table. In each case the underlined olefin was completely reduced before any reduction of the other olefin. The catalyst showed no pronounced specificity toward mixtures of di- and tri-substituted olefins or toward mixtures of symmetrically and asymmetrically disubstituted olefins.

Ruthenium hydrogenated acetylenes readily but showed no selectivity. *Sym*-diphenylacetylene gave, on absorption of one mole of hydrogen, a mixture of starting material and diphenylethane.

In all of these experiments water was used as a solvent. Solvents for ruthenium hydrogenations at low pressure and room temperature seem to be virtually limited to water, water–acetic acid, or water-alcohol mixtures. Occasionally methanol or ethanol may be used satisfactorily. Ruthenium hydrogenations usually show a variable, and sometimes lengthy, induction period. This induction period can usually be eliminated entirely by shaking the catalyst and solvent together with hydrogen at room temperature and atmospheric pressure for an hour or two before adding the substrate.

EXPERIMENTAL

Competitive hydrogenation. One hundred ml. of water, 500 mg. of 5% ruthenium on carbon, and 10.0 ml. (0.064 mole) each of 1-octene and 2-octene were shaken at 32° and 42 p.s.i.g. After an induction period of 2 hr. during which time no hydrogen was absorbed, 0.064 mole of hydrogen was taken up in 20 min. The temperature rose from 32° to 35°. The shaker was stopped, the mixture filtered, the aqueous layer saturated with sodium chloride, and the organic layer separated and dried over sodium sulfate. The infrared spectrum of the product was identical with one of an equimolar mixture of 2-octene and octane. All other hydrogenations followed the same procedure, except that frequently the catalyst was shaken with hydrogen for 1 hr. before adding the substrates.

The catalyst was a commercial preparation, manufactured by Engelhard Industries, of 5% reduced metal on Norit.

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Relative Acidities of Butyrophenone and α-Ethylbutyrophenone[1]

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The ethylation of butyrophenone enolate gives a 90% yield of α-ethylbutyrophenone but no α,α-diethylbutyrophenone. Two factors contribute to this result: the relative rates, k_1 and k_2, for the alkylation of the two enolates and the equilibrium constant, K, for the reaction of butyrophenone enolate with α-ethylbutyrophenone.

$$\mathrm{PhCOCHEt^- + EtX \xrightarrow{k_1} PhCOCHEt_2 + X^-}$$

$$\mathrm{PhCOCHEt^- + PhCOCHEt_2 \overset{K}{\rightleftarrows} PhCOCH_2Et + PhCOCEt_2^-}$$

$$\mathrm{PhCOCEt_2^- + EtX \xrightarrow{k_2} PhCOCEt_3 + X^-}$$

In excess ethyl iodide, independent measurements of specific rates for the alkylations gave $k_1/k_2 = 3.5$. Also, a preliminary experiment indicated that the reaction of sodio-butyrophenone with α-ethylbutyrophenone occurred to only a small extent in 26 hr. in ether solution.[3] There was some doubt as to whether equilibrium had been established in this time, for the reaction of this ketone with sodium triphenylmethide was known to be slow.

The equilibrium has now been approached from both directions and the butyrophenone anion has been studied when paired with both sodium and lithium cations. Equilibrium mixtures were quenched in deuterium oxide and the concentrations of the resulting four ketones determined by infrared spectroscopy. The reactions of both ketone-enolate pairs in equal initial concentrations gave product mixtures with almost identical absorption curves. The equilibrium as written is at least 90% to the left. The concentration equilibrium constant (K) at 30° in ethyl ether is $\lesssim 0.02$, a value which corresponds to at least two pK units difference in acidity for the two ketones. This value was not changed within the limits of the experimental error when lithium was substituted for sodium in the enolate.

These results are in accord with the acid-weakening effects of alkyl groups in other weakly acidic organic compounds.[4] The effect of the α-ethyl group in lowering the acidity of butyrophenone is essentially the same as the 50–100-fold lowering found for this group when in the *alpha*- position of malonic ester in ethanol solution.[5]

EXPERIMENTAL

All operations involving enolates were carried out at 30.00 ± 0.05° under nitrogen in an apparatus described previously.[3]

Materials. Anhydrous ether was Mallinckrodt analytical reagent distilled from ethyl Grignard reagent and stored under a slight positive pressure of nitrogen. The preparations of sodium triphenylmethide, butyrophenone and α-ethylbutyrophenone have been described.[3] Lithium hydride was obtained from Maywood Chemical Co. and ground to a powder in a nitrogen atmosphere. Deuterium oxide (>99.5%) was obtained from the Stuart Oxygen Co.

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[1] Supported in part by a grant from the National Science Foundation.

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[3] H. D. Zook and W. L. Rellahan, *J. Am. Chem. Soc.*, **79**, 881 (1957).

[4] J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932); W. K. McEwen, *J. Am. Chem. Soc.*, **58**, 1124 (1936); A. A. Morton, *Chem. Revs.*, **35**, 11 (1944).

[5] R. G. Pearson, *J. Am. Chem. Soc.*, **71**, 2212 (1949).

Butyrophenone-α-d and α-ethylbutyrophenone-α-d. To 4.05 g. (0.0273 mole) of butyrophenone was added 210 ml. (0.0273 mole) of 0.130*M* ethereal sodium triphenylmethide. The color change from deep red to light yellow was rapid and the end point was sharp when the calculated volume had been added. The enolate solution was stirred for 3 hr. with 1.5 ml. (0.075 mole) of deuterium oxide. The ether layer was washed well with water and distilled through a 6-plate column to give six fractions, 3.7 g., 90%, of butyrophenone-α-*d*, b.p. 61–62° at 2 mm., n_D^{25} 1.5175. The infrared spectrum contained characteristic peaks at 4.63μ and 11.10μ which were lacking in the spectrum of butyrophenone. Several major peaks characteristic of butyrophenone were missing.

The conversion of α-ethylbutyrophenone to its enolate is a slow reaction. An end point was obtained when stoichiometric amounts of ketone and sodium triphenylmethide were stirred for several hours at 30°. The enolate from 4.07 g. (0.0231 mole) of ketone was stirred for 16 hr. with 2 ml. (0.10 mole) of deuterium oxide to give seven fractions, 3.5 g., 83%, of α-ethylbutyrophenone-α-*d*, b.p. 72–73.5° at 1 mm., n_D^{25} 1.5093. The infrared spectrum contained characteristic peaks at 4.65μ and 11.22μ which were lacking in the spectrum of α-ethylbutyrophenone. Major peaks characteristic of this ketone were lacking. All spectra were determined in carbon tetrachloride solution. The spectrum of the deuterated ketone was unchanged by shaking an ethereal solution with dilute aqueous sodium hydroxide for 30 min. at room temperature. This experiment shows the absence of H-D exchange during the washing procedure used in the equilibrium studies.

Equilibrium studies. The reaction of sodio-α-ethylbutyrophenone with butyrophenone is typical. The enolate was prepared from 5.29 g. (0.0301 mole) of the ketone and 203 ml. (0.0301 mole) of 0.148*M* ethereal sodium triphenylmethide. The addition with stirring to give a satisfactory end point required 1 hr. The solution was stirred for an additional 3 hr. after which 4.50 g. (0.0304 mole) of butyrophenone was added. After 28 hr., the reaction was quenched by the addition of 4 ml. of deuterium oxide. The ether layer was washed with five 10-ml. portions of water, the last of which was neutral to litmus. The solution was dried over Drierite and diluted with carbon tetrachloride. All of the ether and a portion of the carbon tetrachloride were removed through a short column, and the residue was diluted to 50.0 ml. with carbon tetrachloride for infrared analysis.

In the reverse process, 0.026 mole of sodio-butyrophenone was stirred for 26 hr. with 0.026 mole of α-ethylbutyrophenone and quenched with 0.10 mole of deuterium oxide.

Lithio-butyrophenone was prepared by stirring and refluxing for 5 days a concentrated ethereal solution of the ketone with excess powdered lithium hydride. The solution was filtered through sintered glass and diluted to 0.107*M* with anhydrous ether. A solution of 181 ml. (0.019 mole) of the enolate was stirred for 117 hr. with 3.42 g. (0.019 mole) of α-ethylbutyrophenone, the reaction quenched with 4 ml. of deuterium oxide and extracted as described.

Spectra were measured on a Perkin-Elmer Model-21 spectrophotometer. The four ketones and triphenylmethane were found to obey Beer's law at the wave lengths used for analysis. When triphenylmethane was present, the concentration of this hydrocarbon was estimated by its absorbance at 6.69μ, a wave length at which the absorbances of the four ketones are negligible. The amounts of triphenylmethane obtained agreed within 3% with those calculated from the quantities of sodium triphenylmethide employed. Spectra of the product mixtures starting with equal concentrations of either ketone-enolate pair were practically identical. The equilibrium is far to the left as indicated by the characteristic peaks of butyrophenone and α-ethylbutyrophenone-α-*d* which appear as small shoulders on the strong peaks of α-ethylbutyrophenone and butyrophenone-α-*d*. Absorbances were measured at peaks characteristic of each of the four ketones. These absorbances were corrected for absorbance due to triphenylmethane when present. Solution of four simultaneous equations gave the equilibrium concentrations from which values of K ranging from 0.006 to 0.02 were calculated for both forward and reverse processes. The equilibrium is too far to the left to obtain a more precise value for the equilibrium constant from these data.

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Use of Girard's Reagent "T" in the Separation of Derivatives of Chlorophylls *a* and *b*

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In view of the continuing interest in the chemistry of chlorophyll, we wish to report a new method for the separation of mixtures of *a* and *b* derivatives. The large scale preparative methods employed in this field separate chlorophyll derivatives according to their hydrochloric acid number[1] and their behavior toward buffers of different *p*H. The latter indicates the number of free carboxylic acid groups present.[2] In the method reported here, Girard's reagent "T" (carboxymethyltrimethylammonium chloride hydrazide)[3] is employed to resolve mixtures into groups of *a* compounds and *b* compounds, irrespective of their hydrochloric acid number or the number of carboxylic acid residues present. The 3-formyl group of the *b* compounds reacts readily with this reagent to form a water soluble derivative, whereas members of the *a* series, even those possessing a keto group, *i.e.*, pheophorbide *a* (I, R = CH_3; R′ = H) or purpurin 7*a* trimethyl ester (II, R = C(O)—$COOCH_3$) react very slowly if at all.

The experimental procedure is as follows: A mixture of *a* and *b* compounds containing about 15 mg. of the *b* member is dissolved in 30 ml. of a 90:10 (v/v) mixture of 95% ethanol:glacial acetic acid containing 150 mg. of Girard's reagent "T". The mixture is refluxed under nitrogen for 5 min., cooled, and poured into 1 l. of peroxide-free ether. (If refluxing is continued indefinitely some of the *a* derivative, if it possesses a keto group, does react.) This is then extracted with small (100 ml.) portions of distilled water until the aqueous extract is colorless. The *a* derivative, free of even traces of *b* contamination, remains in the ether layer. Partial hydrolysis of esterified compounds may occur, but treatment with diazomethane is sufficient to re-esterify them completely. The *b*

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[1] R. Willstätter and A. Stoll, *Investigations on Chlorophyll*, translated from the German by F. M. Schertz and A. R. Merz, The Science Press Printing Co., Lancaster, Pa., 1928, pp. 237–245.

[2] M. J. Hendrickson, unpublished data.

[3] Purchased from Fisher Scientific Co.