Propionylferrocene[4] was converted to the Mannich base in a similar manner; the latter was not isolated but subjected directly to steam distillation. In contrast to the propiophenone analog,[5] it did not pyrolyze to give the desired isopropenyl ketone.

Cinnamoylferrocene has proved polymerizable, and details will be reported later.

EXPERIMENTAL[6]

Cinnamoylferrocene (I). *Method A*. A solution of 46.7 g. (0.35 mole) of anhydrous aluminum chloride and 58.4 g. (0.35 mole) of *trans*-cinnamoyl chloride in 300 ml. of dried methylene chloride was added with stirring and under a nitrogen atmosphere to a solution of 65.2 g. (0.35 mole) of ferrocene in 300 ml. of methylene chloride. During the addition, vigorous evolution of hydrogen chloride occurred and the formation of a blue-green reaction mixture was noted. After stirring for 22 hr. at room temperature following completion of the addition, the reaction mixture was hydrolyzed with 500 g. of ice. The light blue aqueous phase was extracted twice with 50-ml. portions of carbon tetrachloride, the combined organic layer washed to neutrality with 100 ml. portions of water, and then dried over calcium sulfate. Evaporation of the solvent left a dark red crystalline residue which was dissolved in 400 ml. of hot 95% ethanol and chilled overnight at −20°. After filtering and drying, 90.9 g. (81.5% yield) of violet crystals of I was obtained, m.p. 137.0–137.5°. Several recrystallizations from ethanol produced an analytical sample of I, m.p. 139.5–139.7°.

Anal. Calcd. for $C_{19}H_{16}FeO$: C, 72.17; H, 5.10; Fe, 17.66. Found: C, 72.28, 72.31; H, 5.12, 5.14; Fe, 17.56, 17.40.

Method B. A mixture of 2.18 g. (0.01 mole) of acetylferrocene, 1.06 g. (0.01 mole) of benzaldehyde, 5 ml. of 10% sodium hydroxide solution and 30 ml. of methanol was shaken at room temperature for 40 hr. The solvent was then evaporated and the residue recrystallized from methanol to produce 1.50 g. (47% crude yield) of I in the form of red violet crystals, m.p. 130–131°. Recrystallization from methanol raised the melting point to 139.0–139.5°.

A mixture of samples of I prepared by both methods melted at 138.2–139.0°. Furthermore, the infrared spectra of both samples of I (in chloroform solution) were identical.

An oxime, prepared in the usual manner, was recrystallized from a mixture of methanol and water to produce dark orange crystals of melting point 116–118°.

Anal. Calcd. for $C_{19}H_{17}FeNO$: C, 68.92; H, 5.17; Fe, 16.86; N, 4.23. Found: C, 69.02, 68.80; H, 4.97, 5.09; Fe, 16.80, 16.89; N, 4.19, 4.38.

β-Phenylpropionylferrocene. Catalytic hydrogenation of I in 1-butanol solution using 5% platinum on charcoal catalyst produced a 57% yield of β-phenylpropionylferrocene in the form of orange crystals, m.p. 81.5–82.5°. An additional recrystallization from ethanol produced an analytical sample, m.p. 84.5–84.8°.

Anal. Calcd. for $C_{19}H_{18}FeO$: C, 71.72; H, 5.70; Fe, 17.55. Found: C, 71.89, 71.91; H, 5.74, 5.60; Fe, 17.71, 17.57.

Propionylferrocene. In a procedure similar to that described above for the preparation of I (Method A), a methylene chloride solution of 27.8 g. (0.30 mole) of propionyl chloride and 40.0 g. (0.30 mole) of anhydrous aluminum chloride was added to 57.7 g. (0.31 mole) of ferrocene dissolved in the same solvent. After hydrolysis and product workup, a dark oily residue was obtained. The residue was purified by chromatography on an alumina column using chloroform as the eluent. Evaporation of the chloroform and recrystallization of the solid residue from petroleum ether (b.r. 39–51°) produced 34.8 g. (48% yield) of yellow orange needles of propionylferrocene, m.p. 38.0–38.2°.

An oxime, prepared in the usual manner, was recrystallized from a mixture of ethanol and water to yield golden yellow leaflets of melting point 135.4–136.0°.

Anal. Calcd. for $C_{13}H_{15}FeNO$: C, 60.73; H, 5.88; Fe, 21.72; N, 5.45. Found: C, 60.91, 60.98; H, 5.95, 6.09; Fe, 22.09, 21.92; N, 5.35, 5.32.

β-Dimethylaminopropionylferrocene hydrochloride. A mixture of 11.4 g. (0.05 mole) of acetylferrocene, 4.08 g. (0.05 mole) of dimethylamine hydrochloride, 2.25 g. (0.075 mole) of paraformaldehyde, 0.15 ml. of concentrated hydrochloric acid and 50 ml. of absolute ethanol was warmed to reflux. After 1 hr. an additional 1.50 g. of paraformaldehyde was added and refluxing was continued for an additional 2 hr. The mixture was cooled to room temperature, the solvent was evaporated, and the residue extracted repeatedly with ether. From the ether extracts 7.1 g. of acetylferrocene, m.p. 83.5–84.0°, was recovered. The oily ether-insoluble residue was recrystallized from a mixture of ethanol and methyl ethyl ketone to produce 4.1 g. of fine yellow brown crystals of β-dimethylaminopropionylferrocene hydrochloride, m.p. 171–172°, with decomposition. The yield, based on the recovered acetylferrocene, was 68%.

Anal. Calcd. for $C_{15}H_{20}ClFeNO$: C, 56.01; H, 6.27; Cl, 11.02; Fe, 17.36; N, 4.36. Found: C, 56.03, 55.93; H, 6.33, 6.11; Cl, 11.17, 11.32; Fe, 17.13, 17.41; N, 4.65, 4.58.

Steam distillation apparently pyrolyzed this hydrochloride, although no ferrocenyl vinyl ketone could be isolated. A small amount of brown solid was obtained from the distillate, however, and a much larger amount from the distillation flask. After thoroughly washing with water, benzene, and acetone and then drying, the latter solid analyzed as follows:

C, 56.75; H, 4.83; Fe, 25.10; N, 0.63.

Both products appeared to be polymeric in nature and were insoluble in water, benzene, and ether. Addition of a polymerization inhibitor, hydroquinone, during the pyrolysis did not change the result.

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[4] Propionylferrocene has recently been reported by Dr. K. L. Rinehart, Jr., as an intermediate for the preparation of β-ferrocenylpropionic acid; see Abstracts of Papers, 131st Meeting of the American Chemical Society, Miami, Fla., April 7 to 12, 1957, pp. 47–0.

[5] J. H. Burckhalter and R. C. Fuson, *J. Am. Chem. Soc.*, 70, 4184 (1948).

[6] All melting points are corrected; analyses were made by Schwarzkopf Microanalytic Laboratory, Woodside 77, New York, N. Y.

Esterification with Trapping Phase

HENRY KLOSTERGAARD

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Synthesis of an ester from alcohol and acid presents special problems in cases where the ester has a higher boiling point than the alcohol or acid. The method described below is a simple solution to the problems in many cases. It is based on phase separation.

Alcohol and acid are heated with a catalyst and an ester solvent, nonmiscible with water, is added. On the subsequent addition of large amounts of dehydrants phase separation occurs, and it can be

TABLE I

YIELD OF ORGANIC ESTERS USING SULFURIC ACID

Acid	G.	C_2H_5OH, G.	Toluene, Ml.	H_2SO_4, Ml.	Yield, G.	%
Oxalic, 2 aq.	504	463	584 + 146 + 146	288	466	80[a]
Citric, 1 aq.	420	368	640 + 160 + 160	150	442	80
Adipic	292	230	350 + 100 + 100	72	360	89
Succinic	236	230	350 + 100 + 100	72	290	83
Furoic	92	55	100 + 25 + 25	20	83	72
Levulinic	143	77	180 + 45 + 45	23	151	85

[a] Compare H. T. Clarke and Anne W. Davis, *Org. Synthesis*, **2**, 23 (1922) and Joseph Kenyon, *Org. Synthesis*, **5**, 59 (1925)

TABLE II

YIELD OF ORGANIC ESTERS USING $CaCl_2$ METHOD

Acid	G.	C_2H_5OH, G.	Toluene, Ml.	$CaCl_2$, G.	Yield, G.	%
Aconitic	174	184	250	40	165	64
Fumaric	232	230	244	100	306	89[a]
Maleic	232	230	244	50	317	92
Citric, 1 aq.	210	184	275 + 100	100	187	68 + 4[a]
Succinic	118	115	250	50	243	93
Adipic	90	38	110	20	117	94
Furoic	112	59	140	25	95	68[a]
Levulinic	143	77	180	33	158	89[b]

[a] If acid remaining in distillation flask was re-esterified as original the yields were increased to 95%, 91%, and 78%, respectively. [b] Compare L. Ruzicka, *Ber.*, **50**, 1367 (1917).

easily seen that this procedure is favorable for getting a high yield of ester.

The method is useful in laboratory preparation because (a) it uses low excess of alcohol, (b) it is fast, (c) it can use acids without pre-drying, (d) it uses simple equipment, and (e) it gives a good yield. These points will be evident when comparisons are made with standard methods of preparation, a few of which are given by reference in the experimental section.

The method can be followed using either (a) concentrated H_2SO_4 or (b) anhydrous $CaCl_2$ + concentrated HCl. As ester solvent toluene was used, because it has a reasonably high boiling point, yet does not present fractionating problems with the esters.

EXPERIMENTAL

Materials used were obtained from the following sources:

Item	Grade	Manufacturer
Oxalic acid, 2 aq.	Technical	Mallinckrodt
Aconitic acid	Technical	Pfizer
Levulinic acid	Technical	Eastman
Fumaric acid	Technical	Eastman
Maleic acid	Technical	Eastman
Furoic acid	Technical	Quaker Oats
Adipic acid	C. P.	Fischer Scientific Co.
Citric acid, 1 aq.	U. S. P.	Mallinckrodt
Succinic acid	Pure	Merck & Co.
Sulfuric acid	Technical	Braun
Hydrochloric acid	Reagent	Baker
Toluene	Technical	Mefford
Calcium chloride anhydrous	Reagent	Merck & Co.

Method (a) using concentrated sulfuric acid. One equivalent of acid and $1\frac{1}{4}$–$1\frac{1}{3}$ equivalents of alcohol were refluxed with a catalytic amount of concentrated H_2SO_4 until all acid was dissolved or about 15 min. The trapping phase (in these preparations toluene was used) was then added under continued reflux. The volume of toluene was chosen about equal to that of the expected ester. Gradually concentrated H_2SO_4 was added. For every ml. of water present and formed, one ml. of acid should be used. After thorough mixing the toluene layer was taken off in a separatory funnel and the lower phase refluxed with toluene again (about 5 min.). The amount of toluene was about 25% of that used in the first extraction. Again the toluene layer was separated and the extraction repeated once more with the smaller amount of toluene. The combined toluene extracts were washed with a little water, shaken with a little anhydrous Na_2SO_4 and then fractionated under reduced pressure. Examples of this procedure are presented in Table I.

Usual considerations of yield *vs.* size of charge apply. Oxalic acid has been esterified using this procedure in batches of 1500 lbs. with 83% yield.

Tartaric and lactic acids were tried but failed and aconitic acid was somewhat affected by the H_2SO_4.

If speed is more important than high yield certain simplifications can be made.

Starting with 126 g. oxalic acid and 138 g. ethyl alcohol and making one hot extraction after adding 72 ml. concentrated H_2SO_4, a 60% yield of pure distilled ester could be made in 70 min. altogether. Two cold extractions following the hot one, requiring additional 10 min., raised the yield to 73%.

Method (b) using $CaCl_2$ + 38% HCl. One equivalent of acid and $1\frac{1}{4}$–$1\frac{1}{3}$ equivalents of alcohol were refluxed about 15 min. until all acid was dissolved. Catalytic amounts of 38% HCl were added. Under continued reflux toluene was added as under (*a*) and in similar amounts. Additional 38% HCl was added (1 vol. for each 10 vol. alcohol). Anhydrous $CaCl_2$ was then gradually added through the condenser. The amount was chosen equal to the total water present and formed. The whole mixture was then refluxed for some time. In the examples listed the time varied from 1 to 12 hours depending on laboratory hours. Three hours is quite good.

Usually no additional extraction was made. The toluene layer was separated and washed with a small amount of water, shaken clear with a little Na_2SO_4 (anhydrous) and then fractionated.

Examples of this procedure are listed in Table II.

Oxalic and tartaric acid fail to react in this method.

It will be apparent that the methods are not universally applicable, but the number of esters for which they can be expected to work is large and includes many of the common esters. The boiling points (uncorr.) of the esters prepared are listed in Table III.

TABLE III

BOILING POINTS OF ORGANIC ESTERS PREPARED, °C.

	15 mm. Hg	10 mm. Hg	5 mm. Hg
Diethyl oxalate	84	76	66
Triethyl citrate	183	177	164
Diethyl adipate	133	125	111
Diethyl succinate	106	99	88
Ethyl furoate	90		
Ethyl levulinate	96	90	80
Triethyl aconitate	170	160	150
Diethyl fumarate	106	98	87
Diethyl maleate	106	99	86

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Mechanism of the Thermal Isomerization of Bicyclo[2.2.1]heptadiene

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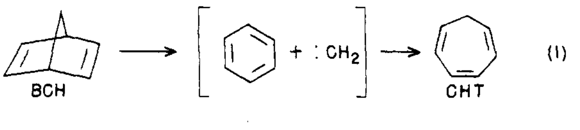
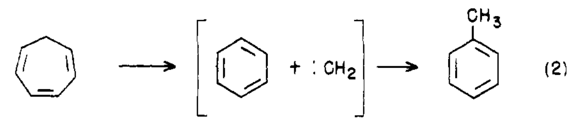
In a recent technical bulletin,[1] the thermal vapor phase isomerization of bicyclo[2.2.1]heptadiene (BCH) at 450–475° and atmospheric pressure was reported to yield about 45% cycloheptatriene (CHT). Toluene, acetylene, and cyclopentadiene (CPD) were identified as the principal side products. In order to elucidate the mechanism of this novel rearrangement, BCH was thermally isomerized and gas-liquid partition chromatography (GLPC) utilized to analyze the pyrolyzates. Product distribution data which show the effect of varying the residence time and the temperature are given in Table I.

The data in Table I indicate that the yield of CHT rapidly decreased with increased residence time (decreased pass rate) at 475°. This effect is apparent from Column 9 which gives the toluene/CHT ratios. At 395° (Run 6) the yield of CHT is markedly higher and that of toluene lower than in the experiments at 475°. These results suggested that CHT was formed initially and subsequently rearranged to toluene. This formulation was verified when a sample of pure CHT was passed through the furnace at 478° (Run 7) and an almost quantitative conversion to toluene resulted. A small amount of benzene and a trace of ethylene were identified as side products (see Experimental, Table IV).

A series of experiments was carried out to test a mechanism involving methylene as an intermediate in the initial isomerization of BCH (Equation 1)



or in the subsequent rearrangement of CHT to toluene (Equation 2). These possibilities were



considered because of the observed benzene and ethylene side products, both in the isomerization of BCH (Run 3) and in the conversion of CHT to toluene (Run 7). Furthermore, photochemically generated methylene is known to add to benzene[2] and to benzene derivatives[3,4] to give cycloheptatrienes and their methylated aromatic isomers.

Pyrolysis of BCH in the presence of a large excess of *n*-butane (*e.g.*, Run 2) gave no trace of pentanes or benzene while the major products of isomerization and reverse Diels-Alder reaction were obtained in the expected proportions (Table I). In order to establish that methylene would actually react with butane under these conditions, diazomethane was passed through the furnace at 475° in the presence of excess butane. These conditions are comparable to those used by Rice and Glasebrook,[5] who established that methylene was formed at these temperatures in the presence of butane. In their experiments,[5] a tellurium mirror was removed and a red $(CH_2Te)_n$ polymer was formed, but the hydrocarbon products were not examined. Table II lists our data for the reaction of methylene with butane at 475°.

The data in Table II show that methylene reacts with *n*-butane at 475° to give a mixture of *n*-pentane and isopentane. Aside from Run 10, the aver-

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[1] Technical data supplied on request by the Shell Chemical Corp., New York, N. Y.

[2] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **72**, 2305 (1950).

[3] W. von E. Doering and F. L. Detert, *J. Am. Chem. Soc.*, **73**, 876 (1951).

[4] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **75**, 297 (1953).

[5] F. O. Rice and A. L. Glasebrook, *J. Am. Chem. Soc.*, **56**, 2381 (1934).