but at temperatures of at least 20°, these intermediates undergo dehydrochlorination of reaction rates evidently faster than the rates of formation of the intermediates themselves. Such dehydrochlorination reactions produce heterocyclic phosphorus compounds predominantly, with formation of five- and six-membered heterorings and, possibly, ten-membered rings (structures II and III). The formation organic, five-membered rings (structure II) evidently is favored by increased electron-attracting power of the halophenyl group as well as by increasing nucleophilicity of the dinucleophile participating. The formation of inorganic, six-membered P—N rings appears to be hindered by increasing electrophilicity of the Ar group. Electron withdrawal by this group from the hydrazine nitrogens may decrease the extent of hydrogen-hydrogen repulsion, which is considered to be the cause for fixation of the hydrazine molecule in *trans* position.[13] With acquisition of free rotation about the N—N axis, hydrazine becomes more likely to form nonheterocyclic polycondensation products instead of heterocyclics of structure III.

EXPERIMENTAL

The *O*-aryl phosphorodichloridothioates employed were of a quality as described previously,[1] while the dinucleophiles were anhydrous, commercial grade products.

Hydrazine derivatives. Anhydrous hydrazine (1.5 gram moles) was added dropwise over a period of 3 hr. at room temperature to an agitated solution prepared from 500 cc. of benzene and 0.5 gram mole of $C_6H_5OPSCl_2$, $C_6H_5OPOCl_2$, or $C_6H_5PSCl_2$, respectively. After completed reaction the reaction mixture was filtered and the solid thus isolated was dissolved in ethanol. Addition of water to this solution gave the crude main product which was recrystallized from methanol. The products obtained showed yields, melting points and analyses as given in Table I. The molecular weights were determined ebullioscopically as indicated in this table.

The compound, $C_6H_5OPS(NHNH)_2PS.OC_6H_5$, was also prepared by dropwise addition of triethylamine (0.225 gram mole) to an agitated solution of $C_6H_5OPSCl_2$ (0.1 gram mole) and $C_6H_5OPS(NHNH_2)_2$ (0.1 gram mole) in 400 cc. of toluene. After completed addition the mixture was slowly heated to reflux over a period of 5 hr., cooled to room temperature, and treated with 400 cc. of water. Separation of the solid phase from this mixture gave 36 grams of a white solid which was recrystallized from aqueous ethanol. Obtained was 33 grams of desired compound, melting at 184–185°. Its infrared analysis showed identity with the compound obtained from $C_6H_5OPSCl_2$ and anhydrous hydrazine.

Reactions involving ethylenediamine. One fourth of a gram mole of ethylenediamine was added dropwise to an agitated solution of one tenth of a gram mole of $ArOPSCl_2$ in 500 cc. of ethylene dichloride at such a rate that the reaction mixture maintained a temperature of +15 to +25° when cooled with ice water. After completed reaction the mixture was washed twice with 200 cc. of water in order to remove ethylenediamine hydrochloride formed. The ethylene dichloride layer was separated and evaporated. The evaporation residues were recrystallized from methanol and gave main products with yields, analyses, and melting points as given in Table II. The molecular weights of these products were determined ebullioscopically in methanol.

Reactions involving ethylene glycol. Mixtures of one-half gram mole of *O*-aryl phosphorodichloridothioate with one-fourth to one gram mole of ethylene glycol, as indicated in Table III, were heated with agitation for eight hours at 55° under a pressure of about 100 mm. The reaction mixtures were taken up with benzene and washed with water in order to remove unreacted glycol. The benzene layers were separated and evaporated. The evaporation residues were recrystallized from methanol to give main products with yields, analyses, and melting points as shown in Table IV. The molecular weights of these products were determined cryoscopically in benzene.

Edgar C. Britton Research Laboratory
The Dow Chemical Co.
Midland, Mich.

---

[13] W. J. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, **2**, 498 (1934).

Selective Hydrogenation of Olefins with Ruthenium

Lewis M. Berkowitz and Paul N. Rylander

Received November 5, 1958

In common with the other platinum metals, ruthenium can be a very active hydrogenation catalyst, but its use has been limited, so far, mainly to carbonyl reduction,[1] to ring hydrogenation, especially where hydrogenolysis is to be avoided,[2] and to reduction of acids to alcohols.[3]

We examined ruthenium catalysts for the hydrogenation of olefins and discovered the catalyst was very selective. Monosubstituted olefins were reduced preferentially in the presence of di- and trisubstituted olefins, as shown in the following

COMPETITIVE HYDROGENATION OF OLEFINS BY RUTHENIUM ON CARBON

4-Methyl-1-pentene and 2-methyl-2-pentene	Selective
4-Methyl-1-pentene and 2-methyl-1-pentene	Selective
4-Methyl-1-pentene and 2-octene	Selective
4-Methyl-1-pentene and cyclohexene	Selective
2-Methyl-2-pentene and 2-methyl-1-pentene	Not selective
2-Methyl-2-pentene and 2-octene	Not selective
2-Methyl-2-pentene and 1-octene	Selective
2-Methyl-2-pentene and cyclohexene	Not selective
2-Methyl-1-pentene and 2-octene	Not selective
2-Methyl-1-pentene and 1-octene	Selective
2-Methyl-1-pentene and cyclohexene	Not selective
2-Octene and 1-octene	Selective
2-Octene and cyclohexene	Not selective
1-Octene and cyclohexene	Selective

---

[1] G. Gilman and G. Cohn, *Advances in Catalysis*, Academic Press Inc., New York, 1957, Vol. IX, pp. 733–742.

[2] (a) L. C. Behr, J. E. Kirby, R. N. MacDonald, and C. W. Todd, *J. Am. Chem. Soc.*, **68**, 1296 (1946). (b) A. E. Barkdoll, D. C. England, H. W. Gray, W. Kirk, Jr., and G. M. Whitman, *J. Am. Chem. Soc.*, **75**, 1156 (1953). (c) M. Freifelder and G. R. Stone, *J. Am. Chem. Soc.*, **80**, 5270 (1958).

[3] T. A. Ford, U. S. Patent **2,607,807** (August 19, 1952).

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.

Chemical Research Laboratories
Engelhard Industries, Inc.
Newark, N. J.

Relative Acidities of Butyrophenone and α-Ethylbutyrophenone[1]

W. L. Rellahan,[2] W. L. Gumby, and H. D. Zook

Received November 6, 1958

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.

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

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

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

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.

---

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

[2] Du Pont Postgraduate Teaching Assistant, The Pennsylvania State University, 1955–56.

(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).