than chloroform was used in the extraction.

Reaction of Chalcone Ketals with TTN in TMOF. General Procedure. Chalcone ketals were prepared in situ by stirring the chalcone (0.01 mol) with 2-6 g of Dowex 50W-X4 cation-exchange resin in 35 mL of TMOF at room temperature. After ketal formation was complete (15-24 h, as determined by TLC monitoring using chloroform and silica gel plates), the reaction mixture was filtered into a solution of 5.0 g (0.011 mol) of TTN·$3H_2O$ in 20 mL of TMOF. After the oxidative rearrangement was complete [6-24 h, as determined by the disappearance of Tl(III)], a small amount of sodium bisulfite was added, followed by 200-300 mL of ether, and the reaction mixture was chilled and filtered to remove $TlNO_3$. It was then worked up as described above. The methyl 2,3-diaryl-3-methoxypropanoates, which were obtained crude (90-98% purity by NMR) in almost quantitative yield, were recrystallized from methanol for analysis.

4-Nitrobenzil. To a slurry of 5.06 g (0.02 mol) of 4-nitrochalcone in 40 mL of 1,2-dimethoxyethane, 20 mL of water, and 10 mL of 70% perchloric acid was added 39.08 g (0.088 mol) of TTN·$3H_2O$. The reaction mixture was heated under reflux for 1 h and cooled, 50 mL of chloroform was added, and the reaction mixture was filtered to remove $TlNO_3$. The filtrate was diluted with saturated sodium chloride solution and extracted with two 50-mL portions of chloroform. The combined extracts were washed with 5% sodium bicarbonate solution and water, dried ($MgSO_4$), and evaporated under reduced pressure to give 3.20 g of crude product which was recrystallized from aqueous ethanol: yield 1.64 g (32%) of 4-nitrobenzil; mp 139.5-140.5 °C (lit.[3] mp 140-141 °C).

Anal. Calcd for $C_{14}H_9NO_4$: C, 65.88; H, 3.56; N, 5.49. Found: C, 66.03; H, 3.51; N, 5.64.

4-Nitro-4′-methoxybenzil was prepared as described above in 52% yield from 4-nitro-4′-methoxychalcone and TTN; mp 154 °C (lit.[7] mp 156 °C).

Anal. Calcd for $C_{15}H_{11}NO_5$: C, 63.15; H, 3.89; N, 4.91. Found: C, 62.94; H, 3.81; N, 5.08.

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE76 16506) for support of this work.

Registry No. 4,4′-Dimethoxychalcone, 2373-89-9; 4-methoxychalcone, 26522-20-3; 4-methoxy-4′-chlorochalcone, 6552-63-2; 4-methoxy-3′-nitrochalcone, 73911-01-0; 4-methoxy-4′-nitrochalcone, 6552-62-1; 3-(4-methoxyphenyl)-1-(2-thienyl)-2-propen-1-one, 6028-93-9; 4,4′-dimethylchalcone, 21551-47-3; 4-methylchalcone, 4224-87-7; chalcone, 94-41-7; 4′-methoxychalcone, 959-23-9; 4′-methylchalcone, 4224-96-8; 4′-bromochalcone, 2403-27-2; 4-chlorochalcone, 956-04-7; 4-chloro-4′-methoxychalcone, 6552-68-7; 2-chlorochalcone, 3300-67-2; 4-nitrochalcone, 1222-98-6; 4-nitro-4′-methoxychalcone, 6552-67-6; 3-nitro-4′-methoxychalcone, 68063-55-8; K (Ar, Ar′ = 4-$CH_3OC_6H_4$), 74007-46-8; K (Ar = 4-$CH_3OC_6H_4$, Ar′ = C_6H_5), 22755-95-9; K (Ar = 4-$CH_3OC_6H_4$, Ar′ = 4-ClC_6H_4), 74007-47-9; K (Ar = 4-$CH_3OC_6H_4$, Ar′ = 3-$O_2NC_6H_4$), 74007-48-0; K (Ar = 4-$CH_3OC_6H_4$, Ar′ = 4-$O_2NC_6H_4$), 74007-49-1; K (Ar = 4-$CH_3OC_6H_4$, Ar′ = 2-C_4H_3S), 74007-50-4; K (Ar, Ar′ = 4-$CH_3C_6H_4$), 74007-51-5; K (Ar = 4-$CH_3C_6H_4$, Ar′ = C_6H_5), 74007-52-6; K (Ar, Ar′ = C_6H_5), 41841-06-9; K (Ar = C_6H_5, Ar′ = 4-$CH_3OC_6H_4$), 74007-53-7; K (Ar = C_6H_5, Ar′ = 4-$CH_3C_6H_4$), 74007-54-8; K (Ar = C_6H_5, Ar′ = 4-BrC_6H_4), 74007-55-9; K (Ar = 4-ClC_6H_4, Ar′ = C_6H_5), 74007-56-0; K (Ar = 4-ClC_6H_4, Ar′ = 4-$CH_3OC_6H_4$), 74007-57-1; K (Ar = 2-ClC_6H_4, Ar′ = C_6H_5), 74007-58-2; E (Ar, Ar′ = 4-$CH_3OC_6H_4$), 74007-59-3; E (Ar, Ar′ = 4-$CH_3C_6H_4$), 74007-60-6; E (Ar = 4-$CH_3C_6H_4$, Ar′ = C_6H_5), 74007-61-7; E (Ar, Ar′ = C_6H_5), 64686-04-0; E (Ar = C_6H_5, Ar′ = 4-$CH_3OC_6H_4$), 64686-06-2; E (Ar = C_6H_5, Ar′ = 4-$CH_3C_6H_4$), 64686-05-1; E (Ar = 4-ClC_6H_4, Ar′ = C_6H_5), 74007-62-8; E (Ar = 4-ClC_6H_4, Ar′ = 4-$CH_3OC_6H_4$), 64686-07-3; E (Ar = 2-ClC_6H_4, Ar′ = C_6H_5), 74007-63-9; E (Ar = 4-$O_2NC_6H_4$, Ar′ = C_6H_5), 64686-08-4; E (Ar = 4-$O_2NC_6H_4$, Ar′ = 4-$CH_3OC_6H_4$), 64686-09-5; E (Ar = 3-$O_2NC_6H_4$, Ar′ = 4-$CH_3OC_6H_4$), 74007-64-0; TTN, 10102-45-1; 4-nitrobenzil, 22711-24-6; 4-nitro-4′-methoxybenzil, 2387-74-8.

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[7] S. Kanno and S. Suzuki, *Yakugaku Zasshi*, 71, 1247 (1951).

Phase-Transfer Catalyzed Reactions. 5.[1] Dramatic Effect of the Concentration of Base on the Dimerization of Crotonaldehyde

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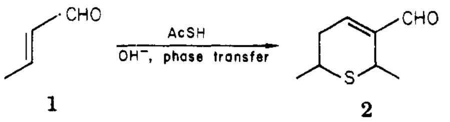
Received October 30, 1979

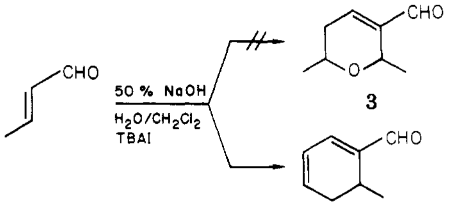
Self-condensation of crotonaldehyde under base-catalyzed phase-transfer conditions leads to aldehydes **3** or **4**, depending only on the concentration of aqueous hydroxide used. Quaternary ammonium fluorides in anhydrous THF is shown to be a useful system for conjugate additions involving base-sensitive aldehydes.

In recent years, we have been exploring the application of phase-transfer catalysis to a variety of reactions. Our interest was triggered initially by the serendipitous observation[3] that conjugated carbonyl compounds [e.g., crotonaldehyde (**1**)] would react with thiolacetic acid and sodium hydroxide in a conjugate addition-aldol condensation sequence to afford thiacyclohexenecarboxaldehydes **2** (eq 1). We now wish to document the amazing plethora of results obtained when changes, some of which are apparently minor, are made in the reagents and reaction conditions.



1 **2** (1)

Although it was known that oxygen anions are both harder and poorer nucleophiles than the analogous sulfur anions,[4] we considered the use of acetic acid as a possible route to dihydropyrans **3**. In the event, this reaction afforded none of **3**, but rather a 49% yield of **4**[5] was obtained.



3

4

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[1] For part 4, see J. M. McIntosh, *Tetrahedron Lett.*, 403 (1979).

[2] NSERC predoctoral fellow, 1974-1977; taken in part from the Ph.D. thesis of H.K., University of Windsor, 1977.

[3] J. M. McIntosh and H. Khalil, *J. Org. Chem.*, 42, 2123 (1977).

[4] J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, 84, 16 (1962).

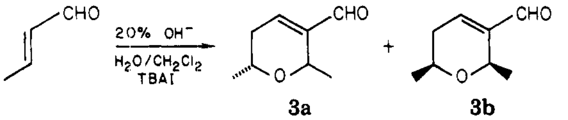
0022-3263/80/1945-3436$01.00/0 © 1980 American Chemical Society

Table I. Self-Condensation of Crotonaldehyde

run	NaOH normality	NaOH vol, mL	NaOH mol	NaOH equiv	catalyst	product	% yield
1	12.4	9	0.11	2.8	TBAI	4	43
2	10.5	9	0.09	2.4	TBAI	4	39
3	10.5	9	0.09	2.4	TEBAC	4	25
4	10.5	9	0.09	2.4	CTMAB	4	37
5	5.4	9	0.05	1.2	TBAI	3	28
6	2.7	9	0.025	0.6	TBAI	3	39
7	5.4	18	0.1	2.4	TBAI	3	22
8	2.7	36	0.1	2.4	TBAI	3	34
9	1.25	9	0.01	0.25	CTMAB	3	25
10	1.25	18	0.02	0.5	CTMAB	3	27
11	1.25	10	0.012	0.3	CTMAB	3	25
12	6.7	9	0.06	1.5	CTMAB	3 + 4	5 + 3
13	17.5	9	0.16	4	CTMAB	4	18

None of the isomeric 4-methyl compound[5d] could be detected by GLC or NMR. The same result was obtained when acetic acid was omitted from the reaction mixture. The reaction is quite clean, any byproducts being water soluble and thus easily separated from **4**. Compound **4** has previously been prepared by other methods, the most effective being that due to Grundmann.[5a] Its further elaboration[5a] into *o*-tolualdehyde and *o*-methylalkylbenzenes and its potential as a diene in the Diels–Alder reaction make **4** a potentially useful synthon.

In an effort to improve the yield of **4**, we attempted the reaction using 20% aqueous sodium hydroxide (eq 2). In this case, none of **4** was formed. The sole product in the organic phase was identified as **3**[6] (as a 45:55 mixture of **3a** and **3b**), the material originally desired. It is noteworthy that **3**, **4**, and a variety of open-chain compounds have been isolated from the acid-catalyzed dimerization of **1**.[6a,7] Systematic investigation of the effect of changing reaction variables on product structure and yield (Table I) led to the following conclusions.

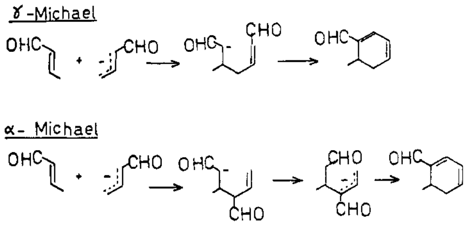


3a **3b** (2)

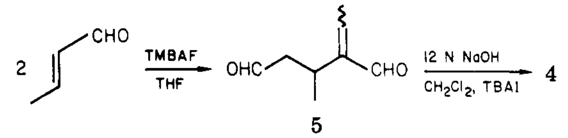
Tetrabutylammonium iodide (TBAI), cetyltrimethylammonium bromide (CMTAB), and triethylbenzylammonium chloride (TEBAC) are all effective catalysts, although the latter is the least active. The nature of the product is affected only by the *concentration* of hydroxide in the bulk aqueous phase and not by either the nature of the catalyst or the molar amount of hydroxide used. The change of product from **4** to **3** occurs over a relatively small range of hydroxide concentration, and the yield of **3** is not materially affected by the molar amount of hydroxide used.

Extensive investigation on the condensation of conjugated aldehydes and ketones under a variety of conditions has been carried out, principally by Weimann.[5b–e] He has pointed out[5c] that four possible mechanisms exist. These are as follows: (1) an initial Michael addition of the γ-carbon atom of **1** with **1** followed by cyclization; (2) a similar condensation using the α-carbon atom of **1** followed by cyclization at the γ-position (Scheme I); (3) a Diels–Alder reaction[8] of **1** with the enolate of **1**; (4) an aldol condensation at the α- or γ-position followed by a Cope-type rearrangement of the trienic product. A fifth possibility lies in the possible Michael addition of the oxygen atom of the enolate of **1** followed by rearrangement.[9] Although the reaction conditions used by Weimann differ considerably from ours (gas phase with alkaline earth oxide catalysts), the same mechanistic possibilities exist. The condensation of methyl vinyl ketone (**9**) and mesityl oxide led to the isolation[5e] of an intermediate which could only be ascribed to the α-Michael sequence, but, in general, they ascribe the majority of their results to the γ-Michael mechanism.[5b]

Scheme I

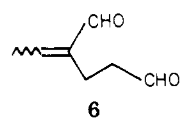


We sought to delineate the operative mechanism in the phase-transfer case by isolating reaction intermediates. Condensation of **1** with trimethylbenzylammonium fluoride (TMBAF) in THF[10] gave, in a slow but clean reaction, 2-ethylidene-3-methylglutaraldehyde (**5**).[7] Exposure of **5** to the usual phase-transfer conditions gave **4** (eq 3). This result appears to rule out all but the α-Michael mechanism. It is important to note that all the products which Weimann obtained can be rationalized on this mechanistic basis.

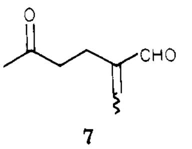


5 (3)

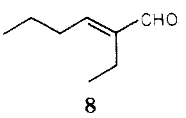
Fluoride-catalyzed reactions of **1** with other acceptor molecules lead to similar results. Thus compounds **6**, **7**, and **8** are obtained in moderate to excellent yields from



6



7



8

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(5) (a) C. Grundmann, *Ber. Dtsch. Chem. Ges.*, **81**, 513 (1948); (b) J. Weimann, J. Riand, and L. Korejzl, *Ann. Chim. (Paris)*, **2**, 399 (1972); (c) J. Weimann and P. Lacroix, *Bull. Soc. Chim. Fr.*, 2257 (1961); (d) J. Weimann and F. Dupayrat, *ibid.*, 209, 757 (1961); (e) J. Weimann and Y. Dubois, *ibid.*, 1813 (1962); (f) J. J. Godfroid, *ibid.*, 2943 (1964).

(6) (a) D. W. Cameron and P. E. Schuetz, *J. Chem. Soc. C*, 1801 (1968); (b) F. E. Bader, *Helv. Chim. Acta*, **36**, 215 (1953).

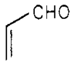
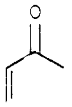
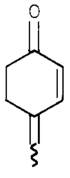
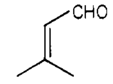
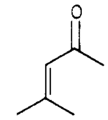
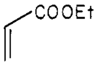
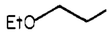
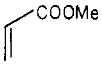
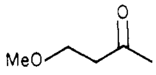
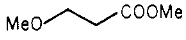
(7) A. Losse, F. Wolf, and J. Muke, *Fresnius' Z. Anal. Chem.*, **232**, 180 (1967).

(8) G. A. Kraus and H. Sugimoto, *Tetrahedron Lett.*, 3929 (1977).

(9) C. R. Engel, V. S. Salvi, and L. Ruest, *Can. J. Chem.*, **48**, 3425 (1970).

(10) I. Kuwajima and E. Nakamura, *J. Am. Chem. Soc.*, **97**, 3257 (1975).

Table II. Mixed Condensations

run	reactants	[OH⁻], N	catalyst	products (yield, %)
1	1 + 	10.5	TBAI	4 (34)
2	1 +  (9)	10.5	CTMAB	 (55) + 4 (34) 10
3	 (11)	10.5	CTMAB	none
4	1 + 11	10.5	CTMAB	4 (35)
5		10.5	TBAI	none
6	9 + 	10.5	CTMAB	 (70%) 12
7	9 + 	10.5	CTMAB	 (28) 13  (10) 14

1 and acrolein or methyl vinyl ketone (9) or from the self-condensation of butanal, respectively. Recent reports[11] on the use of fluoride ion as a catalyst for Michael additions are completely consistent with these results, and it appears that this type of catalyst will find great application in the reactions of base-sensitive aldehydes.

While these experiments delineate the formation of 4, they do not account for the sudden change to 3 when the aqueous hydroxide concentration is lowered below 30%. One possible rationale involves the amount of water of hydration which may be "carried" into the organic phase by the catalyst Q^+OH^-. In Starks' pioneering work on the phase-transfer method, he showed that the amount of water of hydration carried into the organic phase depends on the nature of the anion X^- of the catalyst Q^+X^- and on the concentration of X^- in the aqueous phase.[12] As we have pointed out,[3] the amount of energy associated with removing water molecules from the strongly hydrogen-bonded aqueous phase in concentrated hydroxide solutions suggests that solvation of the catalyst in the organic phase should be minimal and should increase as the concentration of hydroxide decreases. It is well-known that the basicity of anions is dramatically increased by the absence of solvating effects in the reaction medium.[13] Thus it is conceivable that, as the concentration of hydroxide solution decreases, the water concentration in the organic phase changes sufficiently to alter the action of organic-phase hydroxide from that of a base to that of a nucleophile.[16] To our knowledge, this is the first instance where the nature of the product from a phase-transfer reaction is determined by a concentration effect in the aqueous phase. In view of the sudden effect and the possible confusion which exists in referring to, e.g., 50% sodium hydroxide, we recommend that workers in this area use normality or molarity as the standard unit of concentration. The data in Table I reflect this concern.

We are currently investigating crossed condensations. Although the work is still in the preliminary stages, some results are available, and we present them here (Table II) to indicate the remarkable variation in products which can be obtained. Acrolein appears to be too reactive to survive the conditions long enough to undergo addition. Thus only 4 is formed (run 1). The reaction of 1 and 9 leads, in addition to 4, to 10 which has formed by cyclization of 7. None of the product of cyclization in the opposite sense could be detected.

Senecialdehyde (11, runs 3 and 4) and mesityl oxide (run 5) do not react, presumably due to steric hindrance to the conjugate addition. Finally, the methyl group of 9 is not sufficiently acidic to react as the donor (runs 6 and 7).

We are currently exploring other reactions of this type to delineate their scope.

Experimental Section

Infrared spectra were obtained in carbon tetrachloride solution on a Beckman IR-12 instrument, and only the four strongest peaks are given. NMR spectra were run on a Varian EM360 or JEOL C60-HL instrument in deuteriochloroform solution and are reported in parts per million downfield from Me_4Si as internal

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[11] I. Belsky, *J. Chem. Soc., Chem. Commun.*, 237 (1977), and references therein; R. Noyori, K. Yokoyama, J. Sakata, I. Kuwajima, E. Nakamura, and M. Shimizu, *J. Am. Chem. Soc.*, **99**, 1265 (1977).

[12] C. M. Starks and R. M. Owens, *J. Am. Chem. Soc.*, **95**, 3613 (1973).

[13] E. M. Kosower, "Physical Organic Chemistry", Wiley, New York, 1968, p 340 ff.

[14] A. J. Birch, *J. Proc. R. Soc. N.S.W.*, **83**, 245 (1949); *Chem. Abstr.*, **46**, 1118*e* (1952).

[15] G. I. Kiprianov and A. M. Veitsman, *Ukr. Khem. Zh.*, **19**, 662 (1953); *Chem. Abstr.*, **49**, 12320*f* (1955).

[16] The failure to observe carbocyclic products in the reaction of 1 with sulfur nucleophiles[3] using 50% hydroxide reflects the higher nucleophilicity of sulfur relative to oxygen.

standard. Carbon-13 spectra were run in the same solvent on a Bruker CXP-100 spectrometer. Mass spectra were run on a Varian MAT CH5-DF spectrometer in either the electron impact (EI) or field ionization (FI) mode, and only the most intense peaks are reported. Gas chromatographic analyses were performed on a F&M Model 720 instrument using a 10 ft × 0.375 in., 20% SE-30 on Chromosorb W column.

General Reaction Procedure. A mixture of aqueous sodium hydroxide solution, 30 mL of dichloromethane, and 0.1 g of catalyst was cooled to 0 °C under nitrogen. To this mixture was added, dropwise with stirring and cooling, a solution of **1** (0.02 mol) or, in the case of crossed condensations, a mixture of 0.02 mol of each reactant, in 20 mL of dichloromethane. The addition required 20 min. Stirring was continued at 0 °C for 2.5 h, and then the mixture was refluxed for 20 min. The organic phase was separated, diluted with 100 mL of ether, washed with water, and dried over sodium sulfate. Evaporation of the solvents gave the product which was analyzed by GLC. The yields quoted in Tables I and II were obtained by multiplying the weight of crude product by the integrated (disk integrator) area of the peak in the GLC analysis. In each case, the NMR spectrum of the crude product showed no significant extraneous peaks. Variations in the time of cooling or reflux did not significantly affect the product yields.

6-Methylcyclohexa-1,3-dienecarboxaldehyde (4)[5] was obtained as a clear oil: IR 3050, 2800, 1675, 700 cm^{-1}; NMR 9.47 (s, 1 H), 6.69 (t, 1 H, J = 5 Hz), 6.15 (m, 2 H), 2.79 (m, 1 H), 2.30 (m, 2 H), 0.94 (d, 3 H, J = 7 Hz); mass spectrum (FI), m/z 122 (M$^+$), 120, 92, 58, 52, 29.

5,6-Dihydro-2,6-dimethyl-2*H*-pyran-3-carboxaldehyde (3)[6,7] was obtained as a clear oil: IR 2960, 1695, 1255, 865 cm^{-1}. GLC analysis showed the presence of two isomers, **3a** and **3b**, in a ratio of 45:55. These were separated by preparative GLC to give **3a** [NMR 9.57 (s, 1 H), 6.90 (m, 1 H), 4.77–4.33 (m, 1 H), 3.80–3.37 (m, 1 H), 2.43–2.08 (m, 2 H), 1.41 (d, 3 H, J = 7 Hz), 1.30 (d, 3 H, J = 7 Hz); mp (2,4-DNP) 178–179 °C (lit.[6a] mp 180 °C)] and **3b** [NMR 9.60 (s, 1 H), 6.92 (m, 1 H), 4.90–4.50 (m, 1 H), 4.16–3.63 (m, 1 H), 2.53–2.15 (m, 2 H), 1.42 (d, 3 H, J = 7 Hz), 1.23 (d, 3 H, J = 7 Hz); mp (2,4-DNP) 200–201 °C (lit.[6a] 204 °C)]. The mass spectra (EI) of the two isomers were identical: m/z 140 (M$^+$), 125, 111, 83.

4-Ethylidenecyclohex-2-enone[14] **(10)** was obtained with **4** when the condensation of **1** and **9** was effected. These were separated by preparative GLC to give **10** as an oil: IR 1675, 1635, 910, 845 cm^{-1}; NMR 6.95 (d, 1 H, J = 10 Hz), 6.85 (m, 2 H), 2.57 (m, 4 H), 1.82 (d, 3 H, J = 6 Hz); ^{13}C NMR 199.4 (s), 149.4 (d), 133.9 (d), 132.4 (d), 125.3 (d), 36.5 (t), 23.3 (t), 14.3 (q); mass spectrum (FI), m/z 122 (M$^+$), 107, 94, 79, 66, 51. Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.82; H, 8.37. Hydrogenation of **10** over a palladium catalyst at 1 atm led to the uptake of 2 equiv of hydrogen. The product gave a semicarbazone melting point of 173–174 °C (the literature[15] value for the semicarbazone of 4-ethylcyclohexanone is 171 °C).

Ethyl 3-ethoxypropanoate (12): IR 2995, 1730, 1195, 1110 cm^{-1}; NMR 4.10 (q, 2 H, J = 8 Hz), 3.70 (t, 2 H, J = 6 Hz), 3.48 (q, 2 H, J = 8 Hz), 2.55 (t, 2 H, J = 6 Hz), 1.30 (t, 3 H, J = 8 Hz), 1.15 (t, 3 H, J = 8 Hz); mass spectrum (FI), m/z 146 (M$^+$), 100, 58, 29 [identical with an authentic sample (Aldrich)].

4-Methoxy-2-butanone (13): IR 2930, 1705, 1160, 1110 cm^{-1}; NMR 3.62 (t, 2 H, J = 6 Hz), 3.32 (s, 3 H), 2.65 (t, 2 H, J = 6 Hz), 2.15 (s, 3 H); mass spectrum (FI), m/z 102 (M$^+$), 87, 58, 43.

Methyl 3-methoxypropanoate (14): IR 2850, 1720, 1240, 1050 cm^{-1}; NMR 3.70 (s, 3 H), 3.65 (t, 2 H, J = 6 Hz), 3.35 (s, 3 H), 2.55 (t, 2 H, J = 6 Hz); mass spectrum (FI), m/z 118 (M$^+$), 103, 87, 43.

Preparation of Trimethylbenzylammonium Fluoride (TMBAF). The catalyst TMBAF was prepared by neutralizing commercial Triton B solution with 48% hydrofluoric acid to the phenolphthalein end point. The solvents were evaporated, and the residue was dried at 100 °C (0.1 mm) for 24 h. The solid was finely pulverized, dried at 120 °C (0.1 mm) for a further 24 h, and transferred under an inert atmosphere in a drybox.

2-Ethylidine-3-methylglutaraldehyde (5). Crotonaldehyde (0.35 g, 5 mmol), THF (5 mL), and TMBAF (0.3 g) were stirred together under nitrogen at room temperature for 48 h. Hexane (15 mL) was added, the mixture was stirred for 10 min and filtered, and the filtrate was evaporated to leave a yellow oil which GLC analysis showed to be a mixture of **5** and unreacted **1**. The yield of **5**[10] was 60%. A GLC-collected sample of **5** showed the following: n^{25}_D 1.4961; IR 2720, 1725, 1685, 1645 cm^{-1}; NMR 9.71 (s, 1 H), 9.37 (m, 1 H), 6.55 (q, 1 H, J = 6.5 Hz), 2.85 (m, 3 H), 2.10 (d, 3 H, J = 6.5 Hz), 1.20 (d, 3 H, J = 6.5 Hz).

2-Ethylidineglutaraldehyde (6). In a similar manner a mixture of 5 mmol of **1**, 7 mmol of acrolein, 5 mL of dry THF, and 0.3 g of TMBAF at reflux for 10 h led to **6**: 57% yield; n^{25}_D 1.4620; IR 2730, 1725, 1685, 1650 cm^{-1}; NMR 9.79 (s, 1 H), 9.40 (s, 1 H), 6.65 (q, 1 H, J = 6.5 Hz), 2.51 (s, 4 H), 2.05 (d, 3 H, J = 6.5 Hz). Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.51; H, 7.92.

2-Ethylidine-5-oxohexanal (7). With the same amounts of reactants and the same conditions as in the acrolein reaction but with substitution of methyl vinyl ketone for acrolein, a 78% yield of **7** was obtained: n^{25}_D 1.3972; IR 2720, 1715, 1685, 1650 cm^{-1}; NMR 8.38 (s, 1 H), 6.51 (q, 1 H, J = 6.5 Hz), 2.40 (s, 4 H), 2.01 (s, 3 H), 1.90 (d, 3 H, J = 6.5 Hz). Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.41; H, 8.87.

2-Ethyl-2-hexenal (8). A stirred mixture of butanal (7.2 g, 10 mmol), dry THF (30 mL), TMBAF (0.5 g), and 0.3 g of no. 4 molecular sieves was refluxed under a nitrogen atmosphere for 6 h. Workup as usual gave **8** in quantitative yield.

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Reaction of Saturated Organic Compounds with Acetyl and Trifluoroacetyl Nitrate

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The reaction of selected hydrocarbons with trifluoroacetyl nitrate in trifluoroacetic acid results in hydride ion abstraction and formation of alkyl trifluoroacetate. The reaction of reactive alkyl halides and alkyl methyl ethers with protonated acetyl nitrate in acetic acid affords the corresponding alkyl acetates in good yield. The oxidizing reagent in both reactions is ammonium nitrate which is converted in situ to the nitronium acetate by reaction with an anhydride.

Although the numerous addition reactions of electrophilic nitronium compounds to unsaturated substrates containing reactive π electrons have received a considerable amount of attention in the literature, there have only re-

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