Isolation of 1-Bromo-1,2-dichlorotrifluoropropene (8), CF₃-CCl=CClBr.—Compound 1a (13.9 g, 0.0644 mol) was added to aluminum bromide (8.60 g, 0.322 mol) in a 50-ml flask surrounded by an ice–water bath. The mixture was then stirred and heated at 50 ± 5° under an atmosphere of nitrogen for 16 hr. The mixture was hyrolyzed, and the organic material washed with water and dried. The crude product, which contained ca. 7% of the first-eluted unknown compound, was subjected to simple distillation to remove high-boiling compounds.

The distillate was separated by preparative glpc (15% SE-30 0.5 in. × 10 ft) at 70° with a flow rate of 300 ml min⁻¹. The sample of the first-eluted unknown compound gave a single peak on column A: ir 1585 cm⁻¹ (C=C), 1269, 1200, and 1156 cm⁻¹ (CF₃), 999, 883, 798, 791, 688, 667 cm⁻¹ (C–C, C–X).

Anal. Calcd for C₃BrCl₂F₃: C, 14.77; H, 0.00. Found: C, 15.40; H, 0.68.

A small sample of the second-eluted unknown compound was collected, and gave a single peak on column A: ir 1565 (C=C), 1258, 1193, and 1153 (CF₃), 986, 827, 776 cm⁻¹ (C–C, C–X).

Preparation of 17.—Compound 7 (199.5 g, 1.0 mol) and 200 ml of diethylene glycol dimethyl ether (diglyme) were placed in a 2-l. three-necked flask fitted with a thermometer, a pressure-equalized dropping funnel, and a water-cooled condenser, which was in turn connected to a mercury–acetone bubbler. The solution was cooled to 0° in a 1-propanol–Dry Ice bath, and a solution of sodium borohydride (19.3 g, 0.50 mol 98% purity) and water (27.0 g, 1.5 mol) in 600 ml of diglyme was added over a period of 1 hr. Temperature during the addition was maintained at 10–15°.

The mixture was allowed to stir at room temperature for 36 hr after the addition was complete; it was then poured into 2 l. water with vigorous stirring. The organic layer was separated, washed with water, and dried. Fractionation through a 45-cm spinning-band annular still (Column A) gave (a) 14.4 g, bp 55.0–56.0°, cis- and trans-17 containing a trace of 2-chloro-3,3,3-trifluoropropene; (b) 4.8 g, bp 56.0–60.5°, cis and trans 17; and (c) 5.6 g, bp 60.5–61.5°, trans isomer of 17, 99.5+% by glpc.

This procedure was repeated as above, except that the water was contained in the olefin solution. Analysis of the crude mixture by glpc on column B at 25° showed 2-chloro-3,3,3-trifluoropropene 4.3%, low-boiling 17 7.2%, high-boiling 17 27.4%, and

starting olefin 60.8%. Fractionation through column A gave samples of each geometric isomer of 99.9% purity of cis-1,2-dichloro-3,3,3-trifluoropropene: bp 55.5° (750 mm), n²⁰D 1.3672; nmr δ 7.13, J_{HF} = 1.2 Hz [lit.³⁷ bp 51–52° (702 mm), n²⁰D 1.3638; nmr δ 7.08, J_{HF} = 1.1 Hz]; ir 1629 cm⁻¹ (C=C), 1307, 1205–1160 cm⁻¹ (CF₃); high-boiling 17, bp 60.0° (742 mm), n²⁰D 1.3768; nmr δ 6.65, J_{HF} ≤ 0.2 Hz [lit.³⁷ bp 58° (702 mm), n²⁵D 1.3795; nmr δ 6.65, J_{HF} = 0.2 Hz]. Recovery of starting olefin was 90.8 g.

Bromination of 17.—Bromine (10.1 g, 0.063 mol) and 1,2-dichloro-3,3,3-trifluoropropene (10.4 g, 0.063 mol 91% high-boiling isomer, 9% low-boiling isomer) were placed in a flask, which was equipped with a water-cooled condenser and a magnetic stirring bar. The mixture was irradiated by an ultraviolet lamp from a distance of 15 cm for 72 hr. Analysis by glpc on column A indicated the absence of starting olefin, although the color of bromine persisted in the reaction mixture. The crude 1,2-dibromo-1,2-dichloro-3,3,3-trifluoropropane (45) was washed with water and used without further purification.

Dehydrobromination of 45.—Dibromide 45 was treated with a solution of sodium hydroxide (2.90 g, 0.070 mol 97% purity) in 15 ml of water with vigorous stirring for 3 hr. The organic halide was separated, washed with water, and dried (MgSO₄). Fractionation through a 12 × 150 mm Vigreux gave 4.8 g 8: bp 108.0° (740 mm), n²⁰D 1.4402; ir 1582 cm⁻¹ (C=C), 1267, 1196, 1156 cm⁻¹ (CF₃), 998, 876, 796, 789, 689, 665 cm⁻¹ (C–C, C–X); 99.9+% pure by glpc. A small fraction, 0.25 g, bp 108.0°, containing 1.5% low-boiling impurity was also obtained; the residue weighed 4.0 g.

Anal. Calcd for C₃BrCl₂F₃: C, 14.77; H, 0.00; Br, 32.77; Cl, 29.07; F, 23.37. Found: C, 15.16; H, 0.00; Br, 32.90; Cl, 27.63; F, 23.70.

Triarylphosphine-Catalyzed Dimerization of Acrylonitrile and Related Reactions

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In the triarylphosphine-catalyzed dimerization of acrylonitrile to 2-methyleneglutaronitrile (I) and 1,4-dicyano-1-butene (II), the importance of a proper balance between nucleophilicity of the phosphine catalyst and protolytic strength of the solvent is delineated. Best results (85% yield of a mixture of 68% I and 32% II at 36% conversion of acrylonitrile) are obtained with a tri(p-tolyl)phosphine catalyst in triethylsilanol solution at 160°. Reaction of methyl vinyl ketone with a triphenylphosphine catalyst in triethylsilanol solvent gives only one catalytic dimer, 3-methylene-2,6-heptanedione, in 78% yield. Treatment of equimolar amounts of acrylonitrile and ethyl acrylate with a tributylphosphine catalyst at 100° affords only one cross-condensation product, 2-carbethoxy-4-cyano-1-butene, despite the fact that two cross-condensates are possible.

Recently, Baizer, and Anderson[1] have described a novel triphenylphosphine-catalyzed dimerization of acrylonitrile to a mixture of 60% 2-methyleneglutaronitrile (I) and 40% 1,4-dicyano-1-butene (II). The reaction was carried out at 45° in the presence of a small amount of t-butyl alcohol and only a 9% conversion of acrylonitrile to dimers was observed after 198 hr. We discovered[2] this reaction independently and now describe our results which show the triarylphosphine-catalyzed dimerization to be of significantly greater value[3] for the synthesis of II than implied by Baizer and Anderson.

Both the conversion of acrylonitrile and the yields of I and II vary significantly with the reaction temperature, the nature of the triarylphosphine, and the solvent. The results in Table I show that in t-butyl alcohol solvent at 175°[4] with triphenylphosphine as a catalyst, only a 45% yield[5] of dimers (I + II) at 15% conversion of acrylonitrile is obtained. The principal byproducts are an insoluble crystalline hexamer[6] (15–20%) and soluble polymer (25–30%). When tri(p-

(1) M. M. Baizer and J. D. Anderson, *J. Org. Chem.* **30**, 1357 (1965).
(2) J. D. McClure, U. S. Patent 3,225,083 (1965).

(3) The synthetic value of the tributylphosphine-catalyzed dimerization which produces I, exclusively, was emphasized by Baizer and Anderson.[1]
(4) At temperatures greater than 175°, the thermal dimerization to 1,2-dicyanocyclobutane becomes significant.
(5) Yields are based on converted acrylonitrile.
(6) N. Takashina and C. C. Price, *J. Amer. Chem. Soc.*, **84**, 489 (1962).

Catalyst (1 g)	Solvent	Temp, °C	Time, hr	% convn of acrylo-nitrile	% yield of dimer (I + II)	% II in dimer
$(C_6H_5)_3P$	Me_3COH (40 g)	175	8	15	45	39
$(CH_3C_6H_4)_3P$	Me_3COH (80 g)	160	8	30	65	30
$(C_6H_5)_3P$	Et_3SiOH (40 g)	175	8	16	75	40
$(CH_3C_6H_4)_3P$	Et_3SiOH (80 g)	160	11	36	85	32
$(CH_3C_6H_4)_3P$	Et_3SiOH (80 g)	160	4	15	90	38

tolyl)phosphine [$(CH_3C_6H_4)_3P$] is used as catalyst in place of triphenylphosphine at 160°, the acrylonitrile conversion is doubled to 30% and the yield of dimers is increased to 65%. However, the percentage of II in the dimer decreases from 39 to 30. When triethylsilanol[7] (Et_3SiOH) is used as solvent in place of *t*-butyl alcohol with triphenylphosphine as catalyst at 175°, the yield of dimers is increased from 45 to 75%. Finally, with triethylsilanol as the solvent and tri(*p*-tolyl)-phosphine as the catalyst at 160°, an 85% yield of dimers is realized at 36% conversion of acrylonitrile. The dimer composition is 32% II and 68% I. Thus, by

$$ CH_2=CHCN \xrightarrow[Et_3SiOH]{(CH_3C_6H_4)_3P} $$

$$ \underset{\substack{\| \\ CH_2 \\ I}}{NCCCH_2CH_2CN} + \underset{II}{NCCH=CHCH_2CH_2CN} $$

proper choice of triarylphosphine catalyst and solvent, a fourfold increase in acrylonitrile conversion over that reported by Baizer and Anderson[1] is attainable with only a slight decrease (from 40 to 32%) in the percentage of II in the dimer.

Baizer and Anderson[1] also reported that acrylonitrile is dimerized exclusively to 2-methyleneglutaronitrile (I) when treated with a tributylphosphine catalyst at 45°. Rauhut and Currier[8] had disclosed earlier that ethyl acrylate is converted to the dimer, diethyl 2-methyleneglutarate (III), when treated with the same catalyst. We have found that reaction of equimolar amounts of acrylonitrile and ethyl acrylate with a tributylphosphine catalyst at 100° in *t*-butyl alcohol solvent affords only one cross-condensation product (IV) in 48% yield (21% conversion of either reactant) despite the fact that two cross-condensates (IV and V) are possible. I (25% yield) and III (22% yield) are formed as by-products. That IV is a single (>97%)
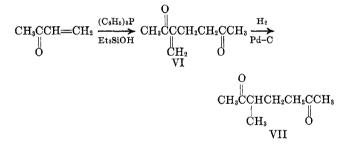
$$ \underset{\substack{\| \\ O \\ IV}}{\overset{\substack{CH_2 \\ \|}}{C_2H_5OCCCH_2CH_2CN}} \qquad \underset{\substack{\| \\ O \\ V}}{\overset{\substack{CH_2 \\ \|}}{C_2H_5OCCH_2CH_2CCN}} $$

(7) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Amer. Chem. Soc.*, **68**, 2282 (1946).

(8) M. Rauhut and H. Currier (to American Cyanamid), U. S. Patent 3,037,999 (1963).

pure) compound and not a mixture of products is evident from spectral studies and capillary (250 ft) gas-liquid chromatographic analysis.

High resolution infrared and mass spectroscopy[9] show unequivocally that the cross-condensate is 2-carbethoxy-4-cyano-1-butene (IV). In the ir spectrum the nitrile absorption at 2250 cm^{-1} is clearly in the range of a saturated alkyl nitrile (2260–2240 cm^{-1})[10] and outside the range of an α,β-unsaturated nitrile (2235–2215 cm^{-1})[10]. The ester carbonyl absorption at 1721 cm^{-1} is within the range of an α,β-unsaturated ester (1730–1717 cm^{-1})[10] and outside the range of a saturated ester (1750–1735 cm^{-1})[10]. The mass spectrum of the cross-condensate shows a molecular formula of $C_8H_{11}NO_2$. A principal fragment at $m/q = 113$, $C_6H_9O_2$, is consistent with structure IV but not with V. The expected cleavage of IV at the bond β to the nitrile group would produce a fragment of $m/q = 113$. No fragment of $m/q = 101$, $C_5H_9O_2$, which would be expected to result from cleavage of the bond β to the nitrile group of V was observed. To our knowledge, IV is a new compound.

We have also examined the catalytic reactions of methyl vinyl ketone with both trialkyl and triarylphosphines. Treatment of methyl vinyl ketone with a catalytic amount of tributylphosphine in dilute triethylsilanol or *t*-butyl alcohol solution affords only a solid polymer (mol wt 1300) even when carried out at 5–10°. However, when triphenylphosphine is used as the catalyst at 118° in triethylsilanol solvent, a single new[11] dimer is isolated in 78% yield at 60% conversion of ketone. With *t*-butyl alcohol as a solvent the yield of dimer is reduced to 60%. The dimer has been identified as 3-methylene-2,6-heptanedione (VI) by spectral means. Compound VI shows the following spectral
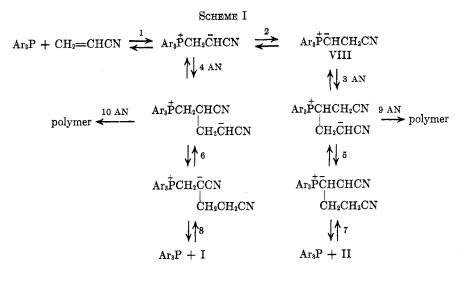
$$ \underset{\substack{\| \\ O}}{CH_3CCH=CH_2} \xrightarrow[Et_3SiOH]{(C_6H_5)_3P} \underset{\substack{\| \\ CH_2 \\ VI}}{\overset{\substack{O \\ \|}}{CH_3CCCH_2CH_2CCH_3}} \xrightarrow[Pd-C]{H_2} $$

$$ \underset{\substack{\| \\ CH_3 \\ VII}}{\overset{\substack{O \\ \|}}{CH_3CCHCH_2CH_2CCH_3}} $$

characteristics: ir, 5.83 μ (saturated ketone), 5.96 μ (α,β-unsaturated ketone), 6.15 μ (carbon–carbon double bond), 10.55 μ (carbon–carbon double bond conjugated with ketone); uv, λ_{max} 218 mμ (ϵ 9500); nmr, singlet at δ 2.12 ppm [3 H, $CH_3C(=O)CH_2$], singlet at 2.32 [3 H, $CH_3C(=O)-C=CH_2$], singlet at 2.55 (4 H, CH_2CH_2), two singlets at 5.85 and 6.10 (1 H each, $CH_2=C$). The presence of a CH_3 doublet at 1.10 ppm in the nmr spectrum of the hydrogenation product (VII) of VI eliminates the alternative structure, 3-octene-2,7-dione, from consideration. To our knowledge, VI has not been reported previously in the literature. In addition to VI, thermal dimer, 6-acetyl-5,6-dihydro-2-methylpyran[11] (7% yield), and an unknown product (3–4% yield) are isolated from the product mixture. The

(9) The nmr of IV which is not definitive is recorded in the Experimental Section.

(10) L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, p 179, 263.

(11) Methyl vinyl ketone has been reported to undergo thermal dimerization at 150° to give 6-acetyl-5,6-dihydro-2-methylpyran: K. Alder, H. Offermanns, and E. Ruden, *Chem. Ber.*, **74B**, 905 (1941).

SCHEME I

$$Ar_3P + CH_2=CHCN \underset{1}{\rightleftharpoons} Ar_3\overset{+}{P}CH_2\overset{-}{C}HCN \underset{2}{\rightleftharpoons} Ar_3\overset{+}{P}\overset{-}{C}HCH_2CN$$

VIII

$\downarrow\uparrow$ 4 AN $\downarrow\uparrow$ 3 AN

$$polymer \overset{10\ AN}{\longleftarrow} Ar_3\overset{+}{P}CH_2CHCN \qquad Ar_3\overset{+}{P}CHCH_2CN \overset{9\ AN}{\longrightarrow} polymer$$
$$\underset{CH_2\overset{-}{C}HCN}{|} \qquad\qquad \underset{\overset{-}{C}H_2\overset{-}{C}HCN}{|}$$

$\downarrow\uparrow$ 6 $\uparrow\downarrow$ 5

$$Ar_3\overset{+}{P}CH_2\overset{-}{C}CN \qquad\qquad Ar_3\overset{+-}{P}CHCHCN$$
$$\underset{CH_2CH_2CN}{|} \qquad\qquad \underset{CH_2CH_2CN}{|}$$

$\downarrow\uparrow$ 8 $\downarrow\uparrow$ 7

$$Ar_3P + I \qquad\qquad Ar_3P + II$$

infrared spectrum of the unknown compound shows that it is not 3-octene-2,7-dione.

Discussion

The mechanism of the triarylphosphine-catalyzed dimerization of acrylonitrile has been discussed by Baizer and Anderson[1] and is shown below in slightly modified form. Support for the presence of the phosphorus ylide intermediate (VIII) has been obtained by both Oda[12] and ourselves[13] through the isolation of Wittig-type reaction products when the dimerization is conducted in the presence of an aromatic[12,13] or aliphatic[13] aldehyde (Scheme I).

The improvement in conversion to dimer that is observed when tritolylphosphine is used in place of triphenylphosphine as catalyst is attributed to the slightly greater nucleophilicity of the methyl substituted phosphine (steps 1 and 2). It is important that the nucleophilicity of the triarylphosphine not be too great because then only a low ($<10\%$) percentage of II in the dimer is observed. Thus, tri(p-anisyl)phosphine which is significantly more nucleophilic than triphenylphosphine gives dimer containing only 9% II.

The improvement in dimer yield that is observed when triethylsilanol is used as a replacement solvent for t-butyl alcohol is particularly noteworthy. The increased dimer yield is at the expense of decreased insoluble (hexamer) and soluble polymer formation. Triethylsilanol has been estimated[14,15] to have a pK_a of about 16 which is about 1000 times as great as that of t-butyl alcohol. Accordingly, the solvent effect is attributed to the fact that triethylsilanol is a stronger protolytic source[16] than t-butyl alcohol and can better terminate polymer chain formation by promoting the proton transfer steps 5 and 6. In the absence of a protolytic source the propagation of the polymer chain (steps 9 and 10) would continue at a much faster rate.

(12) R. Oda, T. Kawabata, and S. Tanimota, *Tetrahedron Lett.*, 1653 (1964).

(13) J. D. McClure, *ibid.*, 2401 (1967).

(14) R. West and R. H. Baney, Abstracts, 133rd National Meeting of American Chemical Society, San Francisco, Calif., April 1958.

(15) C. Eaborn, "Organosilicon Compounds," Academic Press, New York, N. Y., 1960, p 244.

(16) Water or alcohols such as methanol which are stronger protolytic sources than t-butyl alcohol cannot be used as solvents because Michael addition of the alcohol to acrylonitrile occurs. The sterically hindered triethylsilanol does not react with acrylonitrile to give a Michael adduct at temperatures up to 175°.

However, it is important that the solvent not be too protolytic since the basic catalyst can complex with the solvent and be rendered inactive. Thus, the rate of dimerization is reduced tenfold by the presence of 2,6-di-t-butylphenol ($pK_a \cong 10$) in the reaction mixture. It is apparent that a proper balance between nucleophilicity of the phosphine catalyst and protolytic strength of the solvent is quite critical for high yields of II at good conversions of acrylonitrile. The combination of tritolylphosphine catalyst and triethylsilanol solvent is especially propitious.

The isolation of a single cross-condensate, IV, from the tributylphosphine-catalyzed reaction of acrylonitrile with ethyl acrylate is of special interest since it might be expected that two products, IV and V, would be formed. The former (IV) would arise from the reaction of the phosphonium zwitterion, IX, with acrylonitrile (step 11) while the latter (V) would arise from the reaction of X with ethyl acrylate (step 12). Since both I and III are isolated as by-products in approximately equal amounts, intermediates IX and X must be formed in the reaction. The failure to observe V as a product may then be rationalized by assuming that step 12 is much less favorable than step 11. Step 14 which involves proton transfer may also be less favorable than step 13. The results thus indicate that the relative ease of formation of X vs. IX is much less important than the succeeding steps in the ultimate determination of the nature of the products formed (Scheme II).

In contrast to acrylonitrile, methyl vinyl ketone reacts with a tributylphosphine catalyst to give exclusively polymer. The 3-methylene-2,6-heptanedione (VI) which may be initially formed in this system reacts too readily with the tributylphosphine for a selective dimerization to occur. However, if the tributylphosphine is replaced with the much less nucleophilic triphenylphosphine, then a discriminating catalyst is present which reacts primarily with the methyl vinyl ketone and not with VI. Nevertheless, the reaction of the initially formed phosphonium zwitterion, $(C_6H_5)_3$-$P^+CH_2^-CHCOCH_3$ (XI), with another molecule of methyl vinyl ketone is still very rapid in that XI is not significantly transformed to a phosphonium ylide, $(C_6H_5)_3P^{+-}CHCH_2COCH_3$, before reacting as in the case with $(C_6H_5)_3P^+CH_2^-CHCN$. This type of reasoning accounts for the failure to observe any significant
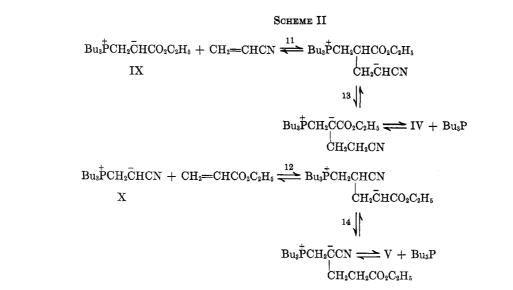
SCHEME II

Bu₃ṖCH₂C̄HCO₂C₂H₅ + CH₂=CHCN ⇌[11] Bu₃ṖCH₂CHCO₂C₂H₅

IX |
                                   C̄H₂CHCN

13 ↓↑

Bu₃ṖCH₂C̄CO₂C₂H₅ ⇌ IV + Bu₃P

|
CH₂CH₂CN

Bu₃ṖCH₂C̄HCN + CH₂=CHCO₂C₂H₅ ⇌[12] Bu₃ṖCH₂CHCN

X |
                                  CH₂C̄HCO₂C₂H₅

14 ↓↑

Bu₃ṖCH₂C̄CN ⇌ V + Bu₃P

|
CH₂CH₂CO₂C₂H₅

amount of 3-octene-2,7-dione in the product mixture.

Experimental Section

Tri(p-tolyl)phosphine-Catalyzed Dimerization of Acrylonitrile. —A solution of 40 g (755 mmol) of acrylonitrile, 1.0 g (3.3 mmol) of tri(p-tolyl)phosphine, and 0.1 g of hydroquinone in 80 g of triethylsilanol[7] in a 350 ml glass-lined reactor sealed under nitrogen was stirred at 160° for 11 hr. The mixture was diluted with 100 ml of benzene and filtered to remove 0.45 g of crude hexamer (3% yield). Benzene and unreacted acrylonitrile were removed by distillation through a Vigreux column at reduced pressure. Analysis of the distillate by gas-liquid chromatography at 80° on a 20-ft column packed with 15%DC-710 on Fluoropak showed the presence of 25.6 g (36% conversion) of acrylonitrile.

The residual liquid separated into two phases on cooling to 0°. Analysis of the lower phase (17.6 g) by gas-liquid chromatography at 150–200° on a 10-ft column packed with 15% Carbowax 20M on Fluoropak showed the presence of 8.3 g of 2-methyleneglutaronitrile[1] (58% yield), 2.1 g of *trans-* and 1.9 g of *cis*-1,4-dicyano-1-butene[1] (27% yield) as well as some triethylsilanol. The upper phase was almost pure triethylsilanol. Distillation of the lower phase through a small Vigreux column separated the dimer, 11.8 g, bp 80–100° (0.5 mm), from triethylsilanol, bp 42–45° (5 mm), and 3.0 g of nonvolatile residue. Separation of the *cis-* and *trans*-1,4-dicyano-1-butene, bp 122–132° (3 mm), from the 2-methyleneglutaronitrile, bp 109–110° (3 mm), was effected by fractional distillation through a 2-ft spinning-band column. Recrystallization of the residue from ethanol recovered 0.7 g (70%) of the tritolylphosphine.

Tributylphosphine-Catalyzed Reaction of Acrylonitrile with Ethyl Acrylate.—A solution of 20 g (378 mmol) of acrylonitrile, 38 g (380 mmol) of ethyl acrylate, 0.9 g (5 mmol) of tributylphosphine, and 0.05 g of hydroquinone in 100 g of *t*-butyl alcohol in a 350 ml glass-lined reactor sealed under nitrogen was maintained at 102 ± 2° for 7 hr. The product mixture was neutralized with 0.35 g of acetic acid. Removal of solvent and unreacted acrylonitrile and ethyl acrylate was effected by distillation under reduced pressure. Analysis of the distillate by gas-liquid chromatography at 70° on the DC-710 column showed the presence of 16 g of acrylonitrile (20% conversion) and 30 g of ethyl acrylate (21% conversion).

Distillation of the residual liquid through a small Vigreux column afforded 9.0 g, bp 70–85° (0.5 mm). Analysis of the distillate by gas-liquid chromatography at 180–200° on a 10 ft by ³/₈ in. column packed with 15% neopentyl glycol sebacate on Chromosorb W showed that the product contained 5.9 g of

2-carbethoxy-4-cyano-1-butane (48% yield), 1.8 g of diethyl 2-methyleneglutarate[8] (22% yield), 1.0 g of 2-methyleneglutaronitrile (25% yield), and 0.3 g of an unknown compound. Separation of IV from the other components was effected by glc trapping on the above described column. Analysis of IV on a 250 ft capillary column packed with Carbowax 20M on Fluoropak showed that it was 97% pure: nmr (CDCl₃) δ 1.30 (t, 3, CH₃-CH₂), 4.17 (q, 2, CH₃CH₂), 2.55 (s, 4, CH₂CH₂CN), 5.70 (s, 1, C=CH₂), and 6.23 (s, 1, C=CH₂).

Anal. Calcd for C₈H₁₁NO₂: C, 62.7; H, 7.20; N, 9.14. Found: C, 62.2; H, 7.45; N, 8.95.

Triphenylphosphine-Catalyzed Dimerization of Methyl Vinyl Ketone.—A solution of 20 g (285 mmol) of methyl vinyl ketone, 0.2 g of hydroquinone, and 1.85 g (7.1 mmol) of triphenylphosphine in 100 g of *t*-butyl alcohol in a 350 ml glass-lined reactor sealed under nitrogen was maintained at 118° for 8 hr. Solvent and unreacted methyl vinyl ketone were removed by distillation under reduced pressure. Analysis of the distillate by gas-liquid chromatography at 80° on a 10-ft column packed with 15% DC-170 on Fluoropak showed the presence of 8.0 g (60% conversion) of methyl vinyl ketone.

Distillation of the residual liquid through a small Vigreux column afforded 8.6 g, bp 55–75° (1–2 mm), along with 4.5 g of residue. Analysis of the distillate by gas-liquid chromatography on the DC-710 column at 180–200° showed the presence of 7.2 g of 3-methylene-2,6-heptanedione (60% yield), 0.8 g of 9-acetyl-5,6-dihydro-2-methylpyran (7% yield), and 0.4 g of an unknown compound. The 3-methylene-2,6-heptanedione, bp 91–92° (5 mm), was isolated in pure form by fractional distillation through a 2-ft spinning-band column, mp 5–7°.

Anal. Calcd for C₈H₁₂O₂: C, 68.5; H, 8.60; mol wt, 140. Found: C, 68.7; H, 8.70; mol wt, 140 (mass spectroscopy).

Recrystallization of the distillation residue from ethanol recovered 1.4 g (75%) of the triphenylphosphine.

Hydrogenation of 3-Methylene-2,6-heptanedione (VI).—A mixture of 1.4 g of VI, 0.5 g of 10% palladium on barium sulfate and 20 ml of tetrahydrofuran shaken at 25° under 100 psi hydrogen pressure absorbed 0.95 mol equiv of hydrogen in 2 hr. After filtration, distillation afforded 1.2 g (85% yield) of VII:[17] bp 56–58° (1 mm); nmr δ 1.10 (d, 3, CH₃CH), 1.70 (m, 2, CHCH₂-CH₂), 2.14 (s, 6, two CH₃CO), 2.4 (m, 3, CH₂CO and CHCO).

(17) K. Alder and R. Muders, *Chem. Ber.* **91**, 1083 (1958).