Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.21; H, 7.07; N, 4.68. Found: C 72.11; H, 7.35; N, 4.46.

Decyanation of Acids 10 and 11. To a stirred solution of each acid (100 mg) in dry tetrahydrofuran (3 ml) and redistilled liquid ammonia (30 ml) was added sodium (80 mg) and the stirring was continued for 5 min. An excess of ammonium chloride (2 g) was added in small portions to the reaction mixture and ammonia was allowed to evaporate. The residue was acidified with 10% hydrochloric acid (10 ml) and extracted with ether. The ethereal layer was washed with water and extracted with 10% sodium hydroxide. After acidification of the above alkaline layer the acid was isolated by extraction with ether. The results are shown below.

The acid (**10**) formed a colorless oil which was chromatographed on silica gel (5 g) using benzene–*n*-hexane (4:1) to give 1α-carboxy-1,2,3,4,4aα,9,10,10aα-octahydro-7-methoxy-1β-methylphenanthrene (**13**), which was recrystallized from methanol to give colorless needles (33 mg): mp 195–196 °C (lit.[10] 197–198 °C); IR (KBr) 1690 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.23 (3, H, s, C_1 CH_3), 3.75 (3 H, s, OCH_3), 6.60 (1 H, d, J = 2 Hz, C_8 H), 6.67 (1 H, dd, J = 8 and 3 Hz, C_6 H), and 6.96 ppm (1 H, d, J = 8 Hz, C_5 H).

Further elution with benzene gave 1α-carboxy-1,2,3,4,4aβ,9,10,10aα-octahydro-7-methoxy-1β-methylphenanthrene (**12**), which was recrystallized from methanol to give colorless prisms (29 mg): mp 174–175 °C (lit.[10] 175 °C); IR (KBr) 1685 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.20 (3 H, s, C_1 CH_3), 3.74 (3 H, s, OCH_3), 6.57 (1 H, d, J = 3 Hz, C_8 H), 6.66 (1 H, dd, J = 9 and 3 Hz, C_6 H), and 7.17 ppm (1 H, d, J = 9 Hz, C_5 H).

Acknowledgment. We thank Dr. U. R. Ghatak, Department of Organic Chemistry, Indian Association for the Cultivation of Science, for a gift of the authentic 1-carboxy-1,2,3,4,4a,9,10,10a-octahydro-7-methoxy-1-methylphenanthrenes. We also thank Mrs. R. Kobayashi, Miss R. Suenaga, Miss E. Nagaoka, Miss M. Tanno, Mrs. C. Koyanagi, Miss K. Mushiake, and Mr. K. Kawamura, Pharmaceutical Institute, Tohoku University, for spectral measurements and microanalyses.

Registry No.—1, 61243-63-8; **2,** 61259-31-2; **3,** 61259-32-3; **4,** 61259-33-4; **5,** 61259-34-5; **8,** 61259-35-6; α-**9,** 61259-36-7; β-**9,** 61259-37-8; **10,** 61259-38-9; **11,** 61259-39-0; **12,** 61259-40-3; **13,** 61259-41-4.

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A Method for the Synthesis of Unsaturated Carbonyl Compounds

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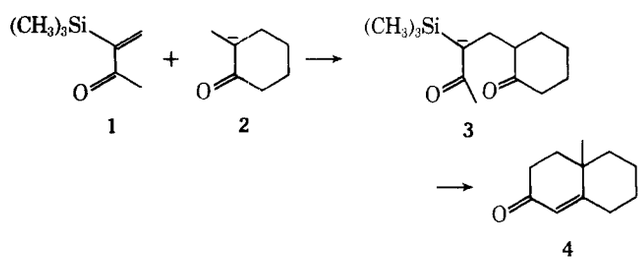
Received July 26, 1976

Unsaturated carbonyl compounds can be prepared by a three-step procedure involving (1) formation of an ethyloxalyl derivative **14**; (2) reaction with an aldehyde to give a diketolactone **15**; and (3) base cleavage to product **16**. Twenty-five examples are reported. Ketones, esters, lactones, lactams, and nitriles all undergo the reaction, although esters and lactones appear to work best. The method has been found to be particularly efficient in preparing α-methylenecyclohexanone (87%), α-methylenebutyrolactone (83%), and α-methylenevalerolactone (93%).

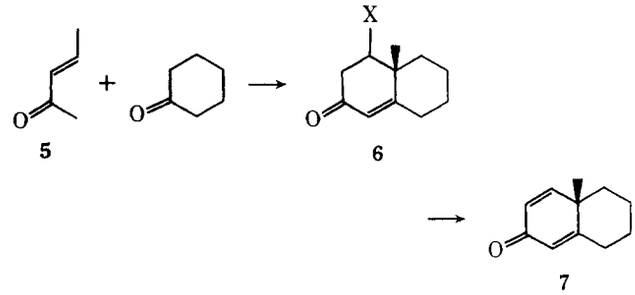
One of the more valuable recent contributions to the methodology of organic synthesis is the work of Stork[1] and Boeckmann[2] in which Robinson annelation reactions are carried out by reacting equivalent amounts of enolate ions with methyl (α-trimethylsilyl)vinyl ketone. Cyclization and desilylation of the initial Michael adducts are then effected by base treatment.



1 2 3 4

The great advantage of this method is that the anion adduct **3** is stable under reaction conditions and does not polymerize the vinyl ketone. This low reactivity of **3** is presumed[1] to be due to the stabilizing effect of silicon on the neighboring carbanion, although steric effects may also play a large role.

For some time, we have been interested in developing general methods of enone synthesis and have reported,[3] for example, the use of β-carboxy ketones as enone equivalents. Our basic idea was to effect Robinson annelation with a substituted vinyl ketone such as **5** and then unmask the enone at

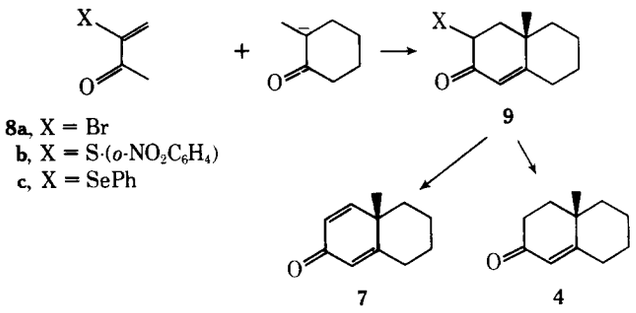


5 6 7

an appropriate time (by oxidative decarboxylation when X = CO_2H).

Combining the Stork–Boeckmann work with our own in-

terest in masked enone synthesis, we felt that it would be worthwhile to synthesize and examine the annelation reactions of other α-substituted vinyl ketones, **8**. The requirements we put on the substituent X are that it stabilize a neighboring carbanion so that Robinson annelations can be carried out with equivalent amounts of enolates; that it be replaceable by H if desired; and that it be readily eliminated to yield an enone if desired.

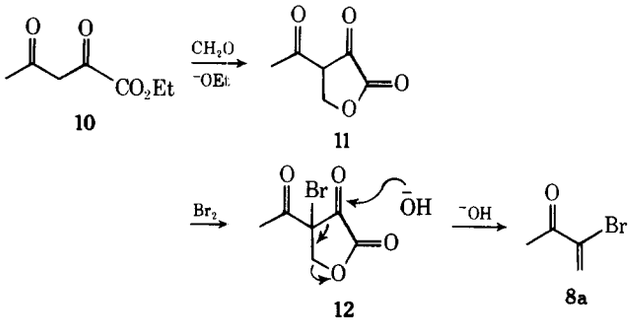


8a, X = Br
b, X = S-(*o*-$NO_2C_6H_4$)
c, X = SePh

9

7 **4**

The obvious choices are X = halogen, SAr, and SeAr, and we therefore attempted the synthesis of the necessary molecules. Methyl α-bromovinyl ketone (**8a**, X = Br) is a known compound[4] which has been prepared from acetone by an unusually clever route. The ethyloxalyl derivative of acetone is condensed with formaldehyde, and the resultant diketolactone (**11**) brominated. Cleavage of the dicarbonyl system and

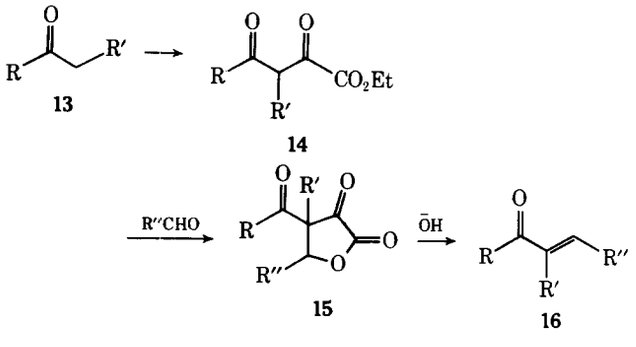


10 **11** **12** **8a**

loss of oxalate is effected by mild base treatment, yielding the desired bromovinyl ketone **8a**.

It occurred to us that the other target compounds **8b** and **8c** might be obtainable by similar routes. When, in fact, a THF solution of the sodium salt of diketolactone **11** was treated either with *o*-nitrophenylsulfenyl chloride or with phenylselenenyl chloride, compounds **8b** and **8c** were obtained in 92 and 90% yields, respectively. Unfortunately, all attempts to carry out Robinson annelation reactions between enolate ions and the vinyl ketones **8a**, **8b**, and **8c** led only to intractable materials, presumably polymerized vinyl ketone.

Our original intentions were therefore stymied, but we became intrigued by the synthetic possibilities of the reaction by which substrates **8a**, **8b**, and **8c** were made, and decided to delve further. In particular, we thought that the two-step



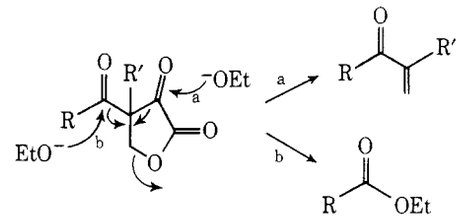
13 **14** **15** **16**

condensation and cleavage of oxalyl derivatives might well prove to be a general method of enone synthesis.

The overall process would, of course, be equivalent to a mixed aldol reaction, but one which is directed by formation of the oxalyl derivative. As can be seen from the results presented in Table I, the reaction is in fact capable of serving as a general synthesis of alkylidene carbonyl compounds, although certain limitations are present.

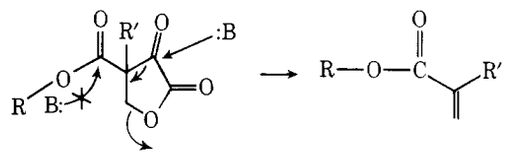
Of the ethyloxalyl ketones examined (reactions 4–10) good yields of products were obtained only in the simplest and most unhindered cases. Condensation of sodioethyl oxalylcyclohexanone[5] with gaseous formaldehyde, followed by treatment with aqueous bicarbonate at 0 °C, gave α-methylenecyclohexanone in 87% yield. This one-pot synthesis constitutes by far the most efficient method for the production of this enone,[6] and the high yield of the thermally sensitive product is undoubtedly due to the extraordinary mildness of the reaction conditions. Methylenecycloheptanone is similarly obtained in good yield (72%) but methylenecyclopentanone cannot be obtained by this method, probably for reasons outlined below.

The reaction works less well when aldehydes other than formaldehyde are used (reactions 5, 6) and when the somewhat more hindered acyclic ketones are used (reactions 9, 10). Attempted methylenation of ethyl phenyl ketone (reaction 10) is particularly instructive since only a low yield of enone is obtained along with much ethyl benzoate when ethoxide is added as base. This demonstrates an inevitable difficulty of the method: since the final step is a β-dicarbonyl cleavage, two different products can be formed depending on which carbonyl is attacked.



In *diketone* cleavages of the type discussed thus far, there is undoubtedly a subtle balance of factors determining the mode of cleavage, and this presumably accounts for some of the low yields obtained, cf. methylenecyclopentanone vs. methylenecyclohexanone.

One ought, however, to be able to control the site of attack and direction of cleavage, by changing the nature of the carbonyl groups. For example, an ester or lactone carbonyl should



be attacked by base less readily than a ketone carbonyl. This means that we may well be able to α-olefinate oxalyl esters or lactones without interference from unwanted cleavages.

Reactions 11–21 show that this expectation can be realized and that both lactones and esters undergo reaction in good yield. The ethyloxalyl derivatives of both butyrolactone and valerolactone react with a variety of primary aldehydes in good to excellent yields. The yields of α-methylenebutyrolactone (83%) and α-methylenevalerolactone (93%) are particularly good and, because of its mildness, this present reaction procedure would seem to compete very favorably with other methods of synthesis.[7]

Acyclic esters (reactions 18–21) also react in good to excellent yields with a variety of primary aldehydes, making

Table I. Synthesis of Some Unsaturated Carbonyl Compounds[b]

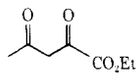
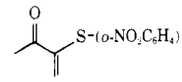
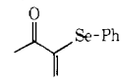
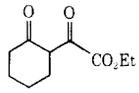
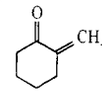
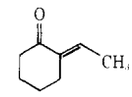
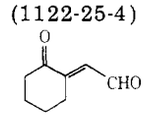
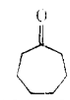
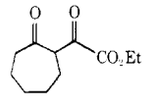
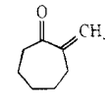
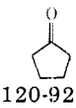
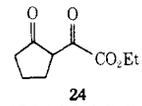
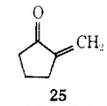
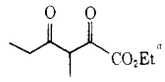
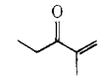
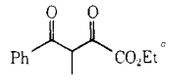
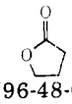
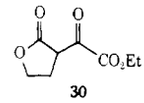
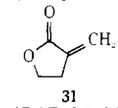
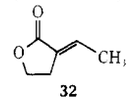
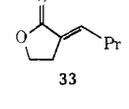
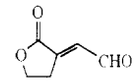
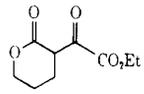
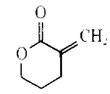
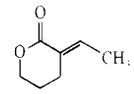
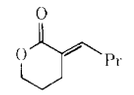
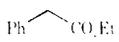
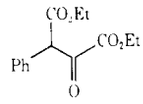
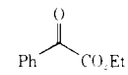
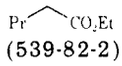
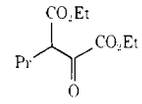
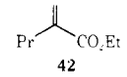
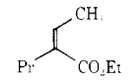
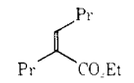
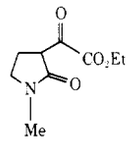
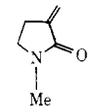
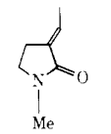
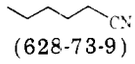
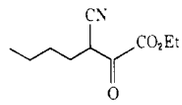
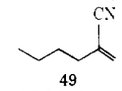
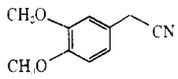
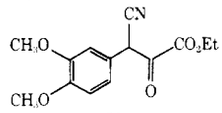
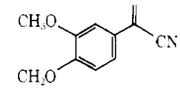
Reaction	Carbonyl compd	Oxalyl derivative	(yield)	Aldehyde	Product	(yield)
1	 (67-64-1)	 17 (615-79-2)	(70)	CH_2O (50-00-0)	 8a (61203-01-8)	(75)
2					 8b (61203-02-9)	(92)
3					 8c (61203-03-0)	(90)
4	 (108-94-1)	 18 (5396-14-2)	(75)	CH_2O	 19 (3045-98-5)	(87)
5				CH_3CHO (75-07-0)	 20 (1122-25-4)	(40)
6				CHOCHO (107-22-2)	 21 (61203-04-1)	(~20)
7	 (502-42-1)	 22 (29800-43-9)	(76)	CH_2O	 23 (3045-99-6)	(72)
8	 (120-92-3)	 24 (39163-39-8)	(80)	CH_2O	 25 (1489-50-5)	(low)
9	 (96-22-0)	 26 (61202-97-9)	*a*	CH_2O	 27 (25044-01-3)	(40)
10	 (93-55-0)	 28 (61202-98-0)	*a*	CH_2O	 29 (769-60-8) [$PhCO_2Et$ (77)]	(13)
11	 (96-48-0)	 30 (42564-36-3)	(90)	CH_2O	 31 (547-65-9)	(83)
12				CH_3CHO	 32	(68)
13				PrCHO (123-72-8)	 33	(62)

Table I (*Continued*)

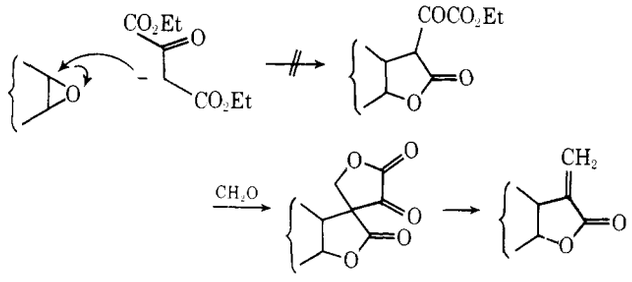
Reaction	Carbonyl compd	Oxalyl derivative	(yield)	Aldehyde	Product	(yield)
14				CHOCHO	 34 (61203-05-2)	(50)
15	 (542-28-9)	 35 (61202-99-1)	(95)	CH_2O	 36 (42023-19-8)	(93)
16				CH_3CHO	 37	(80)
17				PrCHO	 38	(62)
18	 (101-97-3)	 39 (7147-33-3)	(80)	CH_2O	 40 (22286-82-4)	(100)
19	 (539-82-2)	 41 (26103-78-6)	(81)	CH_2O	 42 (3550-06-9)	(71)
20				CH_3CHO	 43	(71)
21				PrCHO	 44	(68)
22	 (872-50-4)	 45 (60044-10-2)		CH_2O	 46 (50586-05-5)	(61)
23				CH_3CHO	 47 (932-26-3)	(low)
24	 (628-73-9)	 48 (61203-00-7)	*a*	CH_2O	 49 (4388-91-4)	(low)
25	 (93-17-4)	 50 (38747-09-0)	(86)	CH_2O	 51 (61203-06-3)	(90)

[a] Oxalyl compound not isolated. [b] Registry no. are in parentheses.

possible the simple syntheses of many structurally diverse unsaturated esters.

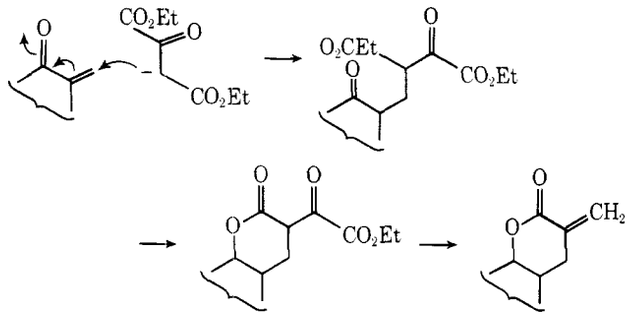
Finally, we have demonstrated that both lactams (reactions 22, 23) and nitriles (reactions 24, 25) may be α-methylenated, although those reactions do not appear to be as general as the ester and lactone cases.

Many other uses of the reaction can be conceived of. For example, a synthesis of fused α-methylenebutyrolactones can be envisioned along the following lines: nucleophilic epoxide



opening by the anion of diethyl oxaloacetate should yield an oxalyl lactone which, on reaction with formaldehyde followed by cleavage, would be expected to result in a one-pot methylene lactone synthesis.

The scheme failed, however, when we were unable to realize the opening of a variety of epoxides under any conditions, a somewhat surprising result since β-keto ester anions react smoothly[8] with epoxides. Diethyl oxaloacetate appears from



this result to be a very poor nucleophile. Further confirmation of this was gained in another unsuccessful scheme which would have resulted in the construction of fused methylenevalerolactones.

Once again, the scheme went unrealized owing to the failure of diethyloxaloacetate to add to a variety of enones, a result noticed before in the literature.[9]

Summary

In summary, although not all of our goals have been met, we have discovered some useful results. This method of synthesis of unsaturated carbonyl compounds which we have exploited has provided excellent syntheses of the sensitive α-methylenecyclohexanone, of methylene lactones, and of other alkylidene lactones and esters.

Experimental Section

NMR spectra were recorded in the solvent indicated (Me_4Si internal standard) on a Varian A-56/60A instrument. IR spectra were obtained on a Perkin-Elmer 337, and mass spectra were taken on a Hitachi Perkin-Elmer RMU6E.

Methyl α-(Phenylselenenyl)vinyl Ketone (8c). Diketolactone 11[4] (1.56 g, 9.7 mmol) was dissolved in 15 ml of ethanol and added to a solution of 1.0 g of $KHCO_3$ in 5 ml of water. Stirring was continued until gas evolution ceased and solvent was then removed at 70 °C under reduced pressure. After drying overnight at 70 °C under high vacuum, phenylselenenyl chloride (0.62 g, 3.25 mmol) in 5 ml of THF was added to the dry salt. After stirring for 10 min at room temperature, $KHCO_3$ (3 g) in 5 ml of water was added. After a further 20 min of stirring, ether was added, and the organic layer drawn off, dried ($MgSO_4$), filtered, and concentrated at the rotary evaporator to yield 0.66 g (90%) of **8c** as a pale oil: IR (neat) 1670, 1600, 1570 cm^{-1}; NMR (CCl_4) δ 7.68 (m, 5 H), 6.57 (d, 1 H), 5.58 (d, 1 H), 2.44 (s, 3 H).

Methyl α-(o-Nitrophenylsulfenyl)vinyl Ketone (8b). Diketolactone 11[4] (1.60 g, 10 mmol) was dissolved in 15 ml of ethanol and 1.0 g of $KHCO_3$ in 5 ml of water was added. Stirring was continued until gas evolution ceased and solvent was removed at 70 °C under vacuum. After drying, o-nitrophenylsulfenyl chloride (0.81 g, 4.3 mmol) in 12 ml of THF was added to the dry salt, and the suspension was stirred for 3 h. After cooling, 3 g of $KHCO_3$ in 10 ml of water was added, and the reaction mixture stirred for an additional 20 min. Ether was added, and the organics were drawn off, dried ($MgSO_4$), filtered, and concentrated to yield 0.87 g (92%) of **8b** as a yellow oil: IR (neat) 1670, 1600, 1570 cm^{-1}; NMR (CCl_4) δ 7.5–8.5 (m, 3 H), 6.75 (s, 1 H), 6.32 (s, 1 H), 2.31 (s, 3 H).

General Procedure for Formation of Oxalyl Derivatives. Ethyl Oxalylbutyrolactone (30). Oxalyl derivatives were prepared according to the general *Organic Syntheses* procedure of Snyder, Brooks, and Shapiro.[5] Sodium metal (3.7 g, 0.16 mol) was cautiously added to 50 ml of absolute ethanol, cooled by an ice/salt bath, and diethyl oxalate (22.0 g, 0.15 mol) was added to the resultant cold solution of sodium ethoxide. Butyrolactone (13.0 g, 0.15 mol) in several milliliters of ethanol was then added dropwise over 15 min, and the reaction mixture was stirred at ice/salt temperature for 1 h. Upon removal of the cooling bath, the solution warmed to room temperature and was further stirred overnight. The solvent was then removed under reduced pressure, and the pasty residue partitioned between ether and water. The aqueous layer was drawn off, cooled with ice, acidified with dilute HCl, and extracted several times with methylene chloride. The extracts were combined, dried ($MgSO_4$), and concentrated at the rotary evaporator to yield the desired ethyl oxalylbutyrolactone (**30**, 25.1 g, 90%) as a colorless oil.

Other oxalyl derivatives used in this work were prepared by similar procedures in the yields specified in Table I.

α-Methylenecyclohexanone (19). Ethyl oxalylcyclohexanone[5] (**18**, 0.79 g, 4.0 mmol) in 10 ml of THF was added to a stirred suspension of degreased sodium hydride (0.17 g of 57% mineral oil dispersion, 4.0 mmol) in 5 ml of THF. Hydrogen evolution was complete after 20 min and the solution was cooled to −10 °C with an ice/salt bath. Excess dry gaseous formaldehyde (obtained by thermal cracking of paraformaldehyde) was swept into the reaction by a stream of nitrogen carrier gas, and after 5 min the reaction mixture was filtered through Celite into a cold flask. The cold filtrate was shaken for 2 min with 50 ml of cold, saturated $NaHCO_3$, then washed with cold brine, dried (Na_2SO_4) at 0 °C, filtered, and concentrated by solvent removal at 5 °C under reduced pressure to yield 0.38 g (87%) of α-methylenecyclohexanone (**19**) as a colorless oil: IR (neat) 1690, 1610 cm^{-1}; NMR (CCl_4) δ 5.7 (m, 1 H), 5.0 (m, 1 H); mass spectrum *m/e* 110 (M^+).

The material as obtained was pure and nearly free of dimer. Dimerization occurred slowly on standing at room temperature.

General Procedure for Formation of Olefins from Oxalyl Derivatives. α-Methylenebutyrolactone (31). Ethyl oxalylbutyrolactone (**30**, 0.80 g, 4.3 mmol) in 10 ml of THF was added dropwise to a suspension of degreased LiH (4.0 mmol) in 10 ml of THF, and the reaction mixture was stirred at room temperature until H_2 evolution ceased (20 min). Anhydrous gaseous formaldehyde (generated by thermal cracking of dry paraformaldehyde) was bubbled through the solution by a stream of N_2 carrier gas. After 5 min at room temperature, the reaction mixture was filtered through Celite to remove formaldehyde polymer, and the solvent was removed from the filtrate under reduced pressure. The residue was taken up in methylene chloride, and 50 ml of saturated $KHCO_3$ was added. After stirring for 20 min, the organic layer was drawn off, dried ($MgSO_4$), filtered, and concentrated at the rotary evaporator to yield 0.35 g (83%) of α-methylenebutyrolactone as a colorless oil: IR (neat) 1750, 1660 cm^{-1}; NMR (CCl_4) δ 6.1 (t, 1 H, J = 3 Hz), 5.6 (t, 1 H, J = 3 Hz), 4.3 (t, 2 H, J = 8 Hz), 2.9 (m, 2 H); mass spectrum *m/e* 98 (M^+).

This general procedure was used for the preparation of the following unsaturated carbonyl compounds with one modification. It is essential that the oxalyl salt be soluble in the reaction medium in order to maximize product yields. In some cases, therefore, bases other than lithium hydride were used to generate the anions. The specific base used in each case is indicated. Product purity was established both by gas chromatography and by NMR.

α-Ethylidenecyclohexanone (20) was prepared as described above (40%) using NaH as base and substituting gaseous acetaldehyde for formaldehyde: IR (neat) 1685, 1610 cm^{-1}; NMR (CCl_4) δ 6.6 (m, 1 H), 2.4 (d, 3H); mass spectrum *m/e* 124 (M^+).

α-Methylenecycloheptanone (23) was prepared as above (72%)

using NaH as base: IR (neat) 1695, 1605 cm^{-1}; NMR (CCl_4) δ 5.8 (d, 1 H, J = 2.5 Hz), 6.2 (m, 1 H); mass spectrum m/e 124 (M^+).

α-Methyl-3-phenylpropen-3-one (29) was prepared as above (13%) using NaH as base. When sodium ethoxide was added to cleave the diketolactone intermediate, rather than $NaHCO_3$, ethyl benzoate was isolated (77%) as the major product.

α-Methylenevalerolactone (36) was obtained (93%) as above using NaH as base: IR (neat) 1720, 1630 cm^{-1}; NMR (CCl_4) δ 6.3 (m, 1 H), 5.4 (m, 1 H), 4.3 (t, 2 H, J = 5.5 Hz), 2.7 (m, 2 H), 2.0 (m, 2 H); mass spectrum m/e 112 (M^+).

Ethyl α-phenylacrylate (40) was obtained as above (100%) using NaH as base: IR (neat) 1720, 1620 cm^{-1}; NMR (CCl_4) δ 7.3 (m, 4 H), 6.2 (d, 1 H, J = 1.5 Hz), 5.8 (d, 1 H, J = 1.5 Hz), 4.2 (q, 2 H, J = 7.5 Hz), 1.2 (t, 3 H, J = 7.5 Hz): mass spectrum m/e 176 (M^+).

Ethyl α-propylacrylate (42) was obtained as above (83%) using NaH as base: IR (neat) 1720, 1630 cm^{-1}; NMR (CCl_4) δ 6.1 (m, 2 H), 4.2 (q, 2 H, J = 7 Hz), 2.25 (t, 2 H, J = 7 Hz); mass spectrum m/e 142 (M^+).

Ethyl α-propylcrotonate (43) was obtained as above (71%) as an 80:20 E:Z mixture using NaH as base and substituting gaseous acetaldehyde for formaldehyde: IR (neat) 1710, 1645 cm^{-1}; NMR (CCl_4) δ 6.7 (q, 0.8 H, E isomer), 5.8 (m, 0.2 H, Z isomer).

Ethyl α-propyl-2-hexenoate (44) was prepared as above (68%) as a 70:30 mixture of E and Z isomers using NaH as base and substituting butyraldehyde for formaldehyde: IR (neat) 1710, 1645 cm^{-1}; NMR (CCl_4) δ 6.6 (t, 0.7 H, E isomer) 5.7 (t, 0.3 H, Z isomer); mass spectrum m/e 184 (M^+).

α-Methylene-*N*-methylpyrrolidone (46) was prepared as above (61%) using triethylamine as base in place of NaH: IR (neat) 1690, 1670 cm^{-1}; NMR (CCl_4) δ 5.7 (m, 1 H), 5.2 (m, 1 H), 2.8 (s, 3 H); mass spectrum m/e 111 (M^+).

3,4-Dimethoxy-α-phenylacrylonitrile (51) was prepared as above (90%) using NaH as base: IR (neat) 2210 cm^{-1}; NMR (CCl_4) δ 7.2 (m, 3 H), 6.25 (s, 1 H), 6.05 (s, 1 H), 3.95 (s, 6 H); mass spectrum m/e 189 (M^+).

When ethyl α-oxalylbutyrolactone and ethyl α-oxalylvalerolactone were condensed with aldehydes other than formaldehyde, an alternate procedure was found necessary.

General Procedure for Formation of α-Alkylidene Lactones. α-Ethylidenebutyrolactone (32). Ethyl oxalylbutyrolactone (**30**, 630 mg, 3.8 mmol) was dissolved in 10 ml of ethanol at room temperature and a solution of NaOH (150 mg, 3.8 mmol) in 5 ml of water was added. Freshly distilled acetaldehyde (2 g, 45 mmol) was added and the reaction mixture was stored for 16 h at room temperature. The solution was then diluted with 30 ml of H_2O and cooled to 5 °C, and 3 g of $KHCO_3$ was added. After 20 min of stirring, the reaction mixture was extracted with methylene chloride. The extracts were dried ($MgSO_4$), filtered through a mat of silica gel, and concentrated to yield the product (68%) as a 70:30 E:Z mixture: IR (neat) 1750, 1675 cm^{-1}; NMR (CCl_4) δ 6.6 (m, 0.3 H, Z isomer), 6.2 (m, 0.7 H, E isomer); mass spectrum m/e 112 (M^+).

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.09; H, 7.34.

α-Butylidenebutyrolactone (33) was prepared as above (62%) substituting butyraldehyde for acetaldehyde. A 70:30 mixture of E:Z isomers was obtained: IR (neat) 1750, 1675 cm^{-1}; NMR (CCl_4) δ 6.7 (m, 0.7 H, E isomer), 6.3 (m, 0.3H, Z isomer); mass spectrum m/e 140 (M^+).

Aldehydolactone 34 was prepared as above (50%) substituting aqueous glyoxal for acetaldehyde: NMR (CCl_4) δ 10.18 (d, 1 H, J = 3 Hz), 6.90 (m, 1 H).

α-Ethylidenevalerolactone (37) was obtained as above (80%). A 70:30 mixture of E:Z isomers was obtained: IR (neat) 1720, 1640 cm^{-1}; NMR (CCl_4) δ 6.9 (m, 0.7 H, E isomer), 6.1 (m, 0.3 H, Z isomer); mass spectrum m/e 126 (M^+).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.41; H, 8.20.

α-Butylidenevalerolactone (38) was obtained as above (62%) as a 70:30 E:Z mixture using butyraldehyde in place of acetaldehyde: IR (neat) 1720, 1675 cm^{-1}; NMR (CCl_4) δ 6.8 (m, 0.7 H, E isomer), 6.0 (m, 0.3 H, Z isomer); mass spectrum m/e 154 (M^+).

Acknowledgment. We thank the National Institutes of Health for their support of this work through Grant GM 19959.

Registry No.—**11**, 61203-07-4; **E-32**, 43142-58-1; **Z-32**, 43142-59-2; **E-33**, 61203-08-5; **Z-33**, 61203-09-6; **E-37**, 61203-10-9; **Z-37**, 61203-11-0; **E-38**, 61203-12-1; **Z-38**, 61203-13-2; **E-43**, 61203-14-3; **Z-43**, 61203-15-4; **E-44**, 61203-16-5; **Z-44**, 61203-17-6; phenylselenyl chloride, 5707-04-0; o-nitrophenylsulfenyl chloride, 7669-54-7.

References and Notes

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(6) C. Mannich, *Chem. Ber.*, **74**, 554 (1941).
(7) For a recent review, see P. A. Grieco, *Synthesis*, 67 (1975).
(8) Cf. J. A. Marshall and N. Cohen, *J. Org. Chem.*, **30**, 3475 (1965).
(9) H. Gault and P. Bouvier, *Bull. Soc. Chim. Fr.*, 711 (1963).