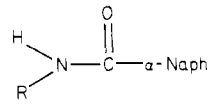
Table II. Resolution of α-Naphthamides of Carbocyclic Amines on CSP 1b



R	α	k_1' [a]
trans-2-phenylcyclopropyl	1.14	13.7
cis-2-phenylcyclopropyl	1.04	10.3
trans-2-hydroxycyclohexyl	1.33	11.2
cis-2-hydroxycyclohexyl	1.20	13.7
trans-2-methylcyclohexyl	1.04	9.6
cis-2-methylcyclohexyl	1.05	10.6
trans-2-cyclohexylcyclohexyl	1.17	6.9
cis-2-cyclohexylcyclohexyl	1.18	7.5

[a] The mobile phase was 10% 2-propanol in hexane.

in the amine portion of the molecule. A variation of the "stacked" model is shown in Figure 2. Here, the solute is repositioned on the CSP to allow hydrogen bond formation to occur between the DNB amide hydrogen and the carbonyl oxygen of the solute. Once again, the most stable diastereomeric absorbate is the one pictured, where R_2 is smaller than R_1, or, alternatively, the one more capable of bonding to proximate portions of the CSP. Although $\pi-\pi$ bonding between the dinitrobenzoyl and naphthoyl groups can stabilize the stacking modes shown in Figures 1 and 2, $\pi-\pi$ interaction is not absolutely essential; a number of simple acyl groups (acetyl, butanoyl) may be used in place of the α-naphthoyl group. Thus, the chiral model(s) presented above can be extended to cover the elution orders reported by Dobashi et al. for acylated amino acid esters on a valine-derived CSP.[10]

The α-naphthamides of aminocycloalkanes are also resolvable on CSP **1b**. Table II provides data pertinent to the resolution of several such compounds. No elution order data is yet available for these compounds.

CSP **1c**, derived from (*S*)-leucine, is often more efficacious for the resolution of enantiomers than is CSP **1b**. However, this is typically not the case for the α-naphthamides studied, the major difference between the two CSP's being the expected difference in elution orders, since the two CSP's differ in absolute configuration.

CSP **1a** is quite similar to **1b** in its ability to resolve acylated amines. In any individual instance, **1a** may perform either slightly better or slightly worse than **1b**.

(10) For example, see: Dobashi, A.; Oka, K.; Hara, S. *J. Am. Chem. Soc.* **1980**, *102*, 7122.

Experimental Section

General Methods. Chromatography was conducted by using a Beckman 100A pump, a Model 210 injector, and a Model 165 detector and a Kipp-Zonen BD41 dual-pen recorder. A Regis Covalent Pirkle 1A column was employed. Rudolph Auto-pol III fitted with a 20-cm flow cell was used as a polarimetric detector in most instances to complement the dual wavelength (usually 254 and 280 nm) ultraviolet detector.

The amines used were available from prior studies and were acylated with α-naphthoyl chloride by using standard procedures. Since most were made from partially resolved amines, they were not crystallized prior to use. The use of dual-wavelength ultraviolet and polarimetric detection ensures that the peaks attributed to the amide enantiomers do, in fact, so arise.

Covalently Bound (*S*)-*N*-(3,5-Dinitrobenzoyl)leucine Stationary Phase (1c). To a slurry of 2 g of finely powdered (*S*)-*N*-(3,5-dinitrobenzoyl)leucine in 60 mL of dry methylene chloride was added 2 g of powdered *N*-(ethoxycarbonyl)-2-ethoxy-1,2-dihydroquinoline. The mixture was swirled until solution was complete, and the solution was suction filtered to remove any residual solids. This solution was immediately pumped through a Regis aminopropyl column at a flow rate of 2 mL/min. This solution was followed by 50 mL of methylene chloride, 100 mL of methanol, and 10% 2-propanol in hexane until the base line stabilized. Columns of this type are available from both Regis and J. T. Baker.

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α-Alkoxyallylation of Activated Carbonyl Compounds. A Novel Variant of the Michael Reaction

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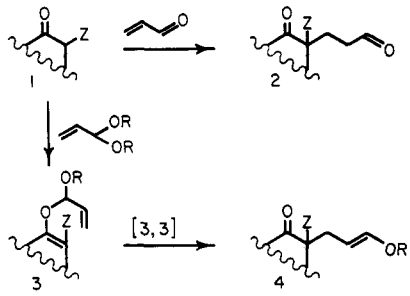
Enolic or readily enolizable carbonyl compounds undergo α-alkoxyallylation upon reaction with acetals of α,β-enals or ethoxyallene at temperatures ranging from 200 °C to ambient. Whereas reactions of the highly enolic or acidic carbonyl compounds (endocyclic β-diketones, α-cyano ketones, α-nitro carbonyl compounds, and α-hydroxymethylene derivatives) occurred simply upon heating, alkylation of the less acidic exocyclic β-diketones and β-keto esters was best carried out in the presence of 1 mol % of $Ni(acac)_2$ as a catalyst. Pyridinium *p*-toluenesulfonate was employed as a catalyst for alkylations with acrolein ethylene acetal. Although ethoxyallylation of acylic substrates (e.g., ethyl acetoacetate, diethyl malonate, and ethyl cyanoacetate) with acrolein diethyl acetal proved to be slow, these and related alkylations could be conveniently accomplished by use of the corresponding α-hydroxymethylene derivatives. Unsaturated acetals bearing a methyl or phenyl substituent at C-2 can be employed for alkoxyallylation, but the reaction appears to be incompatible with a methyl group at C-3. The mechanism of these reactions probably involves either direct C-allylation of the carbonyl compound on the γ-position of an alkoxyallyl carbocation intermediate or an indirect pathway via O-allylation at the α-position of the carbocation followed by Claisen rearrangement.

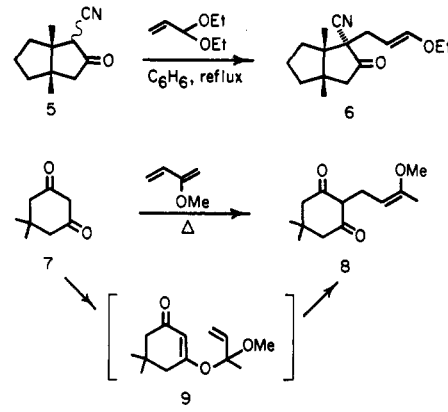
The Michael reaction of β-dicarbonyl compounds with α,β-enones and other electron-deficient olefins is an important synthetic method for carbon–carbon bond formation.[1] Although typically carried out in protic solvents

0022-3263/84/1949-0140$01.50/0

Scheme I



Scheme II



with various basic catalysts, these alkylation reactions may also be catalyzed by acids,[2] fluoride ion,[3] metal chelates (e.g., nickel acetylacetonate),[4] and tri-*n*-butylphosphine.[6] Procedures for Michael addition of preformed enolate and related carbanions to appropriate olefin acceptors under aprotic conditions at low temperatures have been developed recently.[7,8] Another modern innovation involves Lewis acid catalyzed conjugate addition of enol silanes to α,β-enones.[9] Despite the broad scope and utility of these methods for α-alkylation, complications and side reactions are not unknown.[1] For example, Michael reactions of α,β-unsaturated aldehydes may proceed in low yield owing to competing dimerization or polymerization of the enal,[1a,c] subsequent aldol cyclization to the α′-position,[1a,10,11] or α,α-dialkylation of active methylene compounds.[1a]

In an earlier investigation we required a method to attach a propionaldehyde residue at the α-position of an α-cyano ketone (**5**).[11] It seemed reasonable to expect that the equivalent of a Michael reaction could be realized by condensation of enolizable carbonyl compounds with acetals of α,β-enals (**1** → **3** → **4**, Scheme I). Thus, acetal exchange with the enol form of **1** followed by Claisen rearrangement of the resulting allyl vinyl ether **3** would give rise to alkoxyallyl ketones **4**. Aldol-type condensations with acetals and ketals as the electrophilic component have been reported.[12] Potential advantages of this variant of the Michael reaction would include the use of mildly acidic conditions, a presumably reduced risk of aldol cyclization, and delivery of the product in a protected (or activated) form. These considerations, and the precedents cited below, led to the discovery that efficient alkylation of cyano ketone **5** to ethoxyallyl ketone **6** (Scheme II) could be effected simply by heating in the presence of acrolein diethyl acetal.[11]

Encouraging precedent for this transformation was available in the literature.[12-14] Dolby and co-workers had previously postulated that the alkylation of dimedone with 2-methoxy-1,3-butadiene proceeded by a similar mechanism, namely, addition of the enol form to the diene and subsequent Claisen rearrangement (**7** → **9** → **8**).[13] The annelation of phenols with acrolein acetals to give chromanes,[14a] and more recently with orthoacrylate to give dihydrocoumarins,[14b] might reasonably occur by related pathways. Claisen rearrangements of vinyl and propenyl 2,3-dehydroglycosides have been applied to the synthesis of branched-chain sugars.[15]

The objectives of the present research were to develop suitable procedures for alkoxyallylation of various enolizable carbonyl compounds and to explore the scope of the reaction with respect to the two reactants. We have found that β-diketones, β-keto nitriles, β-keto esters, α-nitro carbonyl compounds, and related α-hydroxymethylene derivatives undergo alkylation with acetals of α,β-enals and ethoxyallene.

Results and Discussion

The reactions of activated carbonyl compounds with acrolein acetals and ethoxyallene were carried out at temperatures ranging from 200 °C to ambient by four principal procedures: (A) neat or suspension at 200, 125, or 25 °C; (B) in 1,2-dichloroethane solvent at reflux (~84 °C) or 25 °C; (C) neat, 1 mol % of $Ni(acac)_2$ at 200 °C; (D) neat, 1 mol % of pyridinium *p*-toluenesulfonate at 200 °C. Four equivalents of the acetal or allene was used to minimize the time required to reach high or complete conversion and to facilitate heat transfer in the heterogeneous reactions.

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(4) (a) Nelson, J. H.; Howells, P. N.; De Lulle, G. C.; Landen, G. L. *J. Org. Chem.* **1980**, *45*, 1246–1249. (b) Watanabe, K.; Miyazu, K.; Ibe, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3212–3215. (c) Irie, K.; Miyazu, K.; Watanabe, K. *Chem. Lett.* **1980**, 353–354. (d) Saegusa, T.; Ito, Y.; Tomita, S.; Kinoshita, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 496–499.

(5) Footnote deleted in revision.

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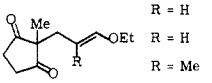
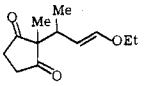
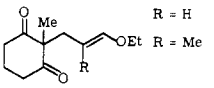
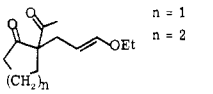
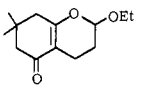
(13) Dolby, L. J.; Elliger, C. A.; Esfandri, S.; Marshall, K. S. *J. Org. Chem.* **1968**, *33*, 4508–4511.

(14) (a) Clarke, D. G.; Crombie, L.; Whiting, D. A. *J. Chem. Soc., Perkin Trans 1* **1974**, 1007–1015. (b) Panetta, J. A.; Rapoport, H. *J. Org. Chem.* **1981**, *47*, 946–950.

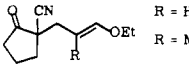
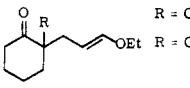
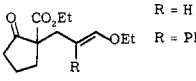
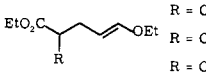
(15) (a) Heyns, K.; Hohlweg, R. *Chem. Ber.* **1978**, *111*, 1632–1645. (b) Cottier, L.; Remy, G.; Descotes, G. *Synthesis*, 1979, 711–712.

Table I. Ethoxyallylation of β-Diketones with Acetals of α,β-Enals

entry	method[a]	time, h	product	yield, %	E/Z ratio
1	A	0.25	 R = H	67	65:35
2	B	33	R = H	82	
3	A	1.5	R = Me	87	
4	A	0.5	R = Ph	88	80:20
5	A	0.25		8 (22)[b]	20:80
6	A	0.5	 R = H	71	90:10
7	A	2	R = Me	54	
8	C	1.5	 n = 1	60	90:10
9	C	2	n = 2	65	80:20
10	B	24		54	

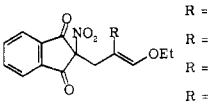
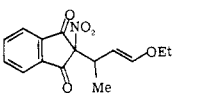
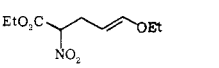
[a] Method A: neat, sealed tube, 200 °C. Method B: in 1,2-dichloroethane, reflux. Method C: neat, 1 mol % of $Ni(acac)_2$, 200 °C. [b] Yield in parentheses is corrected for recovered diketone.

Table II. Ethoxyallylation of β-Keto Esters, β-Keto Nitriles, Diethyl Malonate, and Ethyl Cyanoacetate with Acetals of α,β-Enals at 200 °C

entry	method[a]	time, h	product	yield, %	E/Z ratio
1	A	0.75	 R = H	71	90:10
2	A	2	R = Me	68	
3	A	0.5	 R = CN	81	85:15
4	C	3.5	R = CO_2Et	41	80:20
5	C	5.5	 R = H	50	90:10
6	C	7.5	R = Ph	51	
7	C	0.5	 R = $COCH_3$	43	85:15
8	A	38	R = CO_2Et	16	80:20
9	A	10.5	R = CN	31	60:40

[a] For an explanation of the conditions see Table I, footnote a.

Table III. Ethoxyallylation of α-Nitro Carbonyl Compounds with Acetals of α,β-Enals

entry	method[a]	time, min	product	yield, %	E/Z ratio
1	A	50	 R = H	58	~100:0
2	B	120	R = H	68	~100:0
3	A	45	R = Me	70	
4	A	5	R = Ph	41	
5	A	7		43	~100:0
6	A[b]	60		15	90:10

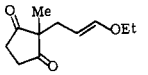
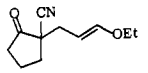
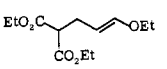
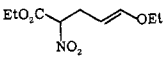
[a] Method A: neat, room temperature unless denoted otherwise. Method B: 1,2-dichloroethane, room temperature. [b] 200 °C.

However, the excess of the acetals (or allenes) may not be necessary for satisfactory yields. It was shown that the yield (by NMR analysis with an internal standard) of ethoxyallylation product from acrolein diethyl acetal and carbethoxycyclopentanone (method B) decreased only slightly when the molar ratio was reduced from 4.0 (reaction time 1.5–2 h) to 1.1 (reaction time 5–8 h).

Although ethoxyallylation might occur at either carbon or oxygen to form any of four possible isomers, only 3-ethoxyallyl C-alkylation products (C_γ coupling) were isolated from the reactions. The structures of the products are clear from their ^1H and ^{13}C NMR spectra. For example, the ^1H NMR spectrum of the ethoxyallyl product (11, R = H) from acrolein diethyl acetal and 2-methyl-1,3-cyclopentanedione exhibits two vinyl protons characteristic of an enol ether (δ 4.20 and 6.05). The symmetry of the compound is shown by the appearance of only nine signals in its ^{13}C NMR spectrum.

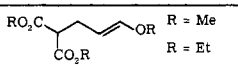
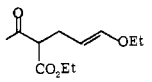
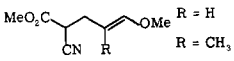
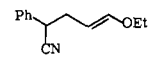
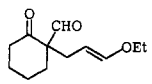
The scope of the alkoxyallylation reaction was investigated with a series of β-diketones, β-keto esters, β-keto nitriles, and α-nitro carbonyl compounds. The conditions, product structures, isolated yields and isomer ratios are

Table IV. Ethoxyallylation of Activated Carbonyl Compounds with Ethoxyallene

entry	method[a]	time, h	product	yield, %	E/Z ratio
1	B	14		58	90:10
2	A	0.33		70	90:10
3[b]	A	4		60	90:10
4	A	5		26	~100:0

[a] Method A: neat, sealed tube, 125 °C. Method B: 1,2-dichloroethane, reflux. [b] The α-hydroxymethylene derivative of diethyl malonate was used.

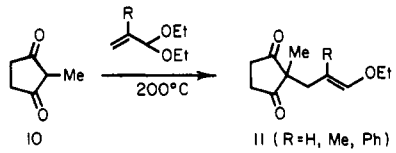
Table V. Alkoxyallylation of α-Hydroxymethylene Derivatives with Acetals of α,β-Enals

entry	method[a]	time, h	product(s)	yield, %	E/Z ratio
1	C	1	 R = Me	58	70:30
2	C	1	R = Et	72	90:10
3	A	0.25		77	80:20
4	A[b]	5	 R = H	67	95:5
5	A	0.08	R = CH_3	86	
6	A	1		62	70:30
7	A[b]	11.5		48[c]	90:10

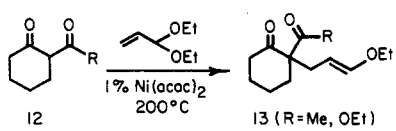
[a] Method A: neat, sealed tube, 200 °C except as noted. Method C: neat, 1 mol % $Ni(acac)_2$, 200 °C. [b] Refluxing acetal (108–120 °C). [c] A small amount (2%) of deformylated product was also isolated.

collected in Tables I–V. Most reactions were conducted without solvent in sealed tubes at either 200 (acetals) or 125 °C (ethoxyallene). Notable exceptions were the condensations of 2-nitro-1,3-indandione with the acetals which occurred readily at room temperature. Since rather long times were required for reactions run in refluxing 1,2-dichloroethane, this procedure (method B) was used infrequently.

The highly enolic endocyclic β-diketones, 2-methyl-1,3-cyclopentanedione (10) and its six-membered-ring relative, and the α-cyano ketones underwent smooth ethoxyallylation with the acrolein acetals at 200 °C in the absence of catalyst. In contrast, the exocyclic β-diketones and the



10 11 (R=H, Me, Ph)



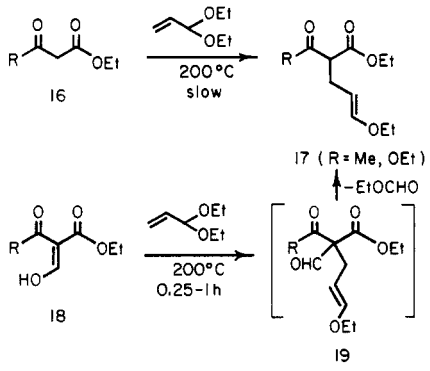
12 13 (R=Me, OEt)

β-keto esters reacted sluggishly under the same conditions. Fortunately these reactions were effectively catalyzed by nickel(II) acetylacetonate ($Ni(acac)_2$).[4a,16] For example, the condensation of carbethoxycyclopentanone with acrolein diethyl acetal, which was incomplete after 24 h at 200 °C (TLC analysis), required only 1.5–2 h to reach completion in the presence of 1 mol % of $Ni(acac)_2$. Since the nickel catalyst had only a slight effect on the rate of ethoxyallylation of α-cyanocyclopentanone (14) in comparative runs at 150 °C, it is reasonable to suppose that the nickel chelate of the dicarbonyl compounds is an intermediate in the catalytic mechanism.

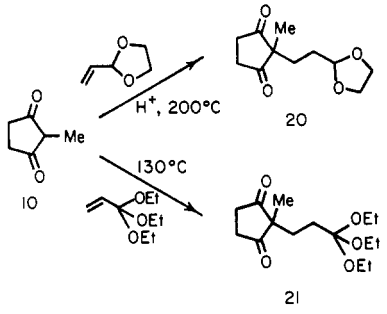
The alkoxyallylation reaction is compatible with substituents at C-2 (methyl and phenyl) of the unsaturated acetal but not with a methyl group at C-3. Thus, similar yields and rates were observed with methacrolein and atropaldehyde acetals. However, with the exception of the α-nitro diketone, only low yields of alkylation products could be isolated when crotonaldehyde diethyl acetal was employed. The intolerance to substitution at C-3 is similar to the sensitivity of the normal Michael reaction to steric

(16) The efficiency of other metal acetylacetonates as catalysts for the condensation of 2-carbethoxycyclopentanone with acrolein diethyl acetal was surveyed in a preliminary way (1 mol % at 200 °C). The rates of disappearance of the β-keto ester with various transition metals [Co(II), Co(III), Mn(II), Mn(III), and Zn(II)] and lanthanides [Ce(IV) and La(III)] were comparable to, or somewhat greater than, that observed with Ni(acac)$_2$. However, inferior absolute yields were indicated by NMR analysis of the crude products. Little or no catalysis was observed with $Al(acac)_3$ and $Cr(acac)_3$ while $Fe(acac)_3$ and $VO(acac)_2$ both displayed some catalytic activity. The chelates of Pt(II), Pd(II), and Cu(II) apparently decomposed under the reaction conditions.

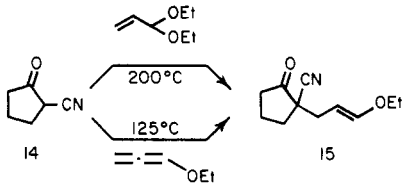
Scheme III



Scheme IV



hindrance in the β-position of the olefin acceptor.[1] The readily available 1-ethoxyallene[17] proved to be a suitable alternative to acrolein diethyl acetal (see Table IV). The greater reactivity of the allene allowed these reactions to be conducted at 125 °C.

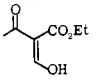
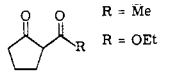


Direct ethoxyallylation of acylic activated carbonyl compounds (i.e., ethyl acetoacetate, diethyl malonate, and ethyl cyanoacetate) with acrolein diethyl acetal proved to be slow and/or to result in low yields. However, this limitation was circumvented by use of the corresponding α-hydroxymethylene derivatives (see Table V). In all but one case the presumed aldehyde intermediates (e.g., **19**, Scheme III) underwent spontaneous deformylation under the reaction conditions. The major product (48%) obtained from α-(hydroxymethylene)cyclohexanone was the α-ethoxyallyl aldehyde (entry 7) which was accompanied by a small amount of deformylated ketone. A statistical mixture of methyl and ethyl esters was obtained from a reaction of dimethyl (hydroxymethylene)malonate with acrolein diethyl acetal. Thus, acid-catalyzed transesterification with the ethanol liberated from the acetal was evidently relatively rapid at ca. 125 °C.

The possibility of using a cyclic acetal was briefly investigated. Although the uncatalyzed reaction of acrolein ethylene acetal with activated carbonyl compounds was rather slow, satisfactory rates and yields of alkylation products were obtained in the presence of 1 mol % of pyridinium *p*-toluenesulfonate at 200 °C (method D): Thus, α-[3,3-(ethylenedioxy)-1-propyl] adducts (e.g., **20**, Scheme IV) were prepared from 2-methyl-1,3-cyclopentanedione (15 min, 77%), 2-methyl-1,3-cyclohexanedione (15 min, 70%), and α-cyanocyclopentanone (3.5 h, 51%). It is quite likely that (β-hydroxyethoxy)allyl products are formed initially but undergo rapid cyclization to reconstitute the acetal. A single example of an orthoacrylate condensation was carried out. Reaction of diketone **10** with triethyl orthoacrylate at ca. 125 °C afforded orthopropionate **21** in 85% yield. The addition of ethanol to a ketene acetal intermediate provides a logical mechanism for this reaction.

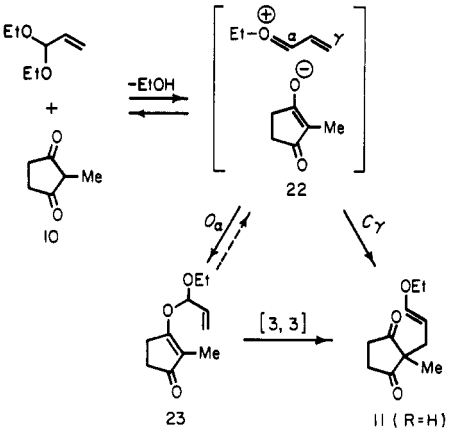
The rates and reaction times for ethoxyallylation with acrolein diethyl acetal varied widely according to the activated carbonyl component employed. Since the mechanism undoubtedly involves acid-catalyzed cleavage of the acetal, it is reasonable to suppose that the rate would be a function of the enol content and acidity of the activated carbonyl compound. This assumption is borne out by the data given in Table VI. Although the estimates of reaction times are based on TLC analyses and are only approximate, there seems to be a clear correlation of reactivity with the pK_a of the carbonyl compound.[18]

Table VI. Approximate Correlation of Reaction Times for Ethoxyallylation by Acrolein Diethyl Acetal with pK_a's of Activated Carbonyl Compounds

carbonyl compd	pK_a[a]	estimated reaction time
	2.5	<1.5 min
	4.6	5-15 min
	6.05	15-30 min
 R = Me R = OEt	7.8 10.2	1-4 h >23 h

[a] The sources of these values for the five entries are as follows: ref 18a, 18b, 18c, 18d, 18d. [b] From TLC analyses during the reaction.

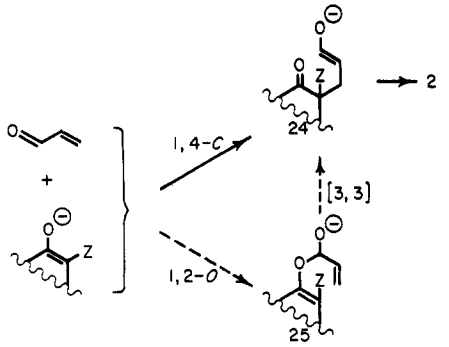
Scheme V



(17) Hoff, S.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 916–924.

(18) (a) Gregoire de Bellmont, E. *Bull. Soc. Chim. Fr.* **1901**, *25*, 28–38. (b) Fernandez, J. E.; Whitaker, R. D.; Brana, M. F.; Simon, J. *Fla. Sci.* **1973**, *36*, 75–77; *Chem. Abstr.* **1975**, *82*, 124480*u*. (c) Meek, E. G.; Turnbull, J. H.; Wilson, W. *J. Chem. Soc.* **1953**, 2891–2896. (d) Jones, J. R. "The Ionization of Carbon Acids"; Academic Press: New York, 1973; p 29.

Scheme VI



The two most likely mechanisms for the ethoxyallylation reaction are depicted in Scheme V. Proton transfer from the activated carbonyl compound (keto or enol form) to the acetal followed by elimination of ethanol would give rise to an allyl oxonium cation and an enolate anion (**22**). O-Alkylation at the α-position of the oxonium ion and subsequent Claisen rearrangement of the mixed acetal would lead to the ethoxyallyl product as originally postulated. However, the same product might also be formed directly by C-alkylation at the γ-position.

It is appropriate to note that the oxonium ion bears a close resemblance to acrolein. Consequently the well-established tendency of α,β-unsaturated carbonyl compounds to undergo kinetic 1,2-addition of nucleophiles[19] may be cited in favor of the O-alkylation–rearrangement pathway. This analogy may not be valid, however, if nucleophilic capture is reversible. That is, the mixed acetal **23** might be formed initially but undergo rapid reionization to the carbocation–enolate anion pair which eventually combines by the C_γ-allylation to give the product.

Although no evidence for the formation of the mixed acetals (e.g., **23**) as intermediates or side products was obtained from TLC analyses during the reactions or from NMR spectra of chromatographic or distillation fractions, it now appears that the Claisen rearrangement of α-ethoxyallyl vinyl ethers such as **23** occurs rapidly even at room temperature.[20] Despite the precedent for C_α-alkoxy alkylation of carbonyl compounds by acetals and ketals,[12,21] no products of this type were encountered in the present investigation.

There is in fact no particular reason to assume that all ethoxyallylations must occur by one mechanism to the exclusion of the other. Indeed, it seems reasonable to suppose that the highly enolic carbonyl substrates (e.g., β-diketones and α-hydroxymethylene derivatives) react by O-allylation–rearrangement whereas diethyl malonate and ethyl cyanoacetate (Table II) might undergo direct ethoxyallylation at carbon.

The preceding discussion raises the interesting question of whether the normal base-catalyzed Michael reaction might in some cases take place by a similar indirect mechanism. Thus, 1,2-addition of the enolate oxygen to the carbonyl group of the Michael acceptor would give rise to an alkoxide adduct which would undergo anion-accelerated [3,3]-sigmatropic rearrangement[22] to the C-alkylated enolate isomer usually proposed (Scheme VI). Although base-catalyzed Michael reactions with acrylonitrile and acrylate esters surely occur by direct 1,4-addition at carbon, the 1,2-addition–rearrangement pathway appears to be quite reasonable when the Michael acceptor is acrolein or other α,β-enals.

In summary, this research has shown that α-alkoxyallylation of enolizable carbonyl compounds with acetals of α,β-enals or ethoxyallene affords a reasonably general alternative to the Michael reaction. Alkylation of highly enolic and/or acidic substrates (endocyclic β-diketones, α-cyano ketones, α-nitro carbonyl compounds, and α-hydroxymethylene compounds) was effected simply by heating the reactants (25–200 °C) whereas reactions of less highly enolic substrates (exocyclic β-diketones and β-keto esters) were conducted in the presence of $Ni(acac)_2$ as a catalyst. Pyridinium *p*-toluenesulfonate was used as a catalyst for the slower condensations with acrolein ethylene acetal. The alkoxyallylation reaction proved to be compatible with a methyl or phenyl substituent at C-2 of the unsaturated acetal, but methyl substitution at C-3 was not tolerated. It is not clear whether the products are formed by direct C-allylation at the γ-position of an alkoxyallyl carbocation intermediate or by an indirect pathway involving O-alkylation at the α-position followed by Claisen rearrangement.

Experimental Section

Spectral and Analytical Data. Unless otherwise stated, ^1H NMR spectral data were recorded at 90 MHz and locked to tetramethylsilane. Proton NMR spectra at 90, 220, and 360 MHz were measured with Varian EM-390 and HR-220 and Nicolet NTC-360 spectrometers, respectively, and ^{13}C NMR spectra were recorded on a JOEL FX-60 spectrometer. Perkin-Elmer 237B and 137 IR spectrometers were used to determine IR spectra. Low-resolution (at 70 and 10 eV) and high-resolution mass spectroscopy was performed by the Mass Spectrometry Service at the University of Illinois. Melting points were measured on a Thomas-Hoover capillary melting point apparatus. Melting points and boiling points are both uncorrected.

Yields are based on isolated weights of products, the purity of which was judged satisfactory (usually >90%) from inspection of the ^1H NMR spectrum or from other physical properties such as melting point or boiling point. *E* to *Z* isomer ratios were determined by integration of the olefinic or allylic protons in the ^1H NMR spectra of the alkoxyallyl products. In some cases, peak height was used as an estimate of the integration for a given resonance. Spectral and physical data are not necessarily based on the run described. If a ratio of isomers is stated in the run appearing in the Experimental Section, then the analytical data are for mixtures of isomers of comparable ratios. All other cases are assumed to be for a single compound. In cases in which geometric isomers were separated during chromatography, the ^1H NMR spectrum for each isomer is listed separately.

Analytical samples, unless noted otherwise, were obtained by preparative TLC on 20 × 20 cm, 2-mm-thick commercial silica gel F-254 plates from E. Merck or Brinkmann Instruments or by flash chromatography on Woelm 32–63-μm silica gel. A Varian 90-P Aerograph with a 0.95 × 229 cm column of 20% SE-30 on 60/80-mesh AW DMCS Chromosorb P was used for preparative GC. Elemental analyses were provided by the microanalytical laboratory of the University of Illinois.

Apparatus. The reusable glass pressure tubes used in the sealed-tube reactions were modeled after the acylation tubes supplied by the Regis Chemical Co. (catalog no. 201 040). The container consists of a heavy-walled glass tube with a pipe flange, a Teflon sealing disk, rubber and aluminum spacing disks, and a male and female threaded coupling. The hand-tight seal used

(19) (a) Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: Oxford, 1974; pp 133–134, 139. (b) Streitwieser, A., Jr.; Heathcock, C. H. "Introduction to Organic Chemistry", 2nd ed.; Macmillan: New York, 1981; pp 602–604. (c) Schultz, A. G.; Yee, Y. K. *J. Org. Chem.* **1976**, *41*, 4044–4045.

(20) Attempts to generate mixed acetals such as **23** by selenoxide elimination at room temperature have given instead the Claisen rearrangement products (e.g., **11**, R = H): unpublished results of S. J. Hobbs.

(21) (a) Klein, J.; Bergman, E. D. *J. Am. Chem. Soc.* **1957**, *79*, 3452–3454. (b) Aleskerov, M. A.; Yufit, S. S.; Kucherov, V. F. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1972**, *21*, 2279–2280.

(22) (a) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765–4766. (b) Evans, D. A.; Nelson, J. V. *Ibid.* **1980**, *102*, 774–782.

on these reusable pressure tubes was adequate for the pressures encountered during the ethoxyallylations. Kugelrohr distillations were performed in a Büchi GKR-50 apparatus and another metal-oven apparatus made by the same company.

Starting Materials. Acetals. Acrolein diethyl and dimethyl acetals were obtained from commercial sources. The following acetals were prepared from trimethyl or triethyl orthoformate and the corresponding aldehyde by the method of Van Allen.[23] Methacrolein dimethyl acetal: yield 35.0 g (50%); bp 102–105 °C (lit.[24] bp 103–110 °C). Methacrolein diethyl acetal: yield 131 g (54%); bp 126–132 °C (lit.[25] bp 143–148 °C). Crotonaldehyde diethyl acetal: yield 282 g (75%); bp 145–150 °C (lit.[23] bp 145–147 °C). Atropaldehyde diethyl acetal was prepared from 1,1-dichloro-2-phenylcyclopropane by the method of Crossland.[26] The yield was 23.8 g (57%), bp 77–82 °C (0.15–0.20 mm) [lit.[27] bp 121 °C (13 mm)]. 1,1-Dichloro-2-phenylcyclopropane was prepared from styrene and chloroform by a procedure also by Crossland:[26] yield 73 g (78%); bp 84–87 °C (0.32–1.4 mm) [lit.[26] bp 100–105 °C (8 mm)].

Acrolein Ethylene Acetal (2-Vinyl-1,3-dioxolane). A solution of 147 mL (123 g, 2.2 mol) of acrolein, 113 mL of ethylene glycol (126 g, 2.0 mol), and 1.51 g (6 mmol) of pyridinium *p*-toluenesulfonate[28,29] in 300 mL of pentane and 100 mL of ethyl ether was heated at reflux for 95 h with continuous collection of water in a Dean–Stark trap. The solvent was distilled off, and the resulting residue was distilled to give 116 g (57%) of acrolein ethylene acetal: bp 110–115 °C (lit.[30] bp 114–116 °C); IR (neat) ν_{max} 1104 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.79–4.02 (m, 4 H, OCH_2CH_2O), 5.16 (d, 1 H, J = 6 Hz, acetal methine), 5.40 (dd, 2 H, CH=CH_2), 5.79 (qd, 1 H, J = 6, 10, 17 Hz, CH=CH_2).

1-Ethoxyallene was prepared from ethyl propargyl ether by the procedure of Brandsma et al.:[17] yield 70.8 g (75%); bp 75–76.5 °C (lit.[17] bp 76–77 °C). Ethyl propargyl ether was prepared from diethyl sulfate and propargyl alcohol by the method of Reppe:[31] yield 52.6 g (31%); bp 78–82 °C (lit.[17] bp 80 °C). **Caution**: An aged sample of this compound which had been stored at −20 °C exploded during distillation at atmospheric pressure.

Catalysts. Pyridinium *p*-toluenesulfonate [mp 119–122 °C (lit.[28] mp 120 °C)] was prepared by the procedure of Grieco.[28] Nickel(II) 2,4-pentanedionate was purchased commercially and dried for 70 h in an Aberhalden apparatus over phosphorus pentoxide at 100 °C prior to use.

Activated Carbonyl Compounds. 2-Acetylcyclopentanone, 2-acetylcyclohexanone (**12**, R = Me), 5,5-dimethyl-1,3-cyclohexanedione, and 2-methyl-1,3-cyclohexanedione were obtained commercially. 2-Methyl-1,3-cyclopentanedione (**10**) was obtained commercially and also prepared by the procedure of Grenda et al.:[32] yield 10.8 g (48%); mp 211–215 °C (lit.[32] mp 212–214 °C). 2-Nitro-1,3-indanedione was prepared by the procedure of Fieser:[33] yield 3.35 g (73%); mp 123 °C dec (lit.[34] mp 113 °C dec).

2-Oxocyclopentanecarbonitrile (14), bp 103–120 °C (2.8–4.8 mm) [lit.[35] bp 126 °C (2.0 mm)], was prepared in 78% yield by the hydrolysis of 2-amino-1-cyclopentene-1-carbonitrile,[36] mp 142–147.5 °C (lit.[37] mp 147–148 °C), obtained in 81% yield by Thorpe–Ziegler condensation of 1,4-dicyanobutane.[37] 2-Oxocyclohexanecarbonitrile, bp 82–98 °C (0.35–0.40 mm) [lit.[38] bp 87 °C (0.5 mm)], was prepared in 39% overall yield by the isoxazole method as described by Kuehne[39] and modified by Mason[35] for 2-(hydroxymethylene)cyclohexanone.

2-Carbethoxycyclopentanone, 2-carbethoxycyclohexanone, ethyl acetoacetate, diethyl and dimethyl malonate, ethyl and methyl cyanoacetate, and ethyl nitroacetate were all purchased from commercial sources.

2-(Hydroxymethylene)cyclohexanone was prepared by the procedure of Ainsworth:[40] yield 80.7 g (64%); bp 51.5–57 °C (2.7 mm) [lit.[40] bp 70–72 °C (5 mm)]. α-Formylphenylacetonitrile was prepared by a literature procedure:[41] yield 46.9 g (65%); mp 157–161.5 °C (lit.[41] mp 159–160 °C).

Ethyl (Ethoxymethylene)acetoacetate. In accordance with the procedure of Claisen,[42] a mixture of 188 mL (203 g, 2.00 mol) of acetic anhydride, 166 mL (148 g, 1.00 mol) of triethyl orthoformate, and 128 mL (131 g, 1.00 mol) of ethyl acetoacetate was stirred and heated at reflux temperature for 0.5 h. The more volatile components were removed on a rotary evaporator at temperatures of 25–82 °C over 1 h. The resulting residue was fractionally distilled to give 97.5 g of reddish viscous oil, bp 78–97 °C (0.20–0.30 mm). Futher purification of the product was accomplished by a second fractional distillation which gave 34.2 g of a pinkish, viscous oil, bp 95 °C (0.025 mm). This fraction was found to be a 90:10 mixture of geometric isomers by ^{1}H NMR. The lower boiling fractions of the second distillation were consolidated and fractionally distilled to give an additional 38.1 g of a pinkish, viscous oil, bp 86–89.5 °C (0.025 mm) [lit.[41] bp 173–174 °C (45 mm)]. This fraction was a 60:40 mixture of geometric isomers according to ^{1}H NMR analysis. The total yield of ethyl (ethoxymethylene)acetoacetate was 72.3 g (39%): IR (neat) ν_{max} 1709 (C=O), 1626 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 60:40 mixture of isomers) δ 1.28–1.50 (four overlapping t, 6 H, OCH_2CH_3), 2.33 (s, 1.8 H, major isomer $COCH_3$), 2.40 (s, 1.2 H, minor isomer $COCH_3$), 4.07–4.43 (m, 4 H, COH_2CH_3), 7.62 (s, 0.6, minor isomer =CHOEt), 7.67 (s, 0.4 H, major isomer =CHOEt); ^{13}C NMR (C_6D_6, 90:10 mixture of isomers) 14.6, 15.2 (OCH_2CH_3), 27.7 (major isomer $COCH_3$), 31.6 (minor isomer $COCH_3$), 60.5, 72.4 (OCH_2CH_3), 114.3 (minor isomer C=CHOEt), 116.1 (major isomer C=CHOEt), 163.6, 164.5, 165.4, 165.6 (minor isomer C=CHOEt or major and minor isomer ester C=O), 193.9, 195.7 (major and minor ketone C=O).

Ethyl (Hydroxymethylene)acetoacetate (18, R = CH_3). In accordance with the procedure of Claisen,[42] 81.9 g (0.440 mol) of ethyl(ethoxymethylene)acetoacetate was treated dropwise with 500 mL of saturated aqueous copper(II) acetate over 3–15 min. The resulting suspension of bluish precipitate was stirred for 3 h at room temperature. The copper salt was filtered and washed with 400 mL of ether cooled to −15 °C. The yield of the copper salt was 72.3 g (95%).

A suspension of 76.8 g (0.222 mol) of the copper(II) salt in 500 mL of ether was treated with 200 mL of aq. 2 N sulfuric acid dropwise over 1.5 h with magnetic stirring. The ether phase was separated, dried (Na_2SO_4), and evaporated at aspirator pressure. Distillation of the residue gave 51.9 g (74%) of a colorless oil, bp 45–67 °C (0.15–0.60 mm) [lit.[42] bp 95 °C (21 mm)]. The hydroxymethylene compound **18** (R = CH_3) proved to be a 90:10 mixture of two tautomers:[43] IR (neat) ν_{max} 1709 (C=O), 1570 (C=C and C=O), 1260 (C—O), 773 (C=CH) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.04 (t, 3 H, J = 8 Hz, OCH_2CH_3), 2.37 (s, 3 H, CH_3CO), 3.97 (q, 2 H, J = 8 Hz, OCH_2CH_3), 8.97 (br s, 0.9 H, major tautomer, C=CHOH), 9.97 (s, 0.1 H, minor tautomer, CHO), 14.07 (s, 0.1 H, minor tautomer, C=CHOH), 16.78 (br s, 0.9 H, major tautomer, C=CHOH).

Dimethyl (Hydroxymethylene)malonate. The procedure

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(24) Patel, B. A.; Kim, J.-I. I.; Bender, D.; Kao, L.-C.; Heck, R. F. *J. Org. Chem.* **1981**, *46*, 1061–1067.
(25) Hamer, F. M.; Rathbone, R. J. *J. Chem. Soc.* **1945**, 595–600.
(26) Crossland, I. *Org. Synth.* **1981**, *60*, 6–10.
(27) Normant, H. *C. R. Hebd. Seances Acad. Sci.* **1955**, *240*, 1435–1437.
(28) Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772–3774.
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(30) Fischer, R. F.; Smith, C. W. *J. Org. Chem.* **1960**, *25*, 319–324.
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of Burgoyne[44] was employed. A solution of sodium methoxide prepared from 7.37 g (320 mmol) of sodium and 300 mL of methanol was treated in succession with 35 mL (40.5 g, 306 mmol) of dimethyl malonate and 76 mL (69.7 g, 941 mmol) of ethyl formate. The resulting mixture was heated at reflux for ca. 3 h and evaporated to near dryness. The residue was suspended in 200 mL of ethyl ether and allowed to stand at refrigerator temperature overnight. The solid was collected and dried under high vacuum overnight to give 34.4 (62%) of the sodium salt of dimethyl (hydroxymethylene)malonate as a white solid.

A mixture of chloroform (50 mL) and a solution of 20.0 g (110 mmol) of the sodium salt in 300 mL of water was cooled to 3 °C with an ice bath and stirred as a solution of 7 mL (7.3 g, 122 mmol) of glacial acetic acid in 50 mL of water was added over 21 min. The chloroform phase was separated, and the aqueous phase was extracted with four 100-mL portions of chloroform. The combined chloroform extracts were dried ($MgSO_4$) and evaporated to give 13.7 g of a colorless, viscous oil. Crystallization from pentane–ether at −20 °C provided 10.32 g (58%) of dimethyl (hydroxymethylene)malonate as a white crystalline solid: mp 36–41.5 °C (lit.[45] mp 38–39 °C); IR (neat) ν_{max} 1736 (C=O), 1656 (br, C=O), 1594 (br, C=C?), 1180 (C—O), 782 (C=CH) cm^{-1}; ^1H NMR (C_6D_6) δ 3.51 (s, 6 H, OCH_3), 8.11 (s, 1 H, C=C*H*OH), 12.80 (br s, 1 H, C=CHO*H*).

Diethyl (Hydroxymethylene)malonate (18, R = OEt). The sodium salt of diethyl (hydroxymethylene)malonate was prepared in a similar manner to that described for the dimethyl ester. The yield of the white powdery salt was 61.2 g (64%).

A 35.4-g portion of the salt was acidified with dilute acetic acid, and the product was isolated as described above. Distillation gave 10.63 g (34%) of diethyl (hydroxymethylene)malonate as a colorless oil: bp 58–61 °C (0.15 mm) [lit.[42] bp 107–109 °C (12 mm)]: IR (neat) ν_{max} 1733 (C=O), 1642 (C=O), 1595 (C=C), 1190 (C—O), 792 (C=CH); ^1H NMR (C_6D_6) δ 1.11 (t, 6 H, J = 7 Hz, OCH_2CH_3), 4.04 (q, 4 H, J = 7 Hz, OCH_2CH_3), 8.17 (br s, 1 H, C=C*H*OH), 12.91 (br s, 1 H, C=CHO*H*).

Methyl (Hydroxymethylene)cyanoacetate. The following procedure is based on the method of Rappoport.[45] A solution of sodium methoxide prepared from 11.8 g (0.511 mol) of sodium and 450 mL of methanol was stirred with a mechanical stirrer and maintained under nitrogen as a solution of 39 mL (43.8 g, 0.44 mol) of methyl cyanoacetate and 114 mL (104 g, 1.41 mol) of ethyl formate was added over ca. 1 min. The mixture was stirred and heated at reflux temperature for 1.5 h. When the mixture cooled, a white solid precipitated, which was filtered and washed with ether. The resulting sodium salt of methyl (hydroxymethylene)cyanoacetate was used immediately in the next step.

The salt was suspended in 1 L of dichloromethane and treated dropwise with 250 mL of 2 N aqueous sulfuric acid over 9 min. The organic phase was separated, dried ($MgSO_4$), and evaporated at aspirator pressure to near dryness. Hexane was added, and the solution was allowed to crystallize in a freezer at −20 °C. The yield was 28.5 g (51% from cyano ester) of white needles: mp 132–135 °C (lit.[18a] mp 136–137 °C); IR (KBr) ν_{max} 2237 (C≡N), 1712 (C=O), 1631 (C=C); 220 MHz ^1H NMR (Me_2SO-d_6) δ 3.71 (s, 3 H, OCH_3), 8.34 (s, 1 H, C=C*H*OH), 12.72 (br s, 1 H, C=CHO*H*).

Monitoring Procedures for the Alkoxyallylation Reactions. The reactions were monitored by TLC on commercial silica gel F-254 plates (0.25 mm layer) obtained from Brinkmann Instruments. The rate of the sealed-tube reactions was estimated from small-scale reactions conducted in sealed glass capillaries for various time intervals. The disappearance of starting active carbonyl compound, or the time at which no further change was observed on TLC, was judged to be the end of the reaction. However, run times reported are not necessarily the minimum possible for the reaction.

General Procedures for Alkoxyallylation Reactions. Method A. The following four procedures are representative of alkoxyallylations of carbonyl compounds with 1-ethoxyallene and acetals of α,β-enals. The reactions were carried out without solvent at temperatures ranging from room temperature to 200 °C.

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Example 1. 2-(3-Ethoxy-2-propenyl)-2-methyl-1,3-cyclopentanedione (11, R = H). A heterogeneous mixture of 0.566 g (5.04 mmol) of 2-methyl-1,3-cyclopentanedione (**10**) and 2.61 g (20.1 mmol) of acrolein diethyl acetal in a reusable glass pressure tube (see Apparatus section) was heated in an oil bath at 200 °C. The tube was cooled to room temperature after 2–3-min intervals of heating to withdraw small (<50 μL) samples for TLC analysis. After a total of 15 min at 200 °C the reaction mixture had become homogeneous, and the starting diketone had been consumed. Excess acetal was evaporated under reduced pressure (ca. 0.1 mm) at room temperature overnight and collected in a dry ice–acetone trap. The remaining viscous oil was distilled in a Kugelrohr apparatus at 175–202 °C (0.20 mm) to give the crude ethoxyallyl ketone as a pale yellow oil, 0.855 g. The product was further purified by flash chromatography on a 70-g, 30 × 200 mm column of silica gel with 30% ethyl acetate–hexane as eluant and a second Kugelrohr distillation. *C*-Ethoxyallyl diketone **11** (R = H) was obtained in 0.65 g (67%) yield as a colorless oil, which proved to be a 65:35 mixture of *E* and *Z* isomers. The presence of the *Z* isomer was inferred from the appearance of the following resonances in the ^1H NMR spectrum ($CDCl_3$): δ 2.35 (d, 2 H, J = 9 Hz, CH_2CH=CH), 2.74 (s, 4 H, CH_2CH_2), 4.20 (q, 1 H, J = 8 Hz, C*H*=CHOEt), 6.05 (d, 1 H, J = 6 Hz, CH=C*H*OEt). The spectral data for the *E* isomer are as follows: IR (neat) ν_{max} 1720 (C=O), 1670 and 1650 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, unlocked) δ 1.07 (s, 3 H, CH_3), 1.21 (t, 3 H, J = 8 Hz, OCH_2CH_3), 2.20 (d, 2 H, J = 9 Hz, CH_2CH=CH), 2.69 (s, 4 H, CH_2CH_2), 3.62 (q, 2 H, J = 8 Hz, OCH_2CH_3), 4.47 (dt, 1 H, J = 9, 12 Hz, C*H*=CHOEt), 6.14 (d, 1 H, J = 12 Hz, CH=C*H*OEt); ^{13}C NMR ($CDCl_3$) δ 14.6, 18.6 (CH_3 at C-2 and OCH_2CH_3), 34.9, 35.6 (CH_2CH_2 and CH_2CH=CH), 57.5 (C-2), 65.0 (OCH_2CH_3), 96.4 (*C*H=CHOEt), 149.8 (CH=*C*HOEt), 198.8 (2 C=O); mass spectrum (70 eV), m/e (relative intensity) 196 (M^+, 6), 85 (68), 57 (base). An analytical sample was prepared from an eariler run by distillation. This sample had bp 80–83 °C (0.15 mm) and was a 90:10 mixture of *E* and *Z* isomers. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.05; H, 8.39.

Example 2. 1-(3-Ethoxy-2-propenyl)-2-oxocyclopentanecarbonitrile (15). Procedure A (example 1) was performed with 1.10 g (10.1 mmol) of 2-oxocyclopentanecarbonitrile (**14**) and 3.38 g (40.1 mmol) of 1-ethoxyallene except that the solution was heated for 20 min in an oil bath at 125 °C, and the excess allene was removed at aspirator pressure. The product was partially purified by two Kugelrohr distillations, which afforded 2.03 g of a pale yellow oil. Flash chromatography on a 116-g, 40 × 200 mm column of silica gel with 30% ethyl acetate–hexane as the eluant, followed by Kugelrohr distillation at 180–182 °C (0.10 mm) provided 1.37 g (70%) of ethoxyallyl cyano ketone **15** as a colorless oil, which was a 90:10 mixture of *E* and *Z* isomers.

Enol ether **15** was also prepared by method A, example 1, from 2.64 g (20.3 mmol) of acrolein diethyl acetal and 0.544 g (4.98 mmol) of 2-cyanocyclopentanone (**14**). The weight of partially purified product after Kugelrohr distillation was 0.912 g. Additional purification by flash chromatography on a 70-g, 30 × 200-mm column of silica gel with 30% ethyl acetate–hexane as the eluant provided 0.735 g of colorless oil. A second flash chromatography was performed in order to separate the *E* and *Z* isomers. A silica gel column of the same dimensions was eluted with 1.24 L of 10% ethyl acetate–hexane and 340 mL of ethyl acetate–hexane while 20-mL fractions were collected. Fractions 28–31 provided 35.8 mg of (*Z*)-**15**. Fractions 40–71 upon Kugelrohr distillation at 178–190 °C (0.10 mm) gave 0.432 g of (*E*)-**15**. The mixed fractions 32–39 upon Kugelrohr distillation provided 0.220 g of an 80:20 mixture of *E* and *Z* isomers of **15**. The overall yield was 0.688 g (71%) (overall *E* to *Z* ratio 90:10). The analytical data are as follows (boiling points and IR data are for mixtures of 90:10 *E*/*Z* isomers): bp 105–110 °C (0.15–0.21 mm); IR (neat) ν_{max} 2252 (C≡N), 1757 (C=O), 1675, 1653 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, *E*-isomer) δ 1.27 (t, 3 H, J = 7 Hz, OCH_2CH_3), 1.79–2.67 (m, 8 H, CH_2CH=CH and 3 ring CH_2), 3.74 (q, 2 H, J = 7 Hz, OCH_2CH_3), 4.91 (dt, 1 H, J = 8, 13 Hz, C*H*=CHOEt), 6.33 (d, 1 H, J = 12 Hz, CH=C*H*OEt); ^1H NMR ($CDCl_3$, *Z* isomer) δ 1.27 (t, 3 H, J = 8 Hz, OCH_2CH_3), 1.63–2.67 (m, 8 H, CH_2CH=CH and ring CH_2), 3.81 (q, 2 H, J = 8 Hz, OCH_2CH_3), 4.40 (q, 1 H, J = 8 Hz, C*H*=CHOEt), 6.18 (d, 1 H, J = 6 Hz, CH=C*H*OEt); ^{13}C NMR ($CDCl_3$) δ 14.6 (OCH_2CH_3), 19.1, 32.7, 33.1, 36.6 (ring

CH_2 and CH_2CH=CH), 49.5 (CCN), 64.9 (OCH_2CH_3), 95.6 (CH=CHOEt), 119.2 (C≡N), 150.4 (CH=CHOEt), 209.4 (C=O); mass spectrum (70 eV), m/e (relative intensity) 193 (M^+, 3), 85 (67), 57 (base).

An analytical sample was prepared from an eariler run using 1-ethoxyallene and was purified by preparative TLC on silica gel followed by Kugelrohr distillation. Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.11; H, 7.92; N, 7.22.

Example 3. 1-(3-Ethoxy-2-propenyl)-2-oxocyclohexanecarboxaldehyde. Method A (example 1) was followed with 2.54 g (20.1 mmol) of 2-(hydroxymethylene)cyclohexanone and 10.5 g (80.3 mmol) of acrolein diethyl acetal except that the solution was heated and stirred at reflux for 11.5 h in a flask fitted with reflux condenser. Evaporation of the acetal under reduced pressure, followed by Kugelrohr distillation, afforded 3.28 g of a pale yellow oil. Further purification was accomplished by flash chromatography on a 116-g, 40 × 200-mm column of silica gel, eluting with 1.2 L of 20% ethyl acetate–hexane and collecting 30-mL fractions. Fractions 16–25 upon Kugelrohr distillation at 175–192 °C (0.15 mm) gave 2.02 g (48%) of product as a colorless oil, which was a 90:10 mixture of *E* and *Z* isomers. The presence of the *Z*-isomer was inferred from the following ^1H NMR resonances ($CDCl_3$): δ 4.27 (q, 1 H, CH=CHOEt), 6.03 (d, 1 H, CH=CHOEt).

Fractions 13 and 14 upon Kugelrohr distillation at 155–160 °C (0.15 mm) gave 0.292 g of a pale yellow oil. A 0.213-g sample of this oil was further purified by flash chromatography on a 70-g, 30 × 200-mm column of silica gel with 800 mL of 10% ethyl acetate–hexane as the eluant, collecting 20-mL fractions. Fractions 13–15 upon Kugelrohr distillation gave 69 mg (3%) of a colorless oil tentatively identified by ^1H NMR and IR spectra as (**E**)-2-(3-ethoxy-2-propenyl)cyclohexanone: IR (neat) ν_{max} 1712 (C=O), 1678, 1656 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (t, 3 H, J = 7 Hz, OCH_2CH_3), 1.00–2.68 (m, 11 H, ring protons and CH_2CH=CH), 3.61 (q, 2 H, J = 7 Hz, OCH_2CH_3), 4.64 (dt, 1 H, J = 8, 12 Hz, CH=CHOEt), 6.15 (d, 1 H, J = 15 Hz, CH=CHOEt); mass spectrum (70 eV), m/e (relative intensity) 182 (M^+, 17), 85 (80), 57 (base); exact mass, m/e 182.1307 (calcd for $C_{11}H_{18}O_2$ 182.1307).

The properties of the major product are as follows (all data were obtained with a 90:10 *E*/*Z* mixture of isomers): bp 102–108 °C (0.20–0.22 mm), IR (neat) ν_{max} 1727, 1703 (C=O), 1669, 1650 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, *E* isomer) δ 1.22 (t, 3 H, J = 7 Hz, OCH_2CH_3), 1.40–2.61 (m, 10 H, ring CH_2 and CH_2CH=CH), 3.63 (q, 2 H, J = 7 Hz, OCH_2CH_3), 4.57 (dt, 1 H, J = 8, 13 Hz, CH=CHCOEt), 6.23 (d, 1 H, J = 13 Hz, CH=CHOEt), 9.50 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$) δ 14.6 (OCH_2CH_3), 21.4, 26.4, 30.9, 31.3, 41.0 (ring CH_2 and CH_2CH=CH), 64.6, 64.8 (OCH_2CH_3 and CCHO), 96.7 (CH=CHOEt), 149.0 (CH=CHOEt), 201.5, 209.1 (aldehyde and ketone C=O); mass spectrum (10 eV), m/e (relative intensity) 210 (M^+, 5), 85 (base), 57 (40).

An analytical sample was prepared by distillation followed by Kugelrohr distillation in an eariler run. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.16; H, 8.74.

Example 4. 2-(3-Ethoxy-2-methyl-2-propenyl)-2-nitro-1,3-indandione. Methacrolein diethyl acetal (5.78 g, 40.1 mmol) was stirred under nitrogen as 1.92 g (10.1 mmol) of 2-nitro-1,3-indandione was added over ca. 1 min. The solution was stirred at room temperature for 47 min after which the excess acetal was removed as described in method A, example 1. Recrystallization of the yellowish solid residue from pentane–ether following treatment with decolorizing charcoal gave 2.03 g (70%) of yellow prisms: mp 113–117 °C, IR (KBr) ν_{max} 1754, 1718 (C=O), 1658 (C=C), 1545 (N—O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (t, 3 H, J = 7 Hz, OCH_2CH_3), 1.30 (s, 3 H, CH_3), 3.20 (s, 2 H, CH_2C=CH), 3.61 (q, 2 H, J = 7 Hz, OCH_2CH_3), 5.83 (s, 1 H, C=CHOEt), 7.81–8.20 (m, 4 H, aromatic H). An analytical sample was prepared in an earlier run by recrystallization. Anal. Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.16; H, 5.17; N, 4.84.

Method B. The three sample procedures below are representative of runs with ethoxyallene and acetals of α,β-enals conducted at room temperature or at reflux in 1,2-dichloroethane.

Example 1. 2-(3-Ethoxy-2-propenyl)-2-methyl-1,3-cyclopentanedione (11, R = H). A heterogeneous mixture of 2.24 g (19.8 mmol) of 2-methyl-1,3-cyclopentanedione (**10**) and 7.82 g (92.9 mmol) of ethoxyallene in 60 mL of 1,2-dichloroethane was heated at reflux for 14 h in an apparatus similar to that used in method A, example 3. Removal of the solvent and the excess allene on a rotary evaporator gave 7.48 g of viscous oil. Further purification by distillation gave 2.26 g (58%) of product, bp 89–95 °C (0.17–0.20 mm). This sample was found to be a 90:10 *E*/*Z* mixture by its ^1H NMR spectrum.

Example 2. 2-Ethoxy-3,4,6,7,8,9-hexahydro-8,8-dimethyl-6-oxo-2*H*-chromene. A suspension of 2.8 g (20 mmol) of dimedone and 12.1 g (93.3 mmol) of acrolein diethyl acetal in 60 mL of 1,2-dichloroethane was heated and stirred at reflux for 24 h in a small round-bottomed flask fitted with a modified Dean–Stark trap and condenser which permitted a continuous flow of condensate through a column of ca. 10 g of Linde 4A molecular sieves. The solvent was removed at aspirator pressure to give 6.82 g of yellowish oil as residue. Further purification of the product by distillation at 91–110 °C (0.12–0.15 mm) gave 2.42 g (54%) of the chromene: IR (neat) ν_{max} 1658 (C=O), 1634 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 (s, 3 H, C-8 methyl), 0.84 (s, 3 H, C-8 methyl), 1.04 (t, 3 H, J = 7 Hz, OCH_2CH_3), 1.34–1.84 (m, 2 H, C-3 CH_2), 1.94–2.11 (m, 4 H, allylic H), 2.24–2.51 (m, 2 H, C-7 CH_2), 3.49 (16 line symmetrical m, 2 H, OCH_2CH_3), 4.70 (t, 1 H, J = 4 Hz, acetal methine); ^{13}C NMR ($CDCl_3$) δ 13.8, 15.2 (2 C-8 CH_3 and OCH_2CH_3), 26.1, 28.2, 32.1, 42.2 (C-3, C-4, C-7 and C-9), 50.6 (C-8), 64.4 (OCH_2CH_3), 98.8 (C-2 acetal methine), 110.6 (C=C—O), 166.7 (C=C—O), 197.3 (C=O); mass spectrum (70 eV), m/e (relative intensity) 224 (M^+, 79), 195 (base), 179 (34). An analytical sample was prepared by distillation at 91–99 °C (0.15 mm). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.98. Found: C, 69.68; H, 9.05.

Example 3. 2-(3-Ethoxy-2-methyl-2-propenyl)-2-nitro-1,3-indandione. To a suspension of 1.91 g (10.0 mmol) of 2-nitro-1,3-indandione in 30 mL of 1,2-dichloroethane was added 6.77 g (47.0 mmol) of methacrolein diethyl acetal over 6 min. After 2.5 h at room temperature the solvent was removed on a rotary evaporator, and the excess acetal was removed as in method A, example 1. Recrystallization of the solid residue from pentane–dichloromethane gave 1.42 g (49%) of the product as yellow prisms, mp 107–112 °C.

Method C. The following example is representative of alkoxyallylations with acrolein diethyl acetal with $Ni(acac)_2$ as the catalyst.

Ethyl 1-(3-Ethoxy-2-propenyl)-2-oxocyclopentanecarboxylate. Method A (example 1) was followed with 0.794 g (5.09 mmol) of 2-carbethoxycyclopentanone and 2.61 g (20.1 mmol) of acrolein diethyl acetal except for the addition of 14 mg (0.053 mmol) of $Ni(acac)_2$ to the initial reaction mixture. After the glass pressure tube was heated in an oil bath at temperatures from 180 to 200 °C for a total of 5.5 h, the reaction mixture was allowed to cool to room temperature. The crude product was dissolved in ether, and the solution was filtered through a 10-g pad of silica gel to remove the metal catalyst. Evaporation of the ether from the filtrate on a rotary evaporator and removal of the excess acetal from the residue as in method A, example 1, afforded 1.36 g of a viscous oil. Further purification of a 0.626-g sample by flash chromatography on a 31-g, 20 × 200 mm column of silica gel with 20% ethyl acetate–hexane, followed by Kugelrohr distillation at 172–184 °C (0.10 mm), afforded 0.283 g (50%) of product as a colorless, viscous oil which proved to be a 90:10 *E*/*Z* mixture: bp 111–113 °C (0.35 mm); IR (neat) ν_{max} 1754, 1727 (C=O), 1678, 1656 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 90:10 *E*/*Z*) δ 1.27 (t, 6 H, J = 7 Hz, ether and ester OCH_2CH_3), 1.57–2.70 (m, 8 H, CH_2CH= and ring CH_2), 3.69 (q, 2 H, J = 7 Hz, ether OCH_2CH_3), 4.15 (q, 2 H, J = 7 Hz, ester OCH_2CH_3), 4.62 (dt, 1 H, J = 8, 12 Hz, CH=CHOEt), 6.04 (d, 0.1 H, J = 7 Hz, CH=CHOEt, *Z* isomer), 6.24 (d, 0.9 H, J = 13 Hz, CH=CHOEt, *E* isomer); ^{13}C NMR ($CDCl_3$) δ 14.2, 14.7 (ester and ether OCH_2CH_3), 19.6, 32.1, 38.2 (3 ring CH_2 and CH=CHOEt), 60.7, 61.2, 64.7 (CCO_2Et, ester and ether OCH_2CH_3), 97.8 (CH=CHOEt), 149.3 (CH=CHOEt), 171.0 (ester C=O), 214.1 (ketone C=O); mass spectrum (70 eV), m/e (relative intensity) 240 (M^+, 6), 85 (base), 57 (94). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.19; H, 8.43.

Method D. The procedure below is representative of runs with acrolein ethylene acetal with pyridinium *p*-toluenesulfonate as the catalyst.

2-[3,3-(Ethylenedioxy)-1-propyl]-2-methyl-1,3-cyclopentanedione (20). Method A (example 1) was followed with

0.562 g (5.01 mmol) of 2-methyl-1,3-cyclopentanedione (**10**) and 2.01 g (20.1 mmol) of acrolein ethylene acetal except that 14 mg (0.054 mmol) of pyridinium *p*-toluenesulfonate was added as the catalyst prior to heating. After the glass pressure tube was heated in an oil bath at 200 °C for 15 min, the excess acetal was removed as in method A, example 1, and the residue was distilled in a Kugelrohr apparatus to give 1.07 g of a pale yellow oil. Additional purification of the product was effected by flash chromatography on a 70-g, 30 × 200 mm column of silica gel with 70% ethyl acetate–hexane as the eluant, followed by Kugelrohr distillation at 180–189 °C (0.10–0.15 mm). Acetal **20** was obtained as a pale yellow oil: yield 0.824 g (77%); bp 143–148 °C (0.15–0.20 mm); IR (neat) ν_{max} 1770, 1730 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (s, 3 H, CH_3), 1.37–1.90 (m, 4 H, side chain CH_2), 2.74 (s, 4 H, ring CH_2), 3.67–4.00 (m, 4 H, dioxolane ring CH_2), 4.65 (t, 1 H, J = 4 Hz, acetal CH); ^{13}C NMR ($CDCl_3$) δ 20.5 (CH_3), 28.3, 28.5, 34.8 (ring and side chain CH_2), 55.8 (C-2), 64.6 (dioxolane ring CH_2), 103.6 (acetal methine), 215.9 (2C=O); mass spectrum (70 eV), m/e (relative intensity) 99 (16), 73 (base). An analytical sample was prepared by preparative GC at 190 °C. The retention time was 9.6 min. Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 61.88; H, 7.42.

Other Alkoxyallylation Reactions. The conditions used for the other alkoxyallylation reactions are presented in the following abbreviated format, where possible: method (reaction time, temperature) and reactants; purification procedure (weight of silica gel, column dimensions, solvent system for flash chromatography; solvent system for recrystallization; boiling point range for distillation); yield (%); E/Z isomer ratio; boiling or melting point; spectral and analytical data.

2-(3-Ethoxy-2-propenyl)-2-methyl-1,3-cyclopentanedione (11, R = H): method B-2 (33.5 h, reflux temperature) with 2-methyl-1,3-cyclopentanedione (**10**) and acrolein diethyl acetal; distillation [bp 85–94 °C (0.15–0.20 mm)]; yield 3.21 g (82%).

2-(3-Ethoxy-2-methyl-2-propenyl)-2-methyl-1,3-cyclopentanedione (11, R = CH_3): method A-1 (1.5 h, 200 °C) with 2-methyl-1,3-cyclopentanedione and methacrolein diethyl acetal; flash chromatography (70 g, 30 × 200 mm, 30% ethyl acetate–hexane); yield 0.915 g (87%); isomer ratio 70:30. The following spectral data are for a single isomer: IR (neat) ν_{max} 1718 (C=O), 1675 (C=C) cm^{-1}; ^1H NMR (CCl_4) δ 0.98 (s, 3 H, CH_3), 1.18 (t, 3 H, J = 8 Hz, OCH_2CH_3), 1.39 (s, 3 H, C=CCH_3), 2.14 (s, 2 H, C=CCH_2), 2.57 (s, 4 H, ring CH_2), 3.68 (q, 2 H, J = 8 Hz, OCH_2CH_3), 5.67 (s, 1 H, C=CH); ^{13}C NMR ($CDCl_3$) δ 14.4, 15.2, 19.8 (CH_3, C=CCH_3 and OCH_2CH_3), 35.8, 42.0 (ring CH_2 and C=CCH_2), 57.2 (C-2), 67.4 (OCH_2CH_3), 107.7 (C=CH), 144.8 (C=CH), 198.2 (2 C=O); mass spectrum (70 eV), m/e (relative intensity) 210 (M^+, 8) 99 (75), 71 (base). The presence of isomers in the product at 200 °C was inferred from the following ^1H NMR resonances ($CDCl_3$, integration estimated by peak height): δ 2.24 (s, 1.40 H, CH_2C=C), 2.30 (s, 0.60 H, CH_2C=C). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.19; H, 8.59.

2-(3-Ethoxy-2-phenyl-2-propenyl)-2-methyl-1,3-cyclopentanedione (11, R = Ph) was prepared by method A-1 (0.25 h, 200 °C) from atropaldehyde diethyl acetal and 2-methyl-1,3-cyclopentanedione (**10**), with the exception that flash chromatography (116 g silica gel, 40 × 200 mm column dimensions, 20% ethyl acetate–hexane as the eluant) was used both to purify the compound and to remove excess acetal. The product was obtained as an 80:20 mixture of geometric isomers: yield 1.22 g (88%); IR (neat) ν_{max} 1733, 1724 (C=O), 1647 (C=C), 1602, 770, 701 (phenyl ring) cm^{-1}; 220-MHz ^1H NMR (C_6D_6, 60:40 mixture) δ 0.87 (t, 0.6 H, J = 7.0 Hz, minor isomer OCH_2CH_3), 0.94 (t, 2.4 H, J = 7.0 Hz, major isomer OCH_2CH_3), 0.98 (s, 2.4 H, major isomer CH_3), 0.99 (s, 0.6 H, minor isomer CH_3), 1.83 (s, 0.8 H, minor isomer ring CH_2), 2.08 (14-line symmetrical m, 3.2 H, major isomer ring CH_2), 2.64 (s, 0.4 H, minor isomer CH_2C=C), 2.90 (s, 1.6 H, major isomer CH_2C=C), 3.32 (q, 0.4 H, minor isomer OCH_2CH_3), 3.34 (q, 1.6 H, major isomer OCH_2CH_3), 5.95 (s, 0.2 H, minor isomer C=CH), 6.03 (s, 0.8 H, major isomer C=CH), 6.88–7.36 (m, 5 H, aromatic H). Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97, H, 7.40. Found: C, 74.79; H, 7.46.

2-(3-Ethoxy-1-methyl-2-propenyl)-2-methyl-1,3-cyclopentanedione: method A-1 (0.25 h, 200 °C) with crotonaldehyde diethyl acetal and 2-methyl-1,3-cyclopentanedione (**10**); flash chromatography (70 g, 30 × 200 mm, 20% ethyl acetate–hexane); yield 85 mg (8% or 22% based on recovered diketone); 20:80 E/Z mixture; IR (neat) ν_{max} 1764, 1718 (C=O), 1658 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 20:80 E/Z mixture) δ 0.94 (d, 3 H, J = 7 Hz, $CHCH_3$), 1.10 (s, 3 H, ring CH_3), 1.23 (t, 3 H, J = 7 Hz, OCH_2CH_3), 2.40–2.98 (m, 4 H, CH_2CH_2), 3.10 (dq, 1 H, J = 7, 10 Hz, CH—CH=CH), 3.74 (q, 2 H, J = 7 Hz, OCH_2CH_3), 4.23 (dd, 0.80 H, J = 6, 10 Hz, Z isomer CH=CHOEt), 4.61 (dd, 0.20 H, J = 10, 13 Hz, E isomer CH=CHOEt), 5.98 (d, 0.80 H, J = 6 Hz, Z isomer CH=CHOEt), 6.21 (d, 0.20 H, J = 13 Hz, E isomer CH=CHOEt); mass spectrum (70 eV), m/e (relative intensity) 210 (M^+, 1), 99 (97), 71 (base). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.41; H, 8.49.

2-(3-Ethoxy-2-propenyl)-2-methyl-1,3-cyclohexanedione: method A-1 (0.5 h, 200 °C) with acrolein diethyl acetal and 2-methyl-1,3-cyclohexanedione; flash chromatography (70 g, 30 × 200 mm, 30% ethyl acetate–hexane); yield 0.754 (71%); 90:10 E/Z; bp 103–106 °C (0.20–0.22 mm); IR (neat) ν_{max} 1730, 1695 (C=O), 1672, 1650 (C=C) cm^{-1}; ^1H NMR (unlocked in $CDCl_3$, E isomer) δ 1.18 (s, 3 H, ring CH_3), 1.19 (t, 3 H, J = 8 Hz, OCH_2CH_3), 1.64–2.04 (m, 2 H, $CH_2CH_2CH_2$), 2.31 (d, 2 H, J = 8 Hz, CH—CH=CH), 2.56 (apparent t, 4 H, $CH_2CH_2CH_2$), 3.56 (q, 2 H, J = 7 Hz, OCH_2CH_3), 4.37 (dt, 1 H, J = 8, 12 Hz, CH=CHOEt), 6.07 (d, 1 H, J = 12 Hz, CH=CHOEt); ^1H NMR ($CDCl_3$, Z isomer) δ 1.20 (s, 3 H, ring CH_3), 1.21 (t, 3 H, J = 8 Hz, OCH_2CH_3), 1.60–3.10 (m, 6 H, ring CH_2), 2.54 (d, 2 H, J = 8 Hz, CH_2CH=CH), 3.77 (q, 2 H, J = 8 Hz, OCH_2CH_3), 4.18 (q, 1 H, J = 7 Hz, CH=CHOEt), 6.01 (d, 1 H, J = 6 Hz, CH=CHOEt). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.26; H, 8.44.

2-(3-Ethoxy-2-methyl-2-propenyl)-2-methyl-1,3-cyclohexanedione: method A-1 (2 h, 200 °C) with methacrolein diethyl acetal and 2-methyl-1,3-cyclohexanedione; flash chromatography (70 g, 30 × 200 mm, 20% ethyl acetate–hexane); yield 0.636 g (54%); bp 105–109 °C (0.15 mm); IR (neat) ν_{max} 1721 (C=O), 1689 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24, 1.24 (t and s, 6 H, J = 7 Hz, OCH_2CH_3, ring CH_3), 1.49 (s, 3 H, C=CCH_3), 1.61–2.24 (m, 2 H, $CH_2CH_2CH_2$), 2.41 (s, 2 H, CH_2C=CH), 2.52–2.74 (m, 4 H, $CH_2CH_2CH_2$), 3.70 (q, 2 H, J = 7 Hz, OCH_2CH_3), 5.81 (s, 1 H, C=CHOEt); mass spectrum (70 eV), m/e (relative intensity) 224 (M^+, 7), 99 (97), 71 (base); exact mass, m/e 224.1412 (calcd for $C_{13}H_{20}O_3$, 224.1412).

2-[3,3-(Ethylenedioxy)-1-propyl]-2-methyl-1,3-cyclohexanedione: method D (0.25 h, 200 °C) with acrolein ethylene acetal and 2-methyl-1,3-cyclohexanedione; flash chromatography (70 g, 30 × 200 mm, 70% ethyl acetate–hexane); yield 0.797 g (70%); IR (neat) ν_{max} 1724, 1692 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 3 H, CH_3), 1.37–1.70 (m, 2 H, $CH_2CH_2CH_2$), 1.70–2.24 (m, 4 H, side chain CH_2), 2.53–2.80 (m, 4 H, $CH_2CH_2CH_2$), 3.75–4.00 (m, 4 H, dioxolane ring CH_2), 4.79 (t, 1 H, J = 4 Hz, acetal methine); mass spectrum (70 eV), m/e (relative intensity) 99 (32), 73 (base). An analytical sample was prepared by preparative GC at a column temperature of 200–205 °C. The product had a retention time of 7.8 min. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.58; H, 7.85.

2-Acetyl-2-(3-ethoxy-2-propenyl)cyclopentanone: method C (1.5 h, 200 °C) with acrolein diethyl acetal and 2-acetylcyclopentanone; flash chromatography (31 g, 20 × 200 mm, 25% ethyl acetate–hexane); yield 0.244 g (60%); 90:10 E/Z mixture; IR (neat) ν_{max} 1736, 1701 (C=O), 1650, 1669 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 70:30 E/Z mixture) δ 1.23 (t, 3 H, J = 8 Hz, OCH_2CH_3), 1.40–3.00 (m, 8 H, allylic and ring CH_2), 2.20 (s, 3 H, $COCH_3$), 3.67 (q, 2 H, J = 8 Hz, OCH_2CH_3), 4.47 (dt, 1 H, J = 8, 12 Hz, CH=CHOEt), 6.01 (d, 0.30 H, J = 5 Hz, CH=CHOEt, Z isomer), 6.22 (d, 0.70 H, J = 12 Hz, CH=CHOEt). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.39; H, 8.65.

2-Acetyl-2-(3-ethoxy-2-propenyl)cyclohexanone (13, R = CH_3): method C (2 h, 200 °C) with acrolein diethyl acetal and 2-acetylcyclohexanone; flash chromatography (70 g, 30 × 200 mm, 20% ethyl acetate–hexane); yield 0.780 g (65%); 80:20 E/Z; bp 119–122 °C (0.50–0.65 mm); IR (neat, 90:10 E/Z mixture) ν_{max} 1712, 1689 (C=O), 1669, 1653 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 90:10 E/Z mixture) δ 1.22 (t, 3 H, J = 8 Hz, OCH_2CH_3), 2.10 (s, 3 H, $COCH_3$), 1.47–2.77 (m, 10 H, allylic and ring CH_2), 3.65 (q, 2 H, J = 8 Hz, OCH_2CH_3), 4.52 (dt, 1 H, J = 8, 13 Hz, CH=CHOEt), 5.97 (d, 0.10 H, J = 7 Hz, CH=CHOEt, Z isomer), 6.20 (d, 0.90 H, J = 13 Hz, CH=CHOEt, E isomer); mass spectrum (70 eV), m/e (relative intensity) 224 (M^+, 1), 85 (61), 57 (base). Anal. Calcd

for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.63; H, 8.99.

1-(3-Ethoxy-2-methyl-2-propenyl)-2-oxocyclopentanecarbonitrile: method A-1 (2 h, 200 °C) with methacrolein diethyl acetal and 2-cyanocyclopentanone; flash chromatography (70 g, 30 × 200 mm, 20% ethyl acetate–hexane); yield 0.653 (68%); IR (neat) ν_{max} 2252 (C≡N), 1754 (C=O), 1681 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (t, 3 H, J = 8 Hz, OCH_2CH_3), 1.72 (s, 3 H, CH_3), 1.80–2.67 (m, 8 H, ring and allylic CH_2), 3.79 (q, 2 H, J = 8 Hz, OCH_2CH_3), 5.96 (s, 1 H, C=CHOEt). Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.41; H, 8.28; N, 6.40.

1-[3,3-(Ethylenedioxy)-1-propyl]-2-oxocyclopentanecarbonitrile: method D (3.5 h, 200 °C) with acrolein ethylene acetal and 2-oxocyclopentanecarbonitrile; flash chromatography (31 g, 20 × 200 mm, ethyl acetate); yield, 0.171 g (54%); IR (neat) ν_{max} 2247 (C≡N), 1751 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47–2.73 (m, 10 H, five CH_2), 3.80–4.05 (m, 4 H, dioxolane CH_2), 4.83–5.00 (m, 1 H, acetal methine). An analytical sample was prepared in an earlier run by preparative GC at a column temperature of 200–205 °C. The retention time of the acetal was 7.6 min. Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 62.86; H, 7.30; N, 6.79.

1-(3-Ethoxy-2-propenyl)-2-oxocyclohexanecarbonitrile: method A-1 (37 min, 200 °C) with acrolein diethyl acetal and 2-oxocyclohexanecarbonitrile; flash chromatography (116 g, 40 × 200 mm, 30% ethyl acetate–hexane); yield 1.68 g (81%); 85:15 E/Z mixture; bp 102–110 °C (0.15–0.20 mm); IR (neat) ν_{max} 2247 (C≡N), 1724 (C=O), 1672, 1656 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 90:10 E/Z mixture) δ 1.27 (t, 3 H, J = 8 Hz, OCH_2CH_3), 1.50–3.07 (m, 10 H, ring and allylic CH_2), 3.74 (q, 2 H, J = 8 Hz, OCH_2CH_3), 4.72 (dt, 1 H, J = 8, 12 Hz, CH=CHOEt), 6.14 (d, 0.10 H, J = 7 Hz, CH=CHOEt, Z isomer), 6.34 (d, 0.90 H, J = 12 Hz, CH=CHOEt). Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.29; H, 8.38; N, 6.78.

Ethyl 2-acetyl-5-ethoxy-4-pentenoate (17, R = CH_3): method A-1 (20 min, 200 °C) with acrolein diethyl acetal and ethyl (hydroxymethylene)acetoacetate (18, R = CH_3); flash chromatography (70 g, 30 × 200 mm, 20% ethyl acetate–hexane); yield 0.833 g (77%); 80:20 E/Z mixture. The enol ether was also prepared by method C (0.5 h, 200 °C) with acrolein diethyl acetal and ethyl acetoacetate and purified by flash chromatography (same conditions as above): yield 0.412 g (43%); 85:15 E/Z mixture; bp 85–91 °C (0.30–0.35 mm); IR (neat) ν_{max} 1739, 1715 (C=O), 1678, 1658 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 80:20 E/Z mixture) δ 1.21, 1.24 (t, 6 H, J = 7 Hz, ester and ether OCH_2CH_3), 2.20 (s, 3 H, $COCH_3$), 2.41 (t, 2 H, J = 7 Hz, C=CCH_2), 3.39 (t, 1 H, J = 7 Hz, $COCHCO_2Et$), 3.63 (q, 2 H, J = 7 Hz, ether OCH_2CH_3), 4.13 (q, 2 H, J = 7 Hz, ester OCH_2CH_3), 4.61 (dt, 1 H, J = 8, 13 Hz, CH=CHOEt), 5.93 (d, 0.20 H, J = 6 Hz, CH=CHOEt, Z isomer), 6.24 (d, 0.80 H, J = 13 Hz, CH=CHOEt, E isomer); ^{13}C NMR ($CDCl_3$) δ 14.2, 14.7 (OCH_2CH_3), 26.9, 29.2 ($COCH_3$ and allylic CH_2), 60.8, 61.3, 64.8 (OCH_2CH_3 and COCHCO), 99.2 (CH=CHOEt), 148.3 (CH=CHOEt), 169.3 (ester C=O), 202.7 (ketone C=O); mass spectrum (70 eV), m/e (relative abundance) 214 (M^+, 7), 85 (43), 57 (56). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.60; H, 8.62.

Ethyl 1-(3-ethoxy-2-propenyl)-2-oxocyclohexanecarboxylate (13, R = OEt): method C (3.5 h, 200 °C) with acrolein diethyl acetal and ethyl 2-oxocyclohexanecarboxylate (12, R = OEt); flash chromatography (31 g, 20 × 200 mm, 30% ethyl acetate–hexane); yield 0.203 g (41%); 80:20 E/Z mixture; IR (neat) ν_{max} 1715 (C=O), 1678, 1656 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 90:10 E/Z) δ 1.28, 1.29 (2 t, 6 H, J = 8 Hz, ester and ether OCH_2CH_3), 0.80–2.73 (m, 10 H, allylic and ring CH_2), 3.67 (q, 2 H, J = 8 Hz, ether OCH_2CH_3), 4.18 (q, 2 H, J = 8 Hz, ester OCH_2CH_3), 4.67 (dt, 1 H, J = 8, 12 Hz, CH=CHOEt), 6.00 (d, 0.1 H, J = 7 Hz, CH=CHOEt, Z isomer), 6.20 (d, 0.90 H, J = 12 Hz, CH=CHOEt, E isomer). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.22; H, 8.60.

2-(3-Ethoxy-2-propenyl)-2-nitro-1,3-indandione: method A-4 (50 min, 25 °C) with acrolein diethyl acetal and 2-nitro-1,3-indandione; crystallization (ether–pentane); yield (colorless needles) 1.61 g (58%); all E. The enol ether was also synthesized by method B-3 with the two components above: crystallization (ether–pentane); yield 1.66 g (68%); mp 68–70.5 °C; IR (melt) ν_{max} 1770, 1730 (C=O), 1675, 1660 (C=C), 1550 (N—O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (t, 3 H, J = 8 Hz, OCH_2CH_3), 3.02 (d, 2 H, J = 8 Hz, C=CCH_2), 3.31 (q, 2 H, J = 8 Hz, OCH_2CH_3), 4.09 (dt, 1 H, J = 8, 12 Hz, CH=CHOEt), 5.99 (d, 1 H, J = 12 Hz, CH=CHOEt), 7.50–7.90 (m, 4 H, aromatic H); mass spectrum, m/e (relative intensity) 275 (M^+, 5), 228 (11), 87 (base), 85 (5), 59 (30), 57 (4). An analytical sample was prepared in an earlier run by crystallization. Anal. Calcd for $C_{14}H_{13}NO_5$: C, 61.09; H, 4.76; N, 5.09. Found: C, 61.01; H, 4,57; N, 5.23.

2-(3-Ethoxy-2-phenyl-2-propenyl)-2-nitro-1,3-indandione was prepared by method A-4 (5 min, 25 °C) from atropaldehyde diethyl acetal and 2-nitro-1,3-indandione except that the product was separated from excess acetal by precipitation in ether–pentane. Purification was accomplished by crystallization (ether–pentane): yield (yellow needles, analytically pure) 1.47 g (41%); mp 92–95 °C; IR (melt) ν_{max} 1754, 1718 (C=O), 1653 (C=O), 1548 (N—O) cm^{-1}; 220-MHz ^1H NMR ($CDCl_3$) δ 1.24 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 4.00 (s, 2 H, C=CCH_2), 4.15 (q, 2 H, J = 6.9 Hz, OCH_2CH_3), 6.82 (s, 1 H, C=CH), 7.39–7.75 (m, 5 H, aromatic H), 8.44–8.56 (m, 4 H, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 351 (M^+, 39), 304 (74), 163 (60), 161 (17), 135 (44), 133 (9). Anal. Calcd for $C_{20}H_{17}NO_5$: C, 68.37; H, 4.88; N, 3.99. Found: C, 68.25; H, 4.95; N, 3.84.

2-(3-Ethoxy-1-methyl-2-propenyl)-2-nitro-1,3-indandione was prepared by method A-4 (7 min, 25 °C) with crotonaldehyde diethyl acetal and 2-nitro-1,3-indandione except that the product was separated from excess acetal by precipitation in pentane. Purification was achieved by crystallization from ether–pentane: yield (white powdery solid, analytically pure); 1.25 g (43%). For E isomer: mp 42.5–44 °C; IR (neat) ν_{max} 1760, 1721 (C=O), 1656 (C=C), 1548 (N—O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (t, 3 H, J = 7 Hz, OCH_2CH_3), 1.24 (d, 3 H, J = 8 Hz, $CHCH_3$), 3.31–3.81 (m, 3 H, OCH_2CH_3 and C=CCH), 4.35 (dd, 1 H, J = 10, 12 Hz, CH=CHOEt), 6.32 (d, 1 H, J = 12 Hz, CH=CHOEt), 7.84–8.21 (m, 4 H, aromatic H). Anal. Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.31; H, 5.27; N, 4.74.

Ethyl 5-ethoxy-2-nitro-4-pentenoate: method A-2 (4 h, 125 °C) from 1-ethoxyallene and ethyl nitroacetate; flash chromatography (70 g, 30 × 200 mm, 10% ethyl acetate–hexane); yield 0.177 g (26%); E isomer. The nitro ester was also prepared in lower yield from acrolein diethyl acetal and ethyl nitroacetate by Method A-1 (0.5 h, 200 °C): flash chromatography (same conditions as above); yield 0.166 g (15%); 90:10 E/Z. The analytical data for the nitro ester are as follows: bp 97–101 °C (0.40–0.55 mm); IR (neat) ν_{max} 1751 (C=O), 1678, 1658 (C=C), 1565 (N—O) cm^{-1}; ^1H NMR ($CDCl_3$, E isomer) δ 1.31, 1.37 (2 t, 6 H, ester and ether OCH_2CH_3), 2.81 (t, 2 H, J = 8 Hz, C=CCH_2), 3.71 (q, 2 H, J = 7 Hz, ether OCH_2CH_3), 4.29 (q, 2 H, J = 8 Hz, ester OCH_2CH_3), 4.63 (dt, 1 H, J = 8, 13 Hz, CH=CHOEt), 5.03 (t, 1 H, J = 8 Hz, $CHNO_2$), 6.37 (d, 1 H, J = 13 Hz, CH=CHOEt); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.6 (ester and ether OCH_2CH_3), 29.5 (CH_2CH=CH), 62.9, 65.0 (ester and ether OCH_2CH_3), 88.8 ($CHNO_2$), 95.2 (CH=CHOEt), 150.4 (CH=CHOEt), 164.0 (C=O); mass spectrum (10 eV), m/e (relative intensity) 217 (M^+, 8), 85 (93), 57 (20). Anal. Calcd for $C_9H_{15}NO_5$: C, 49.76; H, 6.96; N, 6.45. Found: C, 50.11; H, 7.19; N, 6.71.

Diethyl 2-(3-ethoxy-2-propenyl)-1,3-propanedioate (17, R = OEt): method C (1 h, 200 °C) with acrolein diethyl acetal and diethyl (hydroxymethylene)malonate (18, R = OEt); flash chromatography (31 g, 20 × 200 mm, 10% ethyl acetate–hexane); yield 0.346 g (72%); 90:10 E/Z. The enol ether was also prepared by method A-2 (4 h, 125 °C) with ethoxyallene and diethyl (hydroxymethylene)malonate: flash chromatography 70 g, 30 × 200 mm, 10% ethyl acetate–hexane); yield 0.503 g (60%); 90:10 E/Z. The ethoxyallyl malonate was also synthesized by method A-1 (38 h, 200 °C) from acrolein diethyl acetal and diethyl malonate (16, R = OEt): flash chromatography (116 g, 40 × 200 mm, 30% ethyl acetate–hexane); yield 0.399 g (16%); 80:20 E/Z; IR (neat) ν_{max} 1751, 1733 (C=O), 1669, 1656 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 90:10 E/Z mixture) δ 1.20, 1.24 (2 t, 9 H, J = 7 Hz, OCH_2CH_3), 2.44 (t, 2 H, J = 8 Hz, allylic CH_2), 3.27 (t, 1 H, J = 7 Hz, $COCHCO$), 3.62 (q, 2 H, J = 7 Hz, ether OCH_2CH_3), 4.12 (q, 4 H, J = 7 Hz, ester OCH_2CH_3), 4.63 (dt, 1 H, J = 8, 13 Hz, CH=CHOEt), 5.93 (d, 0.10 H, J = 6 Hz, CH=CHOEt, Z isomer), 6.24 (d, 0.90 H, J = 13 Hz, CH=CHOEt, E isomer); ^{13}C NMR ($CDCl_3$) δ 14.1, 14.7 (OCH_2CH_3), 27.6 (allylic CH_2), 53.3 (COCHCO), 61.2, 64.6 (OCH_2CH_3), 99.1 (CH=CHOEt), 148.5 (CH=CHOEt), 168.9 (ester C=O); mass spectrum (70 eV), m/e (relative

intensity) 244 (M^+, 12), 85 (base), 57 (69). An analytical sample was prepared from an earlier run by preparative GC at a column temperature of 140–145 °C. The retention time of the product was 11.2 min. Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 58.98; H, 8.21.

Ethyl 2-cyano-5-ethoxy-4-pentenoate: method A-1 (10.5 h, 200 °C) with acrolein diethyl acetal and ethyl cyanoacetate; flash chromatography (116 g, 40 × 200 mm, 20% ethyl acetate–hexane); yield, 1.25 g (31%); 60:40 *E*/*Z* mixture; bp 92–95 °C (0.15 mm); IR (neat) ν_{max} 2262 (C≡N), 1742 (C=O), 1672, 1658 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 65:35 *E*/*Z* mixture) δ 1.32, 1.39 (2 t, 6 H, *J* = 8 Hz, ester and ether OCH_2CH_3), 2.57 (t, 2 H, *J* = 8 Hz, C=CCH_2), 3.50 (t, 1 H, *J* = 8 Hz, CHCN), 3.74 (q, 2 H, *J* = 8 Hz, ether OCH_2CH_3), 4.25 (q, 2 H, *J* = 8 Hz, ester OCH_2CH_3), 4.74 (dt, 1 H, *J* = 8, 12 Hz, C*H*=CHOEt), 6.13 (d, 0.35 H, *J* = 6 Hz, CH=C*H*OEt, *Z* isomer), 6.41 (d, 0.65 H, *J* = 12 Hz, CH=C*H*OEt, *E* isomer). Anal. Calcd for $C_{10}H_{15}NO_5$: C, 60.90; H, 7.67; N, 7.10. Found: C, 61.08; H, 7.65; N, 6.82.

Dimethyl 2-(3-methoxy-2-propenyl)-1,3-propanedioate: method C (1 h, 200 °C) with acrolein dimethyl acetal and dimethyl (hydroxymethylene)malonate; flash chromatography (70 g, 30 × 200 mm, 50% ethyl acetate–hexane); yield 0.482 g (58%); 70:30 *E*/*Z*; IR (neat) ν_{max} 1748 (C=O), 1681, 1661 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 90:10 *E*/*Z* mixture) δ 2.50 (t, 2 H, *J* = 8 Hz, C=CCH_2), 3.37 (t, 1 H, *J* = 8 Hz, COCHCO), 3.48 (s, 3 H, ether OCH_3), 3.79 (s, 6 H, ester OCH_3), 4.66 (dt, 1 H, *J* = 8, 12 Hz, C*H*=CHOEt), 5.92 (d, 0.10 H, *J* = 6 Hz, CH=C*H*OEt), 6.38 (d, 0.90 H, *J* = 12 Hz, CH=C*H*OEt). Anal. Calcd for $C_9H_{14}O_5$: C, 53.45; H, 6.97. Found: C, 53.38; H, 6.92.

5-Ethoxy-2-phenyl-4-pentenenitrile: method A-1 (1 h, 200 °C) with acrolein diethyl acetal and (hydroxymethylene)-phenylacetonitrile; flash chromatography (31 g, 20 × 200 mm, 10% ethyl acetate–hexane); yield 0.332 g (62%); 70:30 *E*/*Z*; IR (neat, *E* isomer) ν_{max} 2252 (C≡N), 1675, 1656 (C=C), 757, 700 (C_6H_5) cm^{-1}; 220 MHz ^1H NMR ($CDCl_3$, *E* isomer) δ 0.98 (t, 3 H, *J* = 7 Hz, OCH_2CH_3), 2.09 (m, 2 H, C=CCH_2), 3.20 (t, 1 H, *J* = 7 Hz, CHCN), 3.31 (q, 2 H, *J* = 7 Hz, OCH_2CH_3), 4.55 (dt, 1 H, *J* = 8, 13 Hz, C*H*=CHOEt), 6.12 (d, 1 H, *J* = 13 Hz, CH=C*H*OEt), 7.04 (br s, 5 H, aromatic H); ^1H NMR ($CDCl_3$, *Z* isomer) δ 1.20 (t, 3 H, *J* = 8 Hz, OCH_2CH_3), 2.62 (t, 2 H, *J* = 8 Hz, C=CCH_2), 3.71 (q, 2 H, *J* = 8 Hz, OCH_2CH_3), 3.81 (t, 1 H, *J* = 8 Hz, CHCN), 4.35 (q, 1 H, *J* = 6 Hz, C*H*=CHOEt), 6.19 (d, 1 H, *J* = 6 Hz, CH=C*H*OEt), 7.32 (br s, 5 H, aromatic H). Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.32; H, 7.52; N, 7.10.

Methyl 2-cyano-5-methoxy-4-pentenoate: method A-3 (5 h, reflux temperature) with acrolein dimethyl acetal and methyl (hydroxymethylene)cyanoacetate except that 4.7 equiv of acetal was used; distillation [82–102 °C (0.20–0.25 mm)]; yield 2.26 g (67%); 95:5 *E*/*Z*. The presence of the *Z* isomer was inferred by the appearance of the following resonance in a ^1H NMR spectrum ($CDCl_3$): δ 6.07 (d, 1 H, *J* = 6 Hz, CH=C*H*OEt). The analytical data for the enol ether are as follows: IR (neat) ν_{max} 2257 (C≡N), 1748 (C=O), 1678, 1658 (C=C) cm^{-1}; 360-MHz ^1H NMR ($CDCl_3$, *E* isomer) δ 2.59 (t, 2 H, *J* = 7.0 Hz, allylic CH_2), 3.53 (t, 1 H, *J* = 6.5 Hz, CHCN), 3.55 (s, 3 H, ether OCH_3), 3.82 (s, 3 H, ester OCH_3), 4.71 (dt, 1 H, *J* = 7.7, 12.6 Hz, C*H*=CHOEt), 6.48 (d, 1 H, *J* = 12.6 Hz, CH=C*H*OEt); ^{13}C NMR ($CDCl_3$) δ 28.9 (allylic CH_2), 39.1 (CCN), 53.4, 56.1 (OCH_3), 96.0 (*C*H=CHOCH$_3$), 116.6 (C≡N), 151.1 (CH=*C*HOCH$_3$), 166.4 (ester C=O); mass spectrum (70 eV), *m*/*e* (relative intensity) 169 (M^+, 5), 71 (base), 57 (1). An analytical sample was prepared from an earlier run by distillation. Anal. Calcd for $C_8H_{11}NO_3$: C, 56.80; H, 6.55; N, 8.28. Found: C, 56.67; H, 6.51; N, 8.57.

Methyl 2-cyano-5-methoxy-4-methyl-4-pentenoate: method A-1 (5 min, 200 °C) with methacrolein diethyl acetal and methyl (hydroxymethylene)cyanoacetate; flash chromatography (70 g, 30 × 200 mm, 20% ethyl acetate–hexane); yield 0.728 g (86%); bp 80–81 °C (0.10 mm); IR (neat) ν_{max} 2257 (C≡N), 1748 (C=O), 1678 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.62 (s, 3 H, C=CCH_3), 2.47 (d, 2 H, *J* = 8 Hz, C=CCH_2), 3.61, 3.61 (t and s, 4 H, ether OCH_3 and CHCN), 3.82 (s, 3 H, ester OCH_3), 5.91 (s, 1 H, C=CH); ^{13}C NMR ($CDCl_3$) δ 12.3 (CH_3), 35.2, 37.3 (CH_2C=C and *C*CN), 53.4, 59.6 (OCH_3), 107.2 (*C*=CHOCH$_3$), 116.3 (C≡N), 146.0 (C=*C*HOCH$_3$), 166.6 (ester C=O). Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.64. Found: C, 58.96; H, 7.25; N, 7.66.

2-(3,3,3-Triethoxypropyl)-2-methyl-1,3-cyclopentanedione (21). A mixture of 1.13 g (10.1 mmol) of 2-methyl-1,3-cyclopentanedione and 6.97 g (40.0 mmol) of triethyl orthoacrylate[46] was heated in a sealed-tube apparatus similar to that used for method A-1 in an oil bath at 125 °C for 1.5 h. The excess ortho ester was removed by Kugelrohr distillation [150 °C (0.10 mm)], and the resulting residue was subjected to two consecutive Kugelrohr distillations at 155–200 (0.10 mm) and 201–205 °C (0.25 mm) to afford 2.43 g (85%) of analytically pure product as a colorless, viscous oil: IR (neat) ν_{max} 1770, 1740 (C=O), 1062 (C—O) cm^{-1}; 220-MHz ^1H NMR (C_6D_6) δ 0.90 (s, 3 H, CH_3), 1.11 (t, 9 H, *J* = 7.1 Hz, OCH_2CH_3), 1.65–1.97 (m, 4 H, CH_2CH_2), 2.01 (s, 4 H, ring CH_2), 3.49 (q, 6 H, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 15.3, 19.1 (OCH_2CH_3 and CH_3), 27.5, 29.1 (side chain CH_2), 35.1 (ring CH_2), 55.7, 57.2 (C-2 and OCH_2CH_3), 114.7 (*C*-(OEt)$_3$), 215.4 (ketone C=O); mass spectrum (70 eV), *m*/*e* (relative intensity) 286 (M^+, 0.1), 241 (29), 167 (22), 147 (37). Anal. Calcd for $C_{15}H_{26}O_5$: C, 62.91; H, 9.15. Found: C, 62.94; H, 9.10.

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Registry No. 10, 765-69-5; (*E*)-**11** (R = H), 87698-07-5; (*Z*)-**11** (R = H), 87698-08-6; (*E*)-**11** (R = Me), 87698-09-7; (*Z*)-**11** (R = Me), 87698-59-7; (*E*)-**11** (R = Ph), 87698-10-0; (*Z*)-**11** (R = Ph), 87698-11-1; **12** (R = Me), 874-23-7; **12** (R = OEt), 1655-07-8; (*E*)-**13** (R = Me), 87698-12-2; (*Z*)-**13** (R = Me), 87698-13-3; (*E*)-**13** (R = OEt), 87698-17-7; (*Z*)-**13** (R = OEt), 87698-18-8; (*E*)-**13** (R = H), 87698-46-2; (*Z*)-**13** (R = H), 87698-47-3; **14**, 2941-29-9; (*E*)-**15** (R = H), 87711-07-7; (*Z*)-**15** (R = H), 87698-14-4; **15** (R = Me), 87698-57-5; (*E*)-**17** (R = Me), 87698-15-5; (*Z*)-**17** (R = Me), 87698-16-6; (*E*)-**17** (R = OEt), 87698-19-9; (*Z*)-**17** (R = OEt), 87698-20-2; (*E*)-**18** (R = Me), 87698-53-1; (*Z*)-**18** (R = Me), 87698-56-4; (*E*)-**18** (R = Me, ethyl ether), 49836-24-0; (*Z*)-**18** (R = Me, ethyl ether), 66975-53-9; **18** (R = OEt), 20734-18-3; **18**·Na (R = OEt), 25165-97-3; **20**, 87698-21-3; **21**, 87698-22-4; (*E*)-$EtO_2CCH(CN)CH_2CH$=CHOEt, 87698-32-6; (*Z*)-$EtO_2CCH(CN)CH_2CH$=CHOEt, 87698-33-7; (*E*)-$EtO_2CCH(NO_2)CH_2CH$=CHOEt, 87698-38-2; (*Z*)-$EtO_2CCH(NO_2)CH_2CH$=CHOEt, 87698-39-3; (*E*)-$(MeO_2C)_2CHCH_2CH$=CHOMe, 87698-40-6; (*Z*)-$(MeO_2C)_2CHCH_2CH$=CHOMe, 87698-41-7; (*E*)-$MeO_2CCH(CN)CH_2CH$=CHOMe, 87698-42-8; (*Z*)-$MeO_2CCH(CN)CH_2CN$=CHOMe, 87698-43-9; (*E*)-$PhCH(CN)CH_2CH$=CHOEt, 87698-44-0; (*Z*)-$PhCH(CN)CH_2CH$=CHOEt, 87698-45-1; CH_2=$CHCH(OEt)_2$, 3054-95-3; CH_2=C=CHOEt, 13077-71-9; CH_2=$C(CH_3)CH(OMe)_2$, 23230-91-3; CH_2=$C(Ph)CH(OEt)_2$, 80234-04-4; CH_3CH=$CHCH(OEt)_2$, 10602-34-3; $EtO_2CCH_2NO_2$, 626-35-7; EtO_2CCH_2CN, 105-56-6; CH_2=$CHCH(OMe)_2$, 6044-68-4; $(MeO_2C)_2C$=CHOH, 27931-91-5; PhC(CN)=CHOH, 22252-92-2; $MeO_2CC(CN)$=CHOH, 87698-54-2; $MeO_2CCH(CN)CH_2C(CH_3)$=CHOMe, 87698-55-3; CH_2=$CHC(OEt)_3$, 42216-96-6; CH_2=CHCHO, 107-02-8; Ni(acac)$_2$, 3264-82-2; $HC(OEt)_3$, 122-51-0; $EtO_2CCH_2COCH_3$, 141-97-9; $(MeO_2C)_2CH_2$, 108-59-8; EtO_2CH, 109-94-4; $MeO_2CC(CN)$=CHOH·Na, 57338-05-3; (*E*)-2-(3-ethoxy-1-methyl-2-propenyl)-2-methyl-1,3-cyclopentanedione, 87698-23-5; (*Z*)-2-(3-ethoxy-1-methyl-2-propenyl)-2-methyl-1,3-cyclopentanedione, 87711-08-8; (*E*)-2-(3-ethoxy-2-propenyl)-2-methyl-1,3-cyclohexanedione, 87698-24-6; (*Z*)-2-(3-ethoxy-2-propenyl)-2-methyl-1,3-cyclohexanedione, 87698-25-7; (*E*)-2-acetyl-2-(3-ethoxy-2-propenyl)cyclopentenone, 87698-26-8; (*Z*)-2-acetyl-2-(3-ethoxy-2-propenyl)cyclopentanone, 87698-27-9; (*E*)-1-(3-ethoxy-2-propenyl)-2-oxocyclohexanecarbonitrile, 87698-28-0; (*Z*)-1-(3-ethoxy-2-propenyl)-2-oxocyclohexanecarbonitrile, 87698-29-1; ethyl (*E*)-1-(3-ethoxy-2-propenyl)-2-oxocyclopentanecarboxylate, 87698-30-4; ethyl (*Z*)-1-(3-ethoxy-2-propenyl)-2-oxocyclopentanecarboxylate, 87698-31-5; (*E*)-2-(3-ethoxy-2-propenyl)-2-nitro-1,3-indandione, 87698-34-8; 2-(3-ethoxy-2-methyl-2-propenyl)-2-nitro-1,3-indandione, 87698-35-9; 2-(3-ethoxy-2-phenyl-2-propenyl)-2-nitro-1,3-indandione, 87698-36-0; (*E*)-2-(3-ethoxy-1-methyl-2-propenyl)-2-nitro-1,3-indandione, 87698-37-1; 2-ethoxy-

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Reductive Dehalogenation of *vic*-Dihaloalkanes to Alkenes with Sodium Sulfide under Phase-Transfer Conditions

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Reductive dehalogenation of *vic*-dihaloalkanes to alkenes with aqueous Na_2S under phase-transfer catalysis conditions is reported. Debromination reaction occurs at room temperature, giving alkenes in ≥90% yields. Meso and erythro *vic*-dihaloalkanes afford only trans olefins and react faster than the corresponding diastereomeric *d,l* and threo derivatives, which are converted into a mixture of cis and trans olefins. *vic*-Dichloroalkanes react much more slowly than the bromo compounds, affording the dehydrochlorination products instead of the reductive dehalogenation ones.

The olefin-forming dehalogenation of vicinal dibromo alkanes (widely used intermediates for the purification of olefins and for the protection of C=C double bonds[1-5]) can be accomplished with a variety of reagents.[6] One of the most recent dehalogenating systems involves the reaction of *vic*-dibromo derivatives with $Na_2S{\cdot}9H_2O$ in DMF solution.[6,7]

Here we report that the latter reaction can be more advantageously performed under liquid–liquid phase-transfer catalysis (PTC) conditions (eq 1).

$$RCXH{-}CXHR' \xrightarrow[\text{catalyst, toluene, 25 °C}]{Na_2S\ \text{aqueous}} RCH{=}CHR' + 2NaX + S \quad (1)$$

$$X = Br,\ \text{catalyst} = n\text{-}C_{16}H_{33}P^+Bu_3Br^-$$

The debrominations were carried out by stirring at room temperature a heterogeneous mixture of a toluene solution of substrate (1 mol) and an aqueous solution of $Na_2S{\cdot}9H_2O$ (2.5 mol) in the presence of catalytic amounts (0.01 mol) of hexadecyltributylphosphonium bromide as phase-transfer agent.

Under these conditions the dehalogenation reaction is complete in 5 min–12 h, and the yields in the olefins are ≥90%. As expected, reaction times increase on decreasing the amount of the catalyst; in the absence of the latter the reaction does not occur. The debromination can be performed even at 0 °C (Table I). As shown in the case of *meso*-1,2-dihalo-1,2-diphenylethanes, the chloro derivative reacts much more slowly than the bromo compound and affords the α-chloro-*cis*-stilbene instead of the *trans*-stilbene. In the case of the *vic*-dibromides the order of reactivity is qualitatively the same as previously found in the reductive dehalogenation with sodium sulfide in DMF[6] or with iodide ion both in a homogeneous organic solution[9] and in an aqueous–organic two-phase system:[10] meso or erythro derivatives react faster than the corresponding diastereoisomeric *d,l* or threo compounds. Moreover the presence of electron-withdrawing groups bound to the halogenated carbon accelerates the reactions (Table I). Also the stereochemical behavior observed under the present conditions is practically the same found by working in DMF solution with Na_2S[6] or by using iodide ion both under PTC conditions[10] and in a homogeneous organic solution.[11-15] In particular, meso and erythro *vic*-dihaloalkanes yield only trans alkenes, whereas the corresponding diastereoisomeric *d,l* and threo derivatives afford a mixture of cis and trans alkenes. The cis/trans ratio strongly depends on the nature of the groups bound to the halogenated carbons (Table I). On the reasonable assumption that a common mechanism is at work[16] in the reductive de-

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