here again a gauche interaction involving the methyl substituent will disfavor the α-product relative to the γ-product.

The effect of temperature on the reaction suggests a pathway that is kinetically controlled at low temperature but becomes reversible as the reaction temperature is raised. The predominant α-alkylation of **1** and **2** at low temperature is consistent with previous observations made on the kinetically controlled alkylation of α,β-unsaturated ester enolates.[12] That the dianion reaction becomes reversible at elevated temperature was demonstrated by isolating the pure hydroxy acid **13** from the α-condensation of tiglate dianion with **5**. When **13** was treated with 2.2 equiv of lithium diisopropylamide at 25 °C for 12 h, a 1:10 mixture of α-(**13**) and γ-(**14**) products was obtained, as determined by ^1H NMR analysis of their methyl esters.

Table III. Comparison of α:γ Product Ratios from Condensation of Crotonic and Tiglic Acids with Carbonyl Compounds at Different Reaction Times and Temperatures

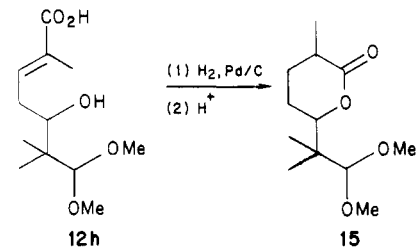
C=O compd	acid	reactn temp, °C	reactn time, h	α:γ ratio	ref
4	**1**	25	6	100:0	this work
4	**1**	45	2	7:3	1
4	**2**	25	6	15:1	this work
4	**2**	25	12	2:1	5
3	**2**	25	6	15:1	this work
C_2H_5CHO	**2**	25	14	2:1	5
8	**1**	−70	6	6:1	this work
$(CH_2)_5CO$	**1**	−70	0.1	9:1	1
$(CH_2)_5CO$	**1**	45	2	6:4	1
$(CH_2)_5CO$	**1**	45	10	1:9	1



13 **14**

Although reaction time was not varied systematically in our study, it was noted that, in those cases where condensation was allowed to proceed beyond the standard 6-h reaction time, an increased amount of γ-product was obtained. This indicates that the ratios in Table II do not in general represent equilibrium distributions. A comparison of our results with those of Casinos and Mestres[1] and of Vedejs and Gapinski[5] (Table III) supports the contention that increased reaction time favors the γ-product.

With optimal conditions established for the condensation of **2** with **6**, the β-hydroxy ester **12h** was available in 88% yield. This substance was hydrogenated to give 91% of the saturated acid, which was converted to δ-lactone **15**



12h **15**

(85%) upon exposure to refluxing benzene containing a catalytic quantity of benzoic acid. Lactone **16** was obtained as a 60:40 trans/cis mixture by this procedure, but equilibration via the enolate converted this to a 80:20 mixture in favor of the trans isomer. This material has provided us with an important building block in our quest for a synthesis of the ionophore boromycin.[9]

Conclusion

The aldollike reaction of α,β-unsaturated acid dianions with aldehydes and ketones under kinetically controlled conditions gives largely the product of condensation at the

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α-carbon. At elevated temperature, where the reaction becomes reversible, the thermodynamically more stable γ-condensation product predominates. The principal factor which determines the position of equilibrium appears to be the steric bulk of substituents around the electrophilic carbonyl group, although the stability of the γ-product is probably reinforced to a small extent by the conjugating effect of the double bond. In spite of the reversibility of this condensation, no isomerization at the double bond of either the crotonate or tiglate products was observed. The generally high efficiency of this condensation, together with the facile control which can be exercised over the distribution of regioisomeric products, makes this a valuable means for adding a butenoate moiety to a carbonyl function.

Experimental Section

Melting points were obtained on a Büchi melting point apparatus and are uncorrected. Infrared spectra (IR) were obtained with a Perkin-Elmer Model 727B infrared spectrometer. Ultraviolet spectra (UV) were obtained on a Varian-Cary Model 210 ultraviolet/visible spectrophotometer. Nuclear magnetic resonance spectra (NMR) were obtained with either a Varian EM-360A, HA-100, or FT-80A spectrometer and are reported in δ units with tetramethylsilane (Me_4Si) as the internal standard; the abbreviations s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet, etc. are used throughout. Mass spectra (MS) were obtained with either a Varian MAT CH-7 or a Finnigan 4500 spectrometer at an ionization potential of 70 eV. Exact mass determinations were made with a CEC-110C spectrometer at an ionization potential of 70 eV. Elemental analyses were done by MicAnal, Tucson, AZ. Column chromatography was carried out with neutral silica gel 60 (230–400 mesh ASTM). Analytical thin-layer chromatography (TLC) plates were obtained from Analtech. For medium-pressure liquid chromatography (MPLC), an FMI solvent pump was used. High-pressure liquid chromatography (HPLC) was performed by using a Waters Model M45 solvent pump, a Waters Model U6K injector, and a Waters semipreparative silica column. The detector used for both high-pressure and medium-pressure liquid chromatography was an Isco UV Model 1850 set at a wavelength of 260 nm. Dry tetrahydrofuran (THF) was obtained by distillation over sodium and benzophenone. All organic solutions were dried over magnesium sulfate and filtered through a sintered glass funnel prior to rotary evaporation at water aspirator pressure. Residual solvent was removed under vacuum, usually at less than 0.2 torr. All reactions were routinely carried out under an inert atmosphere of argon or nitrogen.

3,3-Dimethoxy-2,2-dimethylpropanol (10). 3-Acetoxy-2,2-dimethylpropionaldehyde (**9**)[10] (20.0 g, 139 mmol) was dissolved in methanol (100 mL). Trimethyl orthoformate (30 mL) and *p*-toluenesulfonic acid (1 g) were added, and the solution was stirred at room temperature for 24 h. A saturated solution of sodium chloride (100 mL) was added and the solution was extracted with ether (3 × 100 mL). The ethereal extract was dried and the solvents were removed in vacuo to yield 18.6 g (90%) of **10**: bp_{14} 85 °C (lit.[11] bp_{13} 81 °C); IR (neat) 3450, 1480, 1190, 1100, 1070 cm^{-1}; NMR ($CDCl_3$) δ 4.05 (s, 1 H), 3.55 (s, 6 H), 3.45 (s, 2 H), 0.95 (s, 6 H); MS, *m/e* (relative intensity) 145 (84), 131 (100, M^+ – OH).

3,3-Dimethoxy-2,2-dimethylpropionaldehyde (6). To a slurry of pyridinium chlorochromate (21.8 g, 101 mmol) in dry methylene chloride (200 mL) at 0 °C was added slowly a solution of **10** (10.0 g, 67.5 mmol) in methylene chloride (50 mL). After the mixture had stirred for 8 h at 25 °C, water (100 mL) and ether (100 mL) were added, and the mixture was stirred vigorously. The layers were separated and the organic phase was washed with water (50 mL). The aqueous layer was extracted with ether (3 × 50 mL). The combined organic layer was dried and chromatographed through a 3 cm × 50 cm column filled with 50 g of Florisil. The column was eluted with ether. Solvents were removed *in vacuo* to yield 9.63 g (97%) of **6**; IR (neat) 1730, 1080 cm^{-1}; NMR ($CDCl_3$) δ 9.6 (s, 1 H), 4.3 (s, 1 H), 3.6 (s, 6 H), 1.1 (s, 6 H); MS *m/e* (relative intensity) calcd for $C_7H_{13}O_3$ 145.086, found 145.086 (23, M^+ – H), 131 (100), 115 (40).

General Procedure for Addition of Crotonic and Tiglic Acids to Aldehydes and Ketones. Lithium diisopropylamide (2.2 equiv) was prepared by addition of *n*-butyllithium (1.5 M in hexane, 2.2 equiv) to a solution of diisopropylamine (2.2 equiv) in 5 mL of dry tetrahydrofuran at −78 °C. The solution was stirred for 0.5 h at 0 °C and then cooled to −78 °C. The acid (1 equiv) in 5 mL of dry tetrahydrofuran was added slowly to the lithium diisopropylamide solution and the mixture was stirred at 25 °C for 1 h and then cooled to −78 °C. The aldehyde or ketone (1 equiv) in 5 mL of dry tetrahydrofuran was added slowly to the yellow solution of the acid dianion, and the mixture was stirred at the specified temperature for 6 h. The solution was poured into a mixture of saturated ammonium chloride (10 mL) and ether (10 mL) and was shaken. The ethereal layer was separated and extracted with saturated sodium bicarbonate (3 × 10 mL), and the aqueous layer was acidified with 3 M hydrochloric acid. The acidified, aqueous solution was extracted with ether (3 × 20 mL), and the combined ethereal extracts were dried. Solvent was removed in vacuo to give an oil which was dissolved in ether (10 mL). To this solution was added an ethereal solution of diazomethane until a yellow color persisted. Solvents were removed in vacuo to yield the hydroxy esters as oils. After chromatographic purification, the individual esters were characterized as their 3,5-dinitrobenzoate, which were prepared by dissolving the esters in 2–3 mL of pyridine and adding 2 equiv of 3,5-dinitrobenzoyl chloride. After stirring the mixture for 12 h, ether (2 mL) and 3 M hydrochloric acid (2 mL) were added, and the layers were separated. The organic layer was washed with water and then with saturated sodium bicarbonate solution. The ethereal solution was dried and the solvent was removed in vacuo. Purification of the 3,5-dinitrobenzoates was achieved by flash chromatography on silica (20% ethyl acetate in hexane), which gave these derivatives as either a solid or an oil. The solid products were recrystallized from ethanol, while the oils were purified by high-pressure liquid chromatography.

Methyl 3-hydroxy-2-vinylnonanoate (11a): IR (neat) 3525, 1735, 1640, 1430, 1190, 1160 cm^{-1}; NMR ($CDCl_3$) δ 5.6–6.1 (m, 1 H), 5.05–5.35 (m, 2 H), 3.7 (m, 1 H), 3.71 (s, 3 H), 3.09 (m, 1 H), 1.15–1.7 (m, 10 H), 0.9 (t, *J* = 5, 3 H); MS, *m/e* (relative intensity) 197 (11.89, M^+ – OH), 100 (20.68).

3,5-Dinitrobenzoate: MS, *m/e* 408.154 (calcd for $C_{19}H_{24}N_2O_8$ 408.153).

Methyl 5-hydroxy-2-undecenoate (12a): IR (neat) 3490, 1725, 1660, 1435, 1270 cm^{-1}; NMR ($CDCl_3$) δ 6.92 (dt, *J* = 15, 7, 1 H), 5.85 (d, *J* = 15, 1 H), 3.7 (m, 1 H), 3.71 (s, 3 H), 2.35 (dd, *J* = 7, 7, 2 H), 1.15–1.7 (m, 10 H), 0.9 (t, *J* = 5, 3 H); MS, *m/e* (relative intensity) 197 (15.84, M^+ – OH), 100 (100).

3,5-Dinitrobenzoate: Anal. Calcd for $C_{19}H_{24}N_2O_8$: C, 55.88; H, 5.92; N, 6.86. Found: C, 55.86; H, 5.75; N, 6.72.

Methyl 3-hydroxy-2-methyl-2-vinylnonanoate (11b): IR (neat) 3550, 1730, 1640, 1460, 1240 cm^{-1}; NMR ($CDCl_3$) δ 6.3–5.8 (m, 1 H), 5.4–5.1 (m, 2 H), 3.8 (m, 1 H), 3.7 (s, 3 H), 1.5–1.2 (m, 13 H), 0.9 (t, *J* = 5, 3 H); MS, *m/e* (relative intensity) 229 (7.4, M^+ + H), 211 (35.5), 114 (100).

3,5-Dinitrobenzoate: Anal. Calcd for $C_{20}H_{26}N_2O_8$: C, 56.87; H, 6.20; N, 6.63. Found: C, 56.88; H, 6.19; N, 6.47.

Methyl 5-hydroxy-2-methyl-2-undecenoate (12b): IR (neat) 3470, 1715, 1645, 1435, 1280, 1070 cm^{-1}; NMR ($CDCl_3$) δ 6.8 (t, *J* = 7, 1 H), 3.75 (s, 3 H), 3.7 (m, 1 H), 2.4 (dd, *J* = 7, 7, 2 H), 1.9 (s, 3 H), 1.5–1.2 (m, 10 H), 0.9 (t, *J* = 5, 3 H); MS, *m/e* (relative intensity) 229 (6, M^+ + H), 211 (17), 151 (30), 114 (100).

3,5-Dinitrobenzoate: mp 52–54 °C. Anal. Calcd for $C_{20}H_{26}N_2O_8$: C, 56.87; H, 6.20; N, 6.63. Found: C, 56.98; H, 6.29; N, 6.60.

Methyl 3-hydroxy-3-phenyl-2-vinylpropionate (11c): IR (neat) 3500, 1730, 1640, 1440, 1190, 1155 cm^{-1}; NMR ($CDCl_3$) δ 7.3 (s, 5 H), 6.0–5.5 (m, 1 H), 5.2–5.0 (m, 2 H), 4.9 (m, 1 H), 3.6 (s, 3 H), 3.5 (m, 1 H); MS, *m/e* (relative intensity) 107 (59), 100 (100).

3,5-Dinitrobenzoate: MS, *m/e* 400.090 (calcd for $C_{19}H_{16}N_2O_8$ 400.091).

Methyl 5-hydroxy-5-phenyl-2-pentenoate (12c): IR (neat) 3470, 1710, 1660, 1440, 1275, 1200, 1020 cm^{-1}; NMR ($CDCl_3$) δ 7.27 (s, 5 H), 6.9 (dt, *J* = 16, 7, 1 H), 5.82 (dt, *J* = 16, 2, 2 H), 4.75 (bt, 1 H), 3.62 (s, 3 H), 2.6 (dd, *J* = 7, 7, 2 H); MS, *m/e*

(relative intensity) 189 (29, M^+ – OH), 107 (100), 100 (69).

3,5-Dinitrobenzoate: Anal. Calcd for $C_{19}H_{16}N_2O_8$: C, 57.00; H, 4.03; N, 7.00. Found: C, 57.39; H, 4.33; N, 6.67.

Methyl 3-hydroxy-2-methyl-3-phenyl-2-vinylpropionate (11d): IR (neat) 3450, 1720, 1630, 1245 cm^{-1}; NMR ($CDCl_3$) δ 7.3 (s, 5 H), 5.85–6.45 (m, 1 H), 4.95–5.4 (m, 4 H), 3.75 (s, 3 H), 1.3 (s, 3 H); MS, *m/e* (relative intensity) 221 (2.5, M^+ + H), 203 (100), 114 (49), 107 (19).

3,5-Dinitrobenzoate: Anal. Calcd for $C_{20}H_{18}N_2O_8$: C, 57.97; H, 4.38; N, 6.76. Found: C, 57.86; H, 4.40; N, 6.58.

Methyl 5-hydroxy-2-methyl-5-phenyl-2-pentenoate (12d): IR (neat) 3400, 1700, 1645, 1440, 1280 cm^{-1}; NMR ($CDCl_3$) δ 7.36 (s, 5 H), 6.85 (tq, J = 7, 2, 1 H), 4.8 (t, J = 7, 1 H), 3.7 (s, 3 H), 2.6 (dd, J = 7, 7, 2 H), 1.8 (bs, 3 H); MS, *m/e* (relative intensity) 221 (0.6, M^+ + H), 203 (56), 143 (87), 114 (100), 107 (71).

3,5-Dinitrobenzoate: MS, *m/e* 414.104 (calcd for $C_{20}H_{18}N_2O_8$ 414.106).

Methyl 3-hydroxy-4-methyl-2-vinylpentanoate (11e): IR (neat) 3550, 1730, 1635, 1160 cm^{-1}; NMR ($CDCl_3$) δ 6.2–5.6 (m, 1 H), 5.3–5.1 (m, 2 H), 3.7 (s, 3 H), 3.2 (dd, J = 7, 8, 1 H), 2.67 (dd, J = 7, 8, 1 H), 1.7 (m, 1 H), 0.97 (d, J = 7, 6 H); MS, *m/e* (relative intensity) 157 (8, M^+ + H), 141 (21), 100 (100).

3,5-Dinitrobenzoate: Anal. Calcd for $C_{16}H_{18}N_2O_8$: C, 52.46; H, 4.95; N, 7.65. Found: C, 52.48; H, 4.86; N, 7.63.

Methyl 5-hydroxy-6-methyl-2-heptenoate (12e): UV (MeOH) λ_{max} 211 nm (ϵ 11 000); IR (neat) 3500, 1730, 1635, 1430, 1160 cm^{-1}; NMR ($CDCl_3$) δ 6.97 (dt, J = 16, 7, 1 H), 5.87 (dt, J = 16, 2, 2 H), 3.7 (s, 3 H), 3.45 (dt, J = 1, 6, 1 H), 2.4 (dd, J = 7, 6 H); MS, *m/e* (relative intensity) 159 (s, M^+ + H), 141 (61), 100 (100).

3,5-Dinitrobenzoate: mp 74.5–75 °C. Anal. Calcd for $C_{16}H_{18}N_2O_8$: C, 52.46; H, 4.95; N, 7.65. Found: C, 52.42; H, 4.82; N, 7.38.

Methyl 2,4-dimethyl-3-hydroxy-2-vinylpentanoate (11f): IR (neat) 3550, 1735, 1650, 1240, 1100, 1000 cm^{-1}; NMR ($CDCl_3$) δ 6.3–5.9 (m, 1 H), 5.3–5.0 (m, 2 H), 3.7 (s, 3 H), 3.6 (d, J = 7, 1 H), 1.8 (m, 1 H), 1.35 (s, 3 H), 0.95 (d, J = 7, 6 H); MS, *m/e* (relative intensity) 187 (13, M^+ + H), 169 (40), 114 (100).

3,5-Dinitrobenzoate: MS, *m/e* 380.121 (calcd for $C_{17}H_{20}N_2O_8$ 380.122).

Methyl 2,6-dimethyl-5-hydroxy-2-heptenoate (12f): UV (MeOH) λ_{max} 218 nm (ϵ 12 100); IR (neat) 3540, 1720, 1650, 1280, 1100 cm^{-1}; NMR ($CDCl_3$) δ 6.78 (t, J = 8, 1 H), 3.68 (s, 3 H), 3.48 (dt, J = 4, 1, 1 H), 2.3 (dd, J = 4, 8, 2 H), 1.8 (s, 3 H), 1.75 (m, J = 7, 1, 1 H), 2.3 (dd, J = 4, 8, 2 H); MS, *m/e* (relative intensity) 187 (30, M^+ + H), 169 (60), 114 (100).

3,5-Dinitrobenzoate: mp 86.5–87 °C. Anal. Calcd for $C_{17}H_{20}N_2O_8$: C, 53.68; H, 5.30; N, 7.37. Found: C, 53.36; H, 5.20; N, 7.02.

Methyl 5,5-dimethoxy-4,4-dimethyl-3-hydroxy-2-vinylpentanoate (11g): IR (neat) 3550, 1735, 1640, 1440, 1155, 1060 cm^{-1}; NMR ($CDCl_3$) δ 6.2–5.8 (m, 1 H), 5.3–5.1 (m, 2 H), 4.1 (s, 1 H), 3.8 (d, J = 6, 1 H), 3.7 (s, 3 H), 3.5 (s, 6 H), 3.4 (m, 1 H), 0.95 (s, 6 H); MS, *m/e* (relative intensity) 215 (8, M^+ – OCH_3), 86 (98), 84 (100).

3,5-Dinitrobenzoate: MS, *m/e* 440.139 (calcd for $C_{19}H_{24}N_2O_{10}$ 440.143).

Methyl 7,7-dimethoxy-6,6-dimethyl-5-hydroxy-2-heptenoate (12g): IR (neat) 3525, 1725, 1660, 1270, 1100 cm^{-1}; NMR ($CDCl_3$) δ 7.1 (dt, J = 15, 7, 1 H), 5.9 (d, J = 15, 1 H), 4.02 (s, 1 H), 3.67 (s, 3 H), 3.5 (s, 6 H), 3.45 (t, J = 7, 1 H), 2.3 (dd, J = 7, 7, 2 H), 0.90 (s, 3 H), 0.86 (s, 3 H); MS, *m/e* (relative intensity) 215 (5, M^+ – OCH_3), 100 (52), 86 (100).

3,5-Dinitrobenzoate: MS, *m/e* 409.127 (M^+ – OCH_3) (calcd for $C_{18}H_{21}N_2O_9$ 409.125).

Methyl 5,5-dimethoxy-3-hydroxy-2,4,4-trimethyl-2-vinylpentanoate (11h): IR (neat) 3540, 1730, 1640, 1250, 1095, 1060 cm^{-1}; NMR ($CDCl_3$) δ 6.1 (dd, J = 16, 7, 1 H), 5.2 (m, 2 H), 4.15 (s, 1 H), 3.95 (s, 1 H), 3.65 (s, 3 H), 3.5 (s, 6 H), 1.4 (s, 1 H), 1.0 (s, 3 H), 0.9 (s, 3 H); MS, *m/e* (relative intensity) 229 (21, M^+ + H), 143 (92), 115 (100). The 3,5-dinitrobenzoate of **11h** could not be prepared.

Methyl 7,7-dimethoxy-5-hydroxy-2,6,6-trimethyl-2-heptenoate (12h): IR (neat) 3530, 1710, 1645, 1260, 1060 cm^{-1}; NMR ($CDCl_3$) δ 6.9 (t, J = 7, 1 H), 4.05 (s, 1 H), 3.8 (t, J = 4, 1 H), 3.7 (s, 3 H), 3.5 (s, 6 H), 2.25 (dd, J = 7, 4, 1 H), 1.9 (s, 3 H), 1.0 (s, 3 H), 0.9 (s, 3 H); MS, *m/e* (relative intensity) 229 (7, M^+ + H), 115 (69), 86 (100).

3,5-Dinitrobenzoate: MS, *m/e* 454.159 (calcd for $C_{20}H_{26}N_2O_{10}$ 454.159).

Methyl 3-hydroxy-3-methyl-2-vinylbutanoate (11i): IR (neat) 3530, 1735, 1640, 1435, 1190 cm^{-1}; NMR ($CDCl_3$) δ 6.15–5.7 (m, 1 H), 5.3–5.1 (m, 2 H), 3.7 (s, 3 H), 3.03 (d, J = 8, 1 H), 1.25 (s, 6 H); MS, *m/e* (relative intensity) 173 (7, M^+ + H), 155 (17), 129 (14), 100 (100).

3,5-Dinitrobenzoate: Anal. Calcd for $C_{15}H_{16}N_2O_8$: C, 51.14; H, 4.58; N, 7.95. Found: C, 51.27; H, 4.29; N, 7.93.

Methyl 5-hydroxy-5-methyl-2-hexenoate (12i): IR (neat) 3550, 1725, 1660, 1435, 1270, 1190 cm^{-1}; NMR ($CDCl_3$) δ 6.95 (dt, J = 16, 8, 1 H), 5.82 (dt, J = 16, 2, 2 H), 3.7 (s, 3 H), 2.35 (dd, J = 2, 8, 2 H), 1.25 (s, 6 H); MS, *m/e* (relative intensity) 173 (5, M^+ + H), 155 (9), 100 (100). The 3,5-dinitrobenzoate decomposed upon attempted purification.

Methyl 2,3-dimethyl-3-hydroxy-2-vinylbutanoate (11j): IR (neat) 3540, 1710, 1640, 1260 cm^{-1}; NMR ($CDCl_3$) δ 6.2 (dd, J = 10, 16, 1 H), 5.2 (dd, J = 1, 10, 1 H), 5.1 (dd, J = 1, 16, 1 H); MS, *m/e* (relative intensity) 173 (6, M^+ + H), 155 (68), 114 (100).

3,5-Dinitrobenzoate: Anal. Calcd for $C_{16}H_{18}N_2O_8$: C, 52.46; H, 4.95; N, 7.65. Found: C, 52.66; H, 4.91; N, 7.47.

Methyl 2,5-dimethyl-5-hydroxy-2-hexenoate (12j): IR (neat) 2500, 1710, 1645, 1250 cm^{-1}; NMR ($CDCl_3$) δ 6.84 (t, J = 8, 1 H), 3.76 (s, 3 H), 2.4 (d, J = 8, 2 H), 1.9 (s, 3 H), 1.3 (s, 6 H); MS, *m/e* (relative intensity) 173 (3, M^+ + H), 155 (100), 114 (91).

3,5-Dinitrobenzoate: mp 88–88.5 °C. Anal. Calcd for $C_{16}H_{18}N_2O_8$: C, 52.46; H, 4.95; N, 7.65. Found: C, 52.52; H, 5.01; N, 7.68.

Methyl 3-cyclopentyl-3-hydroxy-2-vinylpropionate (11k): IR (neat) 3550, 1730, 1640, 1435, 1195, 1160, 990 cm^{-1}; NMR ($CDCl_3$) δ 6.2–5.8 (m, 1 H), 5.25–5.05 (m, 2 H), 3.7 (s, 3 H), 3.1 (d, J = 8, 1 H), 1.85–1.5 (m, 8 H); MS, *m/e* (relative intensity) 185 (6, M^+ + H), 135 (35), 107 (100), 101 (99).

3,5-Dinitrobenzoate: Anal. Calcd for $C_{17}H_{18}N_2O_8$: C, 53.97; H, 4.80; N, 7.40. Found: C, 54.10; H, 4.81; N, 7.45.

Methyl 5-cyclopentyl-5-hydroxy-2-pentenoate (12k): IR (neat) 3500, 1720, 1655, 1435, 1270, 1190, 970 cm^{-1}; NMR ($CDCl_3$) δ 7.0 (dt, J = 15, 8, 1 H), 5.85 (dt, J = 15, 1, 1 H), 3.63 (s, 3 H), 2.4 (dd, J = 8, 1, 2 H), 1.7–1.5 (m, 8 H); MS, *m/e* (relative intensity) 100 (100), 85 (73).

3,5-Dinitrobenzoate: mp 83–83.5 °C. Anal. Calcd for $C_{17}H_{18}N_2O_8$: C, 53.97; H, 4.80; N, 7.40. Found: C, 53.92; H, 4.80; N, 7.30.

Methyl 3-cyclopentyl-3-hydroxy-2-methyl-2-vinylpropanoate (11l): IR (neat) 3550, 1730, 1640, 1250, 1110 cm^{-1}; NMR ($CDCl_3$) δ 6.1 (dd, J = 10, 16, 1 H), 5.2 (dd, J = 1, 10, 1 H), 5.1 (dd, J = 1, 16, 1 H), 3.66 (s, 3 H), 1.85–1.45 (m, 8 H), 1.36 (s, 3 H); MS, *m/e* (relative intensity) 145 (5), 114 (100), 82 (60).

3,5-Dinitrobenzoate: MS, *m/e* 392.120 (calcd for $C_{18}H_{20}N_2O_8$ 392.122).

Methyl 5-cyclopentyl-5-hydroxy-2-methyl-2-pentenoate (12l): IR (neat) 3500, 1710, 1645, 1260 cm^{-1}; NMR ($CDCl_3$) δ 6.84 (t, J = 8, 1 H), 3.72 (s, 3 H), 2.5 (d, J = 8, 2 H), 1.88 (s, 3 H), 1.8–1.6 (m, 8 H); MS, *m/e* (relative intensity) 181 (37), 114 (100).

3,5-Dinitrobenzoate: mp 97 °C. Anal. Calcd for $C_{18}H_{20}N_2O_8$: C, 55.10; H, 5.14; N, 7.14. Found: C, 54.94; H, 5.01; N, 7.58.

Equilibration of 2,4-Dimethyl-3-hydroxy-2-vinylpentanoic Acid, Methyl Ester (11f) to 2,6-Dimethyl-5-hydroxy-2-heptenoic Acid, Methyl Ester (12f). A mixture of **11f** and **12f** (0.207 g ratio 3:1, respectively) in tetrahydrofuran (5 mL) was added slowly to a solution of lithium diisopropylamide in tetrahydrofuran (5 mL) at –78 °C. The solution was stirred at 25 °C for 18 h. Standard workup gave 0.10 g (48%) of a mixture of **11f** and **12f** in a ratio of 1:10, respectively.

7,7-Dimethoxy-5-hydroxy-2,6,6-trimethylheptanoic Acid δ-Lactone (16). Tiglic acid (1.3 g, 13 mmol) in 20 mL of tetrahydrofuran was added to a solution of lithium diisopropylamide (28.5 mmol) in tetrahydrofuran (20 mL), prepared from diisopropylamine (3.0 g, 29.6 mmol) and *n*-butyllithium (1.5 M in hexane, 19 mL, 28.5 mmol), at –78 °C. The solution was stirred at 25 °C for 1 h and cooled to –78 °C. Aldehyde **6** (1.7 g, 12 mmol) in tetrahydrofuran (20 mL) was added slowly, and the solution was allowed to warm and was stirred at 25 °C for 18 h. The solution was poured into a mixture of a saturated solution of

ammonium chloride (20 mL) and ether (20 mL) and was shaken. The organic layer was separated and was extracted with a saturated solution of sodium bicarbonate (3 × 10 mL). The aqueous layer was acidified with 3 M hydrochloric acid and extracted with ether (3 × 30 mL). The combined ether extract was dried and the solvent was removed in vacuo to give 2.60 g (88%) of **12h** as an oil. This material was dissolved in methanol (200 mL) and the solution was stirred for 24 h under one atmosphere of hydrogen with 5% palladium-on-carbon (0.26 g) as catalyst. The suspension was filtered through Celite, and the filtrate was concentrated in vacuo to give 2.4 g (91%) of the saturated acid as an oil. This was dissolved in benzene (200 mL) containing benzoic acid (12 mg), and the solution was refluxed for 24 h under 4Å molecular sieves. After removal of the solvent in vacuo, the residual oil was purified by chromatography (40% ethyl acetate in hexane) to give 1.96 g (85%) of **16**: IR (neat) 1740, 1460, 1380, 1180, 1080 cm^{-1}; NMR ($CDCl_3$) δ 4.34 (m, 1 H), 4.24, 4.22 (2 s, 0.5 H, 0.5 H), 3.52, 3.50, 4.99 (3 s, 1.5 H, 3 H, 1.5 H), 2.7–1.5 (m, 5 H), 1.30, 1.22 (2 d, 1.5 H, 1.5 H), 0.94, 0.92 (2 s, 1.5 H, 1.5 H), 0.84 (s, 3 H); MS, *m/e* 199.133 ($M^+ - OCH_3$) (calcd for $C_{11}H_{19}O_3$ 199.133).

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Registry No. 1, 3724-65-0; 1 (lithium dianion), 83439-40-1; 2, 80-59-1; 2 (lithium dianion), 92186-60-2; 3, 111-71-7; 4, 100-52-7; 5, 78-84-2; 6, 18208-39-4; 7, 67-64-1; 8, 120-92-3; 9, 16184-79-5; 10, 87395-22-0; 11a, 56949-93-0; 11a (3,5-dinitrobenzoate), 92186-61-3; 11b, 92186-64-6; 11b (3,5-dinitrobenzoate), 92186-65-7; 11c, 56949-94-1; 11c (3,5-dinitrobenzoate), 92186-68-0; 11d, 92186-70-4; 11d (3,5-dinitrobenzoate), 92186-71-5; 11e, 92186-74-8; 11e (3,5-dinitrobenzoate), 92186-75-9; 11f, 92186-78-2; 11f (3,5-dinitrobenzoate), 92186-79-3; 11g, 92186-82-8; 11g (3,5-dinitrobenzoate), 92186-83-9; 11h, 92186-85-1; 11h (3,5-dinitrobenzoate), 92186-86-2; 11i, 92186-88-4; 11i (3,5-dinitrobenzoate), 92186-89-5; 11j, 92186-92-0; 11j (3,5-dinitrobenzoate), 92186-93-1; 11k, 92186-96-4; 11k (3,5-dinitrobenzoate), 92186-97-5; 11l, 92187-00-3; 11l (3,5-dinitrobenzoate), 92187-01-4; 12a, 92186-62-4; 12a (3,5-dinitrobenzoate), 92186-63-5; 12b, 92186-66-8; 12b (3,5-dinitrobenzoate), 92186-67-9; 12c, 72853-47-5; 12c (3,5-dinitrobenzoate), 92186-69-1; 12d, 92186-72-6; 12d (3,5-dinitrobenzoate), 92186-73-7; 12e, 92186-76-0; 12e (3,5-dinitrobenzoate), 92186-77-1; 12f, 92186-80-6; 12f (3,5-dinitrobenzoate), 92186-81-7; 12g, 92186-84-0; 12g (3,5-dinitrobenzoate), 92219-75-5; 12h, 92187-05-8; 12h (3,5-dinitrobenzoate), 92186-87-3; 12i, 92186-90-8; 12i (3,5-dinitrobenzoate), 92186-91-9; 12j, 92186-94-2; 12j (3,5-dinitrobenzoate), 92186-95-3; 12k, 92186-98-6; 12k (3,5-dinitrobenzoate), 92186-99-7; 12l, 92187-02-5; 12l (3,5-dinitrobenzoate), 92187-03-6; 15, 92187-04-7; trimethyl orthoformate, 149-73-5.

The Synthesis and Selected Chemistry of 6-Alkyl-6-carbalkoxy- and 6-Alkyl-6-(aminocarbonyl)-2,4-cyclohexadien-1-ones and Cyclohexadienone Ketals

Arthur G. Schultz,* James P. Dittami, Frank P. Lavieri, Christina Salowey, Padmanabhan Sundararaman, and Mary Beth Szymula

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

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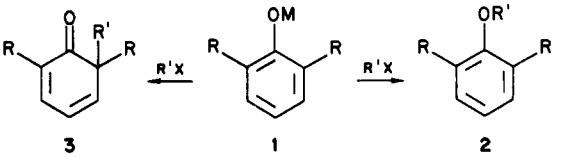
The preparation of several 6-alkyl-6-carbalkoxy-2,4-cyclohexadien-1-ones and corresponding C(1) ketals is described. Birch reduction–alkylation of methyl 2-methoxybenzoates gives 6-alkyl-6-carbomethoxy-1-methoxy-1,4-cyclohexadienes **4a–e** and **5a–d**, and these are converted to bromo ketals **12** and **13**, respectively, by treatment with *N*-bromoacetamide in methanol. Base-catalyzed dehydrobrominations of the bromo ketals produce 2,4-cyclohexadien-1-one dimethyl ketals **15** and **16**; acid-catalyzed ketal hydrolysis gives the title 2,4-cyclohexadienones **17** and **18**. Alternatively, acid-catalyzed enol ether hydrolysis of **4** and **5** gives 2-alkyl-2-carbomethoxy-3-cyclohexen-1-ones **19** and **20**; allylic bromination–dehydrobromination of **19** and **20** (*N*-bromosuccinimide) gives **17** and **18**. Analogous processes with *N,N*-diethylbenzamide derivatives are discussed. Diels–Alder reactions of the 2,4-cyclohexadienones provide a route to bicyclo[2.2.2]oct-5-en-2-ones **29**, from which triplet-sensitized oxa-di-π-methane photorearrangements give tricyclo[3.2.1.$0^{2,8}$]octan-3-ones **30**. The incorporation of optical activity by reduction–alkylation of the *d*-menthol ester of *o*-anisic acid is detailed.

The 2,4-cyclohexadien-1-one ring system embodies a potentially versatile array of functionality in a compact, stereochemically defined environment. Reactions of 2,4-cyclohexadienones include (1) cycloadditions in which the diene unit functions as a two-electron or four-electron component, (2) photochemical rearrangements to diene ketene derivatives and bicyclo[3.1.0]hex-3-en-2-ones, and (3) nucleophilic, electrophilic, and radical additions involving 1,2-, 1,4-, and 1,6-processes. Despite this vast potential for reactivity, 2,4-cyclohexadienones are only occasionally used in multistep organic synthesis. Most likely this situation is a result of an absence of efficient and general methods for the preparation of 2,4-cyclohexadienones.

Carbon alkylation of the alkali metal salts of phenols, **1**, is the most expeditious route to 2,4-cyclohexadienones. Although formation of alkyl aryl ethers, **2**, is favored in



3 **1** **2**

polar or protic solvents, substantial carbon alkylation can occur under nonhomogeneous conditions in hydrocarbon solvents.[1] Only the most reactive alkylation reagents (e.g., methyl iodide, allylic and benzylic halides) are useful under

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