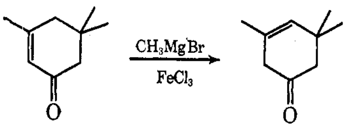
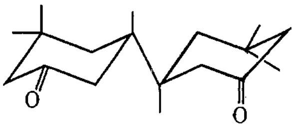
The crystalline by-products (mp 124 and 163°) were recognized from spectral evidence to result from reductive dimerization; their properties are well accounted for on the basis of formulas **3** and **4**, although we were unable to decide which isomer corresponds to the racemic mixture **3** and which to the meso form **4**. Earlier workers[4,5] have described these reductive dimers from the sodium or lithium metal reductions of **1**. In our case, reductive dimerization seems to be brought about by the presence of excess magnesium metal in the methylmagnesium bromide reagent used to bring about the desired deconjugation.



1 **2**



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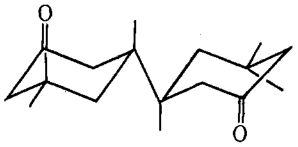

4

On the basis of many experiments, we find that high yields of **2** are obtained when no excess of magnesium is present in the Grignard reagent, when the isophorone is added very rapidly to this reagent, and when other precautions noted in the Experimental Section are observed.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer 257 grating infrared spectrophotometer. The nuclear magnetic resonance spectra were obtained on Varian Associates A-60 and A-60A instruments. Mass spectra were taken on an Associated Electrical Industries MS-902 mass spectrometer.[6]

β-Phorone (2).—To a stirred solution of 51.5 g of Mallinckrodt Grignard magnesium in 300 ml of ether in a 3-l. flask, 200 g of cooled methyl bromide in 300 ml of ether was added. The dropwise addition was carried out over a 3-hr period, keeping the mixture under nitrogen and just below reflux temperature with an ice bath. When all of the magnesium was dissolved, 4 g of anhydrous ferric chloride in 100 ml of ether was added dropwise over 15 min. A solution of 207 g of distilled isophorone (1) [bp ~90° (10 mm)] in 300 ml of ether was added with rapid stirring over a 25-min interval. This step is dangerous and requires adequate venting of methane; moreover, the reaction mixture should not be allowed to cool, since large amounts of polymer are formed under those conditions. The reaction mixture was refluxed for 1 hr and poured into a 6-l. separatory funnel containing 50 g of ammonium chloride and 100 g of ice. After dropwise addition of 120 ml of glacial acetic acid, the mixture was shaken, and the aqueous phase was extracted twice with ether. The combined ether extract was washed with water, 5% aqueous sodium bicarbonate, and again with water. The ether was dried with anhydrous magnesium sulfate and filtered. Evaporation of the solvent and two distillations of the product using a Vigreux column gave 150 g of 96% pure β-phorone (2) [bp ~70° (10 mm)]; the purity was tested by gas chromatography on a 4% SE-30 column at 135°. The yield of β-phorone was 73%; however, reconjugation to isophorone (1) occurred at room temperature. This process was slowed by rapid distillation of the products and subsequent refrigeration.

Isophorone Dimers 3 and 4.—To a suspension of 25 g of magnesium in a 2-l. flask containing 200 ml of ether was added 100 g of cooled methyl bromide in 300 ml of ether. The system was flushed with nitrogen and 2 g of anhydrous ferric chloride in 50 ml of ether was added. (Specks of magnesium metal were visible in the mixture.) A solution of 125 g of isophorone (1) in 150 ml of ether was added carefully over a 1-hr period. A viscous material formed while refluxing for 1 hr which made stirring very difficult. Ice and 60 ml of acetic acid were used to hydrolyze the reaction mixture. After washing with water, 5% aqueous sodium bicarbonate, and water again, the ether layer was dried with anhydrous magnesium sulfate. Evaporation of the solvent yielded a semisolid viscous residue. The oil partially dissolved in pentane yielding 8.5 g of a crystalline dimeric species, mp 163°. Fractional crystallization in pentane yielded 15 g of a more soluble dimeric species, mp 123–124°. The total yield of dimer was about 20%; however, other experiments under varying conditions produced as much as 50% yield of dimers. Spectral data for both isomers were indistinguishable.

The dimer, mp 163°, had the following spectra: mass spectrum (70 eV) m/e 278.2239 ($C_{18}H_{30}O_2$ requires 278.2246), 263.2000 ($C_{17}H_{27}O_2$ requires 263.2010), 245.1875 ($C_{17}H_{25}O_2$ requires 245.1905), 263 $\xrightarrow{m^*\ 228.1}$ 245, 139 ($M - C_9H_{15}O$); nmr ($CDCl_3$) δ 1.05 (s, 6 H), 1.10 (s, 12 H), 1.27, 1.51, 1.70, 1.94 (AB quartet, $J_{AB} \sim 14$ cps, 4 H), 1.94, 2.18, 2.30, 2.54 (AB quartet, $J_{AB} \sim 14$ cps, 4 H), 2.18 (s, 4 H); nmr (pyridine) δ 0.99 (s, 18 H), 1.20, 1.43, 1.72, 1.95 (AB quartet, $J \sim 14$ cps, 4 H), 1.95, 2.18, 2.37, 2.60 (AB quartet, $J \sim 14$ cps, 4 H), 2.18 (s, 4 H); ir (CH_2Cl_2) 5.86 μ.

The dimer, mp 123–124°, had the following spectra: mass spectrum (70 eV) m/e 278, 263, 245, 263 $\xrightarrow{m^*\ 228.1}$ 245, 139; nmr ($CDCl_3$) δ 1.09 (s, 18 H), 1.28, 1.52, 1.71, 1.95 (AB quartet, $J \sim 14$ cps, 4 H), 1.92, 2.15, 2.31, 2.54 (AB quartet, $J \sim 14$ cps, 4 H), 2.18 (s, 4 H); nmr (pyridine) δ 0.99 (s, 18 H), 1.18, 1.42, 1.65, 1.89 (AB quartet, $J \sim 14$ cps, 4 H), 1.92, 2.16, 2.34, 2.58 (AB quartet, $J \sim 14$ cps, 4 H), 2.18 (s, 4 H); ir (CH_2Cl_2) 5.86 μ.

Registry No.—**1,** 78-59-1; **3,** 28192-72-5; **4,** 4994-12-1.

A New Synthesis of Symmetrical Diaroylmethanes

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Sieglitz and Horn[2] prepared a series of symmetrical β-diketones by the reaction of vinyl acetate with the appropriate acid chloride in the presence of aluminum chloride. This method suffers from the disadvantage that appreciable amounts of unsymmetrical diketones, $RCOCH_2COCH_3$, are also formed. Rothman and Moore[3] have reported a route to β-diketones [$(RCO)_2CH_2$; R = alkyl] starting from isopropenyl esters. Recently, we described the preparation of symmetrical and unsymmetrical diaroylmethanes containing the pentafluorophenyl group.[4] We now report a simple general method for the preparation of symmetrical diaroylmethanes.

Vinyl esters of benzoic acids (Table I), prepared in

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(4) W. Baker, *J. Amer. Chem. Soc.*, **47**, 663 (1925)

(5) J. Morizur, B. Furth, and J. Kossanyi, *Bull. Soc. Chim. Fr.*, 1422 (1967).

(6) Cornell High Resolution Mass Spectrometer Facility supported by NIH Grant No. RR00355.

(1) To whom inquiries should be addressed.

(2) A. Sieglitz and O. Horn, *Chem. Ber.*, **84**, 607 (1951).

(3) E. S. Rothman and G. G. Moore, *Tetrahedron Lett.*, 2553 (1969); E. S. Rothman, G. G. Moore, and A. N. Speca, *ibid.*, 5205 (1969).

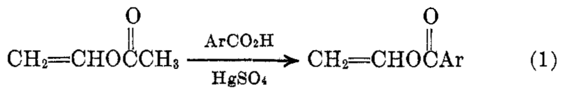
(4) R. Filler, Y. S. Rao, A. Biezais, F. N. Miller, and V. D. Beaucaire, *J. Org. Chem.*, **35**, 930 (1970).

TABLE I

VINYL BENZOATES

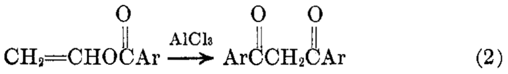
$CH_2{=}CHOCOAr$ Ar =	Registry no.	Yield, %	Bp (mm) or mp, °C	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
$4\text{-}ClC_6H_4$	7561-01-5	74	33 (5)	$C_9H_7O_2Cl$	59.18	3.89	59.32	3.83
$4\text{-}CH_3C_6H_4$	2653-44-3	70	33 (5)	$C_{10}H_{10}O_2$	74.07	6.17	73.9	6.1
$4\text{-}CH_3OC_6H_4$	13351-86-5	75	40 (5)	$C_{10}H_{10}O_3$	67.4	5.6	67.3	5.61
$4\text{-}NO_2C_6H_4$	831-69-6	80	73	$C_9H_7O_4N$	60.3	3.9	60.2	3.87
C_6F_5	28541-28-8	75	80 (5)	$C_9H_3F_5O_2$	45.3	1.26	45.15	1.24

75–80% yield by ester interchange (eq 1),[5] are treated with anhydrous aluminum chloride in tetrachloroethane at 70° to give the diketones in yields of 58–98% (Table II) (eq 2).[6]



$$\mathrm{CH_2{=}CHO\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[HgSO_4]{ArCO_2H} CH_2{=}CHO\overset{O}{\overset{\|}{C}}Ar} \tag{1}$$

Ar = C_6H_5, $p\text{-}ClC_6H_4$, $p\text{-}CH_3OC_6H_4$, $p\text{-}CH_3C_6H_4$, $p\text{-}NO_2C_6H_4$, C_6F_5



$$\mathrm{CH_2{=}CHO\overset{O}{\overset{\|}{C}}Ar \xrightarrow{AlCl_3} Ar\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}Ar} \tag{2}$$

The formation of the diaroylmethanes may proceed through the intermediacy of the diaroylacetaldehyde, $(ArCO)_2CHCHO$, which would then undergo decarbonylation to give the diketone.

Experimental Section

Vinyl Interchange Reaction.—In a three-necked, round-bottomed flask, provided with a thermometer and water-cooled condenser, was placed 42.4 g (0.2 mol) of pentafluorobenzoic acid. Vinyl acetate (110 g, 1.28 mol) was added to the flask along with powdered mercuric sulfate (1.71 g). The contents of the flask were stirred with a magnetic bar and heated under reflux for 3 hr. At the end of this period, the contents of the flask were cooled and diluted with petroleum ether (bp 30–60°). Sodium acetate hydrate was added to remove acidic materials. The organic layer was filtered from the inorganic materials and concentrated on a rotary evaporator. Unreacted vinyl acetate and petroleum ether were thus removed. The residue in the flask was dissolved in ether and the ether solution washed with a solution of sodium bicarbonate to remove last traces of pentafluorobenzoic acid. The oily layer was distilled under reduced pressure to give 32 g (75%) of vinyl pentafluorobenzoate, bp 80° (5 mm). The following benzoates (see Table I) were prepared in the same fashion. Vinyl benzoate was obtained from Monomer-Polymer Labs, Philadelphia, Pa. If, when other other acids are used, the acid does not dissolve in vinyl acetate, it is beneficial to add 10–20 ml of absolute ethyl alcohol to dissolve the acid.

TABLE II

DIAROYLMETHANES

Vinyl ester, $CH_2{=}CHOOCAr$ Ar =	Registry no.	Yield, %	Mp of β-diketone, °C
C_6H_5	120-46-7	95	78[a]
$4\text{-}ClC_6H_4$	18362-49-7	85	159[b]
$4\text{-}CH_3C_6H_4$	3596-36-3	90	127[c]
$4\text{-}CH_3OC_6H_4$	18362-51-1	58	116[b]
$4\text{-}NO_2C_6H_4$	13586-91-9	98	241[b]
C_6F_5	23074-29-5	95	119[d]

[a] F. G. Young, F. C. Frostick, Jr., J. J. Sanderson, and C. R. Hauser, *J. Amer. Chem. Soc.*, **72**, 3635 (1950). [b] See ref 2. [c] A. Behal and V. Auger, *Bull. Soc. Chim. Fr.*, **9**, 699 (1893). [d] See ref 4.

Reaction of Vinyl Ester with Aluminum Chloride.—In a three-necked flask provided with a thermometer, condenser, and a stirrer was placed 4.76 g (0.02 mol) of vinyl pentafluorobenzoate in 150 ml of tetrachloroethane. Anhydrous aluminum chloride (6 g, 0.046 mol) was added. The mixture was heated at 70° for 45 min. The reaction mixture was cooled and decomposed with 100 ml of 10% hydrochloric acid. Tetrachloroethane was removed by steam distillation and the residual organic material in the aqueous layer was recovered by extraction with ether. The ether layer was washed with water and dried over anhydrous sodium sulfate. Ether was removed on a rotary evaporator leaving behind a solid residue which was crystallized from a benzene–methanol mixture to give 3.85 g of bispentafluorobenzoylmethane, mp 119°.

A similar procedure was employed in preparing other diaroylmethanes (Table II).

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[5] W. J. Toussaint and L. G. McDowell, Jr., U. S. Patent 2,299,862 (1942) [*Chem. Abstr.*, **37**, 1722 (1943)]; R. L. Adelman, *J. Org. Chem.*, **14**, 1057 (1949).

[6] After the present work was completed, Rothman and Moore, *ibid.*, **35**, 2351 (1970), have shown that under similar conditions, diacylmethanes, $(RCO)_2CH_2$, where R = $C_{11}H_{23}$, $C_{15}H_{31}$, and $C_{17}H_{35}$, are obtained from vinyl alkanoates. With shorter reaction times, only β-ketoaldehydes were isolated. We have not isolated any β-ketoaldehydes in our work.