genuine sample of 4-nitrobenzophenone.[26] Spectral data for all keto acids may be found in Table III.

TABLE III
SPECTRAL PROPERTIES OF o-KETOBENZOIC ACIDS

Compd	Infrared,[a] cm^{-1} RR'C=O	Infrared,[a] cm^{-1} COOH	Ultraviolet,[b] nm (ε)
2-*p*-Anisoylbenzoic acid	1660	1680	290 (14,400)
2-*p*-Toluylbenzoic acid	1670	1690	264 (19,850)
2-(*p*-Chlorobenzoyl)-benzoic acid	1670	1690	262 (17,200)
5-Methoxy-2-benzoyl-benzoic acid	1675	1690	253 (14,780)
5-Nitro-2-benzoyl-benzoic acid	1680	1692	263 (32,860)

[a] Nujol mulls. [b] In water.

TABLE IV
MELTING POINTS AND ANALYSES OF SUBSTITUTED 3-METHOXY-3-PHENYLPHTHALIDES

Compd	Mp,[a] °C	Analysis,[b] % Calcd	Found
2	77–80	C 70.12	70.40
	lit.[c] 80–81.5	H 5.22	5.11
3	66–67	C 75.57	75.44
	lit.[d] 71–72	H 5.55	5.46
4	100–101	C 65.58	65.82
	lit.[e] 101–102	H 4.04	4.05
5	66–68	C 71.11	71.24
		H 5.19	5.31
6	84–86	C 63.16	62.86
		H 3.86	4.01

[a] Uncorrected. [b] Microanalysis by Alfred Bernhardt, Germany. [c] V. Auwers and K. Heinz, *Ber. Bunsenges. Phys. Chem.*, **52**, 586 (1919). [d] H. Meyer, *Monatsh. Chem.*, **28**, 1236 (1907). [e] E. Egerer and H. Meyer, *ibid.*, **34**, 84 (1913).

(26) We thank Mr. Steven Szucs, a National Science Foundation Undergraduate Research Fellow, for carrying out this delicate and crucial experiment.

All of the substituted 3-methoxy-3-phenylphthalides were synthesized by allowing the appropriate keto acid to react with thionyl chloride followed by treatment with dry methanol containing 1 equiv of urea.[27] Pertinent data on each compound are given in Table IV. Spectral data are given in Table V.

TABLE V
SPECTRAL PROPERTIES OF SUBSTITUTED 3-METHOXY-3-PHENYLPHTHALIDES

Compd	Infrared,[a] cm^{-1} (C=O)	Ultraviolet,[b] nm (ε)	Kinetics wavelength, nm
2	1765	231 (18,100)	295
3	1773	221 (19,600)	260
4	1775	224 (23,500)	260
5	1768	218 (31,350)	260
		304 (2670)	
6	1790	260 (14,340)	260

[a] Nujol mulls. [b] In water.

Rate Determinations.—The hydrolyses of 3-methoxy-3-phenylphthalides were followed in the ultraviolet at wavelengths listed in Table V. It was determined that all the compounds followed Beer's law in the region of concentration used (10^{-4}–10^{-5} *M*). A full spectrum of the hydrolysis run after 10 half-lives was superimposable on a spectrum of the product at the same concentration. A larger sample of each 3-methoxyphthalide was allowed to hydrolyze in aqueous acid containing a suitable cosolvent. In each case the corresponding keto acid was recovered in yields of 95% or greater. The details of the kinetics method have been described previously.[5,14]

Registry No.—**1**, 7335-63-9; **2**, 40893-30-9; **3**, 40893-31-0; **4**, 33433-81-7; **5**, 40893-33-2; **6**, 40893-34-3; 2-*p*-anisoylbenzoic acid, 1151-15-1; 2-*p*-toluoylbenzoic acid, 85-55-2; 2-(*p*-chlorobenzoyl)benzoic acid, 85-56-3; 5-methoxy-2-benzoylbenzoic acid, 2159-48-0; 5-nitro-2-benzoylbenzoic acid, 2159-46-8; 2-methyl-4-methoxybenzophenone, 40893-37-6; 4-nitrophthalic anhydride, 5466-84-2.

(27) V. Auwers and K. Heinz, *Ber. Bunsenges. Phys. Chem.*, **52**, 586 (1919)

A Novel Synthesis of Disubstituted Maleic Anhydrides by the Pyrolysis of 1-Ethoxy-1-alkenyl Esters of α-Keto Acids[1]

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The preparation of a number of 1-ethoxy-1-alkenyl esters of pyruvic acid and benzoylformic acid was accomplished by addition to the corresponding ethoxyacetylenes without the use of a mercury catalyst. Pyrolysis of the esters thus formed produced the corresponding disubstituted maleic anhydride in moderate yields. This method is a general one and has the further advantage of being a one-pot reaction. The synthesis of *n*-butylphenylmaleic anhydride (**20**) and *n*-butylmethylmaleic anhydride (**25**), in yields of 45 and 44%, respectively, is reported for the first time. The major by-products of the reactions are monosubstituted β-keto esters and the ethyl esters of the starting α-keto acids. All of the isolated products of the reactions may be explained by variations of an outlined general reaction scheme. The reactions described represent a new, and possibly the most efficient, method for the synthesis of unsymmetrically disubstituted maleic anhydrides.

Recent studies here indicated that the rearrangement of 1-ethoxy-1-alkenyl esters of carboxylic acids might be a useful route to the synthesis of monosubstituted β-keto esters. The pyrolysis of 1-ethoxyvinyl pyruvate (**1**) to ethyl acetoacetate (**2**) and carbon monoxide and of di-1-ethoxyvinyl oxalate to diethyl acetonedicarboxylate demonstrated a novel synthesis of esters of β-keto acids not substituted in the α position.[3] The thermal decomposition of a variety of 1-ethoxyvinyl esters of carboxylic acids also was shown to give initially β-keto esters which, however, underwent further reaction before isolation.[4] Subsequent studies demonstrated that the heating of the 1-ethoxyvinyl ester of

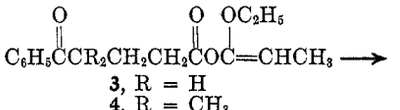
(1) This research was supported in part by Grant 12445 of the National Science Foundation.

(2) Ohio State University Postdoctoral Fellow 1971.

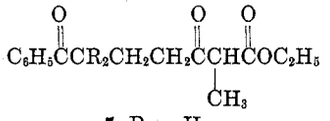
(3) G. R. Banks, D. Cohen, and H. D. Springall, *Rec. Trav. Chim. Pays-Bas*, **83**, 513 (1964). A repetition of this experimental procedure gave only a moderate yield of ethyl acetoacetate (see Experimental Section).

(4) B. Zwanenburg, *ibid.*, **82**, 593 (1963).

one β- and γ-keto acid did not yield any β-keto ester.[5] More recently, however, pyrolysis of 1-ethoxy-1-propenyl 4-benzoylbutanoate (**3**) and 1-ethoxy-1-propenyl 4-benzoyl-4,4-dimethylbutanoate (**4**) was shown to yield ethyl 3,7-diketo-2-methyl-7-phenyl heptanoate (**5**) and ethyl 3,7-diketo-7-phenyl-2,6,6-trimethylheptanoate (**6**),[6] respectively.

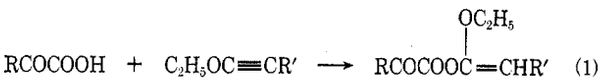


3, R = H
4, R = CH_3



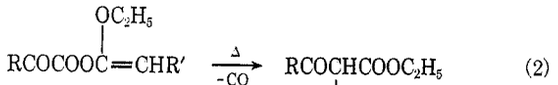
5, R = H
6, R = CH_3

Since new methods for synthesis of monsubstituted β-keto esters are of interest, we undertook a study of the formation and pyrolysis of 1-ethoxy-1-alkenyl esters of pyruvic and benzoylformic acids. The desired 1-ethoxy-1-alkenyl esters (**7**–**11**) were prepared in almost quantitative yield by the addition of the α-keto acids to 1-ethoxy-1-propyne, 1-ethoxy-1-butyne, and 1-ethoxy-1-hexyne (eq 1). Since these 1-ethoxy-1-alkenyl esters were sensitive to heat and hydrolysis, they were isolated rapidly under mild conditions and immediately pyrolyzed. Initial attempts to synthesize monosubstituted β-keto esters (**12**) by this method (eq. 2) gave poor yields (10–35%). However, an unexpected new reaction to produce disubstituted maleic anhydrides (**13**) was discovered (eq 3).



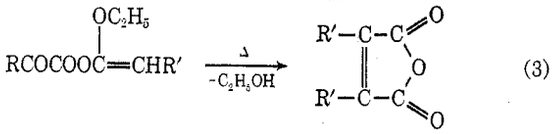
(1)

7, R = C_6H_5; R′ = CH_3
8, R = C_6H_5; R′ = C_2H_5
9, R = C_6H_5; R′ = n-C_4H_9
10, R = R′ = CH_3
11, R = CH_3; R′ = n-C_4H_9



(2)

12



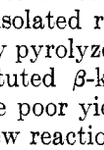
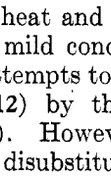
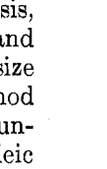
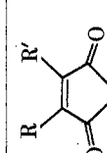
(3)

13

Since an improved method for preparing the needed 1-ethoxy-1-alkynes has been reported recently,[7] a general synthesis for disubstituted maleic anhydrides is at hand (Table I). Because other syntheses of this type of compound leave much to be desired,[8] the method described herein appears to be the method of choice to date.

(5) D. Cohen and G. E. Pattenden, *J. Chem. Soc. C*, 2314 (1967).
(6) M. S. Newman and Z. ud Din, *J. Org. Chem.*, **36**, 2740 (1971).
(7) M. S. Newman, J. R. Geib, and W. M. Stalick, *Org. Prep. Proced. Int.*, **4**, 89 (1972).
(8) J. Schreiber, *Ann. Chim. (Paris)*, **2**, 84 (1947); J. A. Moore and F. Marascia, *J. Amer. Chem. Soc.*, **81**, 6409 (1959).

TABLE I
PRODUCTS FORMED BY THE PYROLYSIS OF 1-ETHOXY-1-ALKENYL ESTERS

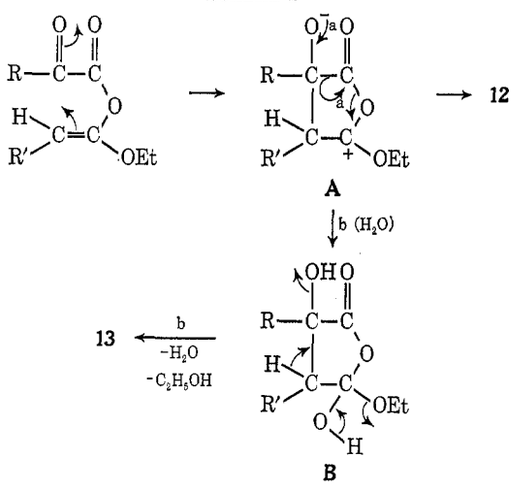
Reactants				Products									
													
R	Registry no.	R′	Catalyst	No.	% yield[a]	No.	% yield[a]	No.	% yield[a]	No.	% yield[a]	No.	% yield[a]
C_6H_5	611-73-4	CH_3		14	41	15	4	16	14	17	1		
C_6H_5		CH_3	$Hg(OAc)_2$	14	40	15	9	16	14	17	*b*		
C_6H_5		C_2H_5		18	44	19	10	16	9				
C_6H_5		C_2H_5	$Hg(OAc)_2$	18	41	19	20	16	8				
C_6H_5		n-C_4H_9		20	45	21	6	16	9	22	3		
CH_3	127-17-3	CH_3		23	35	24	10	25	*c*				
CH_3		CH_3	$Hg(OAc)_2$	23	30	24	35	25	*c*				
CH_3		n-C_4H_9		25	44	26	8	25	*c*				
CH_3		H	$Hg(OAc)_2$		*b*	27	48						

[a] Based on α-keto adid. [b] A small amount was separated by vpc for identification. [c] Not isolated in pure form.

When this study was initiated, the 1-ethoxy-1-alkenyl esters (eq 1) were prepared using a mercuric acetate catalyst as had been previously described.[6,9] However, mercury contamination of the products invariably resulted despite all attempts made to remove the mercury before pyrolysis. We found that 1-ethoxy-1-alkenyl esters could be prepared in essentially quantitative yields without the mercury catalyst. Pyrolysis of mercury-free esters yielded products more easily purified for two reasons: the absence of mercury and the smaller amounts of β-keto esters present.

The formation of the products **12** and **13** by heating of **7–11** may be accounted for by the formation of **A** which decomposes by two paths: a, loss of carbon monoxide to yield β-keto ester (eq 2); and b, reaction with catalytic amounts of water to yield an intermediate **B** which loses ethanol to yield the disubstituted maleic anhydride (**13**).[10] The paths are shown in Scheme I.

SCHEME I



Although a mole of ethanol must be formed for every mole of **13** produced, none was isolated or detected by glpc. Examination of Table I shows two side products that were produced during the pyrolysis. The formation of these ethyl esters (**16** and **25**) of the original starting α-keto acids can be explained if one assumes that the ethanol produced from maleic anhydride formation transesterified the starting 1-ethoxy-1-alkenyl ester to produce ethyl benzoylacetate or ethyl pyruvate, and ethyl propionate, ethyl butyrate, or ethyl hexanoate, all of which were found as by-products of the reaction. Small amounts of ethyl esters were detected but insufficient to account for all of the ethanol expected. The reaction of ethanol with the ethoxyvinyl esters undoubtedly is the cause of the low yields of β-keto esters and disubstituted maleic anhydrides formed. The yields of these products might be improved if, for example, *tert*-butoxyacetylenes were used in place of ethoxyalkynes.

In summary, a number of 1-ethoxy-1-alkynes have been shown to react with α-keto acids without a mercury catalyst to give disubstituted maleic anhydrides in moderate yields. The reaction allows one to produce unsymmetrically disubstituted maleic anhydrides as easily as symmetrically substituted ones. Finally the reaction seems to be general.

(9) H. H. Wasserman and P. S. Wharton, *J. Amer. Chem. Soc.*, **82**, 661 (1960).

(10) It is realized that the timing of the steps is unknown. Hence, no attempt is made to do other than indicate the steps that may occur.

Experimental Section[11]

Reagents.—1-Ethoxy-1-propyne, 1-ethoxy-1-butyne, and 1-ethoxy-1-hexyne were prepared as described previously[7] and used immediately after distillation. Benzoylformic acid was used as received,[12] and pyruvic acid (Aldrich, Gold Label) was distilled immediately before use. Dried CH_2Cl_2 was prepared by storing over CaH_2 and distilling before use.

1-Ethoxy-1-alkenyl Esters (7–11).—These esters were all prepared by the following general method. A 500-ml round-bottomed flask equipped with a large magnetic stirring bar and a pressure-equalizing addition funnel topped with a $CaCl_2$ drying tube was half-immersed in a Dry Ice–acetone bath. Stirring was started after the addition of 50 ml of dry CH_2Cl_2. A solution of 0.375 mol of 1-ethoxy-1-alkyne in 50 ml of dry CH_2Cl_2 was added followed in 5 min by the slow addition (3 hr) of a solution of 0.15 mol of α-keto acid in 150 ml of dry CH_2Cl_2. The reaction was allowed to come to room temperature as stirring was continued overnight. The CH_2Cl_2 chloride solution was rapidly washed with an iced dilute K_2CO_3 solution followed by washing with a saturated NaCl solution. Any emulsions that were formed were dispersed by suction filtration through fine filter paper. The organic layer was percolated through anhydrous $MgSO_4$. At this point the reaction mixture was distilled at reduced pressure, keeping the bath temperature below 70°, to remove the CH_2Cl_2 and 1-ethoxy-1-alkyne which were collected together in a Dry Ice–acetone trap for later separation and recovery of the excess 1-ethoxy-1-alkyne. The 1-ethoxy-1-alkenyl esters were light yellow viscous oils that did not crystallize on standing. Since these oils were sensitive to heat and hydrolysis, they were not characterized.

General Pyrolysis Procedure of 7–11.—All of the 1-ethoxy-1-alkenyl ester obtained from 0.15 mol of α-keto acid as described in the preceding section was placed in a 50–100 ml distillation flask connected through a ground glass joint to a receiver cooled in a Dry Ice–acetone bath and connected to a vacuum pump.[13] Heating was accomplished by immersing the reaction vessel in a silicone oil bath heated to about 100°. A moderate vacuum was applied and the remnants of the 1-ethoxy-1-alkyne were removed in the first fraction. The pressure was then decreased to 0.05–0.5 mm and the bath temperature raised to 130–150° as the pyrolysis was continued for about 2 hr. The receiver was changed sometimes during this period if the head temperature indicated a change in products. If the pyrolysis was continued, small amounts of additional material continued to distil for about 3 hr more.

Pyrolysis of 1-Ethoxy-1-propenyl Benzoylformate (7).—Heating 0.15 mol of this ester as described above yielded the following compounds.

Methylphenylmaleic Anhydride (14).—This was distilled from the pyrolysis mixture at 115–128° (0.3 mm) but was contaminated with ethyl benzoylformate (**16**) and traces of the compound tentatively identified as diethyl methylphenylmaleate (**17**). The distillate crystallized upon collection and **14** was obtained as white needles by recrystallization from pentane. Distillation of the mother liquor yielded more **14**. Total yield of methylphenylmaleic anhydride was 11.0 g (41%): mp 94–4.5° (lit.[8] mp 94.5°);

(11) All melting and boiling points are uncorrected. Analyses were by M-H-W Laboratories, Garden City, Mich. Infrared spectra (samples were neat unless otherwise specified) were recorded on a Perkin-Elmer Infracord and nmr spectra on a Varian A-60 spectrometer using CCl_4 as solvent unless otherwise specified, TMS standard. Gas–liquid phase chromatographic (glpc) analyses and separations were performed on a F & M Model 500 instrument equipped with a thermal conductivity detector and using helium as a carrier gas. The separation and purification of products for identification was accomplished with a 9 ft × 3/8 in. column packed with 15% silicone gum rubber SE-30 on 60–80 mesh Chromosorb W. Identity of compounds with known compounds was established by comparison of spectra and mixture melting point determinations when applicable. All compounds had ir and nmr spectra consistent with the assigned structures. We thank Mr. Richard Weisenberger for the mass spectral determinations, which were carried out on an AEI Model AS9 instrument at an ionization potention of 70 eV.

(12) We thank the S. B. Penick Chemical Co. for a generous supply of benzoylformic acid.

(13) Similar to the apparatus described in M. S. Newman, "An Advanced Organic Laboratory Course," Macmillan, New York, N. Y., 1972, p 23.

nmr (CD_3COCD_3) δ 2.28 (s, 3, CH_3), 7.64 (m, 5, C_6H_5); ir (KBr) 5.70, 7.93, and 10.87 μ; mass spectrum *m/e* 188 (M^+),[11] 188 (M^+).

Anal. Calcd for $C_{11}H_8O_3$: C, 70.2; H, 5.3. Found: C, 70.30; H, 5.3.

Ethyl α-methylbenzoylacetate (15), contaminated with a little ethyl benzoylformate (16) as determined by glpc, was obtained in about 4% yield in the forerun of the fraction which yielded mainly **14**. A sample of **15** was identified by comparison with an authentic sample: bp 94–96° (0.17 mm) [lit.[14] bp 90–94° (0.2 mm)]; nmr δ 1.15 (t, 3, CH_2CH_3), 1.42 (d, 3, $CHCH_3$), 4.12 (q, 2, OCH_2CH_3), 7.50 and 7.98 (m, 5, C_6H_5); ir 5.76, 5.92, 6.25, 6.91 μ; mass spectrum *m/e* 206 (M^+).[11]

Ethyl benzoylformate (16) was found in both of the fractions described above. Its identity was verified by comparison of a sample purified by glpc with an authentic sample made by the acid-catalyzed esterification of benzoylformic acid with ethanol.

Diethyl methylphenylmaleate (17) was found to be present as a high-boiling impurity observed as a shoulder when **14** was analyzed by glpc. A small amount of the compound tentatively identified as **17** was separated and had the following characteristics: ir 3.55, 5.75, 5.90, 6.25, 6.32, 6.85, 6.92, and 7.42 μ; mass spectrum *m/e* 262 (M^+).[11]

Pyrolysis of 1-Ethoxy-1-butenyl Benzoylformate (8).—Heating 0.15 mol of this ester as described in the general pyrolysis procedure produced a low-boiling fraction, bp 40–45° (50 mm), identified as the starting material, 1-ethoxy-1-butyne. The following compounds were isolated from succeeding fractions.

Ethylphenylmaleic anhydride (18) was one of the products isolated from the fraction boiling in the range 103–118° (25 mm). A higher boiling fraction, bp 130–135° (25 mm), yielded a dark yellow liquid that was essentially pure **18**. A fractionation of the lower boiling material and a redistillation of the higher boiling fraction yielded 13.4 g (44%) of a clear light yellow liquid identified as **18**. The liquid crystallized upon standing and recrystallization from ethanol yielded colorless needles: mp 43–43.5° (lit.[8] mp 43°); nmr δ 1.24 (t, 3, CH_3), 2.56 (q, 2, CH_2), and 7.52 (s, 5, C_6H_5); ir 5.67, 8.01, 10.80 (sh), and 10.92 μ; mass spectrum *m/e* 202 (M^+).[11]

Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.3; H, 5.0. Found: C, 71.1; H, 4.9.

Ethyl α-ethylbenzoylacetate (19) was one of the coproducts collected in the fraction, bp 103–118° (25 mm). Redistillation yielded a light yellow liquid analyzed by glpc to contain 2.3 g (9%) of ethyl benzoylformate (16) and 3.2 g (10%) of **19**: $n^{25}D$ 1.5057 [lit.[15] bp 134–135° (3 mm)]; nmr δ 0.98 (t, 3, $CHCH_2CH_3$), 1.15 (t, 3, OCH_2CH_3), 2.00 (p, 2, $CHCH_2CH_3$), 4.13 (m, 3, OCH_2CH_3 and CH), 7.53 and 8.03 (m, 5, C_6H_5); ir 5.75, 5.91, and 6.91 μ: mass spectrum *m/e* 220 (m^+).[11]

Pyrolysis of 1-Ethoxy-1-hexenyl Benzoylformate (9).—A low-boiling fraction [bp 43–45° (8 mm)] was identified as 1-ethoxy-1-hexyne. Decreasing the pressure yielded a second fraction, bp 90–112° (0.5 mm), and left 7 g of dark tan residue.

***n*-Butylphenylmaleic anhydride (20)** was found to be present in the second fraction above, which upon redistillation yielded the following compounds: ethyl hexanoate (1.5 g), as identified by nmr and by comparison to authentic material, bp 38° (2.5 mm); and ethyl benzoylformate (16), 2.4 g (9%), bp 85–92° (1 mm). The fraction, bp 105–110° (0.5 mm), was found to be a mixture of **20** and **21** by glpc, while the highest boiling fraction, bp 110–112° (0.5 mm), was mostly **20** contaminated with a small amount of diethyl *n*-butylphenylmaleate (**22**). A total of 15.5 g (45%) of *n*-butylphenylmaleic anhydride (**20**) was isolated: $n^{25}D$ 1.5531; nmr δ 0.93 (t, 3, CH_3), 1.53 (m, 4, $CH_2CH_2CH_2CH_3$), 2.64 (t, 2, $CH_2CH_2CH_2CH_3$), 7.50 (s, 5, C_6H_5); ir 5.47, 5.70, 7.90, and 10.90 μ; mass spectrum *m/e* 230 (M^+).[11]

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.0; H, 6.1. Found: C, 73.3; H, 5.9.

Ethyl α-butylbenzoylacetate (21) was isolated from the fraction described above [bp 105–110° (0.5 mm)], as a clear, colorless liquid, 2.4 g (6%). Identification was made by comparison to an authentic sample synthesized as previously described:[16] bp 95–100° (0.6 mm); $n^{25}D$ 1.5018 (lit.[16] $n^{20}D$ 1.5044); nmr δ 0.91 (t, 3, $CH_2CH_2CH_2CH_3$), 1.13 (t, 3, OCH_2CH_3), 1.1–1.55 (m, 4, $CH_2CH_2CH_3$), 1.88 (p, 2, $CH_2CH_2CH_2CH_3$), 4.08 (q, 3, OCH_2CH_3 and CH), 7.50, and 7.95 (m, 5, C_6H_5); ir 5.72, 5.89, 6.19, and 6.82 μ; mass spectrum *m/e* 248 (M^+).[11]

Diethyl *n*-butylphenylmaleate (22) was found as a contaminant (3%) when **20** was analyzed by glpc. Separation by preparative glpc using an SE-30 column gave a small amount of material tentatively identified as **22**; ir 3.38, 5.67, 5.81, 6.85, 6.95, and 7.36 μ; mass spectrum *m/e* 304 (M^+).[11]

Pyrolysis of 1-Ethoxy-1-propenyl Pyruvate (10).—A low-boiling fraction, bp 45–50° (150 mm), was identified as 1-ethoxy-1-propyne. Reducing the pressure gave another fraction, bp 40–45° (2 mm), found to contain ethyl propionate and ethyl α-methylacetoacetate (**24**). The third fraction, bp 60–100° (2 mm), was essentially pure ethyl propionate (3.5 g). No ethyl pyruvate (**25**) was isolated from the reaction mixture.

Dimethylmaleic anhydride (23), 6.7 g (35%), was distilled in essentially pure form in the final fraction [bp 100–106° (2 mm)]. The light yellow crystals were recrystallized from heptane to yield colorless plates, mp 90–92° (no depression in melting point when mixed with authentic sample from Aldrich).

Ethyl α-methylacetoacetate (24), 2.1 g (10%), was isolated mainly from the above fraction, bp 40–45° (2 mm), as a clear, colorless liquid identified by comparison to an authentic sample synthesized by a procedure similar to that of Rathke.[17]

Pyrolysis of 1-Ethoxy-1-hexenyl Pyruvate (11).—A low-boiling fraction, bp 53–56° (15 mm), was identified as 1-ethoxy-1-hexyne. A reduction in the pressure while increasing the bath temperature to 150–190° yielded a second fraction, calculated to contain 8.3 g of ethyl hexanoate and 2.2 g of **26** by glpc. Again no ethyl pyruvate was identified in the collected products.

***n*-Butylmethylmaleic anhydride (25)**, 11.2 g (44%), was collected as a pale yellow liquid, bp 110–120° (1 mm). A dark brown amorphous residue (5.7 g) that solidified upon cooling remained. Characterization of *n*-butylmethylmaleic anhyride: $n^{25}D$ 1.4677; nmr δ 0.94 (t, 3, $CH_2CH_2CH_2CH_3$), 1.5 (m, 4, $CH_2CH_2CH_2CH_3$), 2.09 (s, 3, CH_3), 2.48 (t, 2, $CH_2CH_2CH_2CH_3$); ir 5.37 (sh), 5.49 (sh), 5.62 (sh), 5.67, 7.87, 10.85, 11.24, and 13.59 μ; mass spectrum *m/e* 168 (M^+).[11]

Anal. Calcd for $C_9H_{12}O_3$: C, 64.3; H, 7.2. Found: C, 64.0; H, 7.3.

Ethyl α-butylacetoacetate (26),[16] bp 115° (16 mm), $n^{25}D$ 1.4261 (lit.[15] $n^{20}D$ 1.4288), was obtained from the fraction, bp 60–79° (1 mm), and was purified by preparative glpc: nmr δ 0.93 (t, 3, $CH_2CH_2CH_2CH_3$), 1.1–1.5 (m, 7, OCH_2CH_3 and $CH_2CH_2CH_2CH_3$), 1.73 (m, 2, $CH_2CH_2CH_2CH_3$), 3.25 (t, 1, CH), 4.16 (q, 2, OCH_2CH_3); ir 3.40, 5.73 (sh), and 5.82 μ; mass spectrum *m/e* 186 (M^+).

1-Ethoxyvinyl Pyruvate (1).—This compound was prepared essentially as described.[3,9] The dark red-brown oil obtained weighed 6.7 g (85% yield). The oil was heated for 1 hr at 90° and then distilled to give 3.8 g (48%) of a clear, colorless material, bp 65–70° (15 mm), identical with authentic ethyl acetoacetate (**27**) as shown by ir and nmr.

Registry No.—**7**, 40940-27-0; **8**, 40940-28-1; **9**, 40940-29-2; **10**, 40940-30-5; **11**, 40940-31-6; **14**, 41016-29-9; **15**, 10488-87-6; **16**, 1603-79-8; **17**, 40940-54-3; **18**, 40940-34-9; **19**, 24346-56-3; **20**, 40940-36-1; **21**, 6134-71-0; **22**, 40940-55-4; **23**, 766-39-2; **25**, 7541-33-5; **26**, 1540-29-0.

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