

that the magnitudes of the equilibria constants are determined by considerations of potential energy alone. It is clear from the observed large variations in ΔS° that this is not the case and that, in fact, the kinetic energy changes accompanying complex formation are not uniformly the same throughout this series. Under these conditions it becomes hopeless to attempt to correlate structure and reac-

tivity toward complex formation in terms of potential energy considerations alone. The changes in equilibrium constant resulting from a particular substituent could stem from a whole series of effects amongst which we might list polar or inductive effects, resonance effects, steric hindrance effects, polarizability effects and solvent effects.

NORTH ADAMS, MASS.

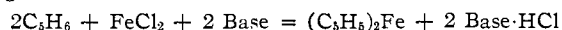
NOTES

A New Preparation of Bis-cyclopentadienyl-Metal Compounds

By J. M. BIRMINGHAM, D. SEYFERTH AND G. WILKINSON
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Three major types of reactions have been used to prepare bis-cyclopentadienyl-iron(II) and other bis-cyclopentadienyl-metal compounds: (a) the reaction of a cyclopentadienyl organometallic reagent: C_5H_5MgBr in benzene¹ or C_5H_5Na in tetrahydrofuran² with transitional metal halides or acetylacetonates, or C_5H_5K in liquid ammonia with a metal thiocyanate.³ Bis-indenyl derivatives of Fe and Co also have been prepared by similar reactions⁴; (b) the reaction of cyclopentadiene vapor with a metallic iron catalyst^{5a} or ferrous oxide at 350°,^{5b} and (c) the reaction of cyclopentadiene vapor with a metal carbonyl.⁶

Method a depends upon the acidic character of the methylene hydrogen of cyclopentadiene which enables the formation of an organometallic derivative with the evolution of hydrogen in the reaction with Na or K, or in the case of the Grignard reagent, where cyclopentadiene reacts with C_2H_5MgBr , of ethane. The dissociation constant of the acidic hydrogen of cyclopentadiene is very small; the pK value for indene has been estimated to have a minimum value of 21⁷ and the minimum pK value for cyclopentadiene should be slightly lower.⁸ Consideration of this slight acidity of cyclopentadiene suggested that a reaction of cyclopentadiene with a metal halide in the presence of a hydrogen halide acceptor might be an alternate route for the preparation of bis-cyclopentadienyl-metal compounds, e.g.



We have found that such reactions do indeed give small yields of ferrocene and of bis-cyclopentadien-

- (1) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).
- (2) G. Wilkinson and F. A. Cotton, *Chemistry and Industry*, 307 (1954).
- (3) E. O. Fischer and R. Jira, *Z. Naturforsch.*, **8b**, 217 (1953).
- (4) (a) P. L. Pauson and G. Wilkinson, *THIS JOURNAL*, **76**, 2024 (1954); (b) E. O. Fisher, *et al.*, *Z. Naturforsch.*, **8b**, 692, 694 (1953).
- (5) (a) S. A. Miller, J. A. Tebbott and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952); (b) G. Wilkinson, unpublished observation.
- (6) (a) G. Wilkinson, *THIS JOURNAL*, **76**, 209 (1954); G. Wilkinson, P. L. Pauson and F. A. Cotton, *ibid.*, **76**, 1970 (1954).
- (7) W. K. McEwen, *ibid.*, **58**, 1124 (1936).
- (8) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

yltitanium(IV) chloride,⁹ $(C_5H_5)_2TiCl_2$. As hydrogen halide acceptors, triethylamine, diethylamine, pyridine and sodium methoxide have been used. The formation of $FeCl_2$ -amine addition compounds that are insoluble in the solvents tried is a competing reaction that has thus far prevented good yields. Sodium methoxide seems to cause polymerization of the cyclopentadiene. It is, however, significant that bis-cyclopentadienyl-metal compounds are formed under these conditions; in the absence of a hydrogen halide acceptor, none of the desired product could be detected.

Experimental

(1) An equimolar mixture of $(C_2H_5)_3N$ and C_5H_6 was slowly added to anhydrous $FeCl_2$ with rapid stirring under a nitrogen atmosphere. Benzene was then added and the mixture was stirred overnight. The reaction mixture was filtered and the yellow filtrate was allowed to evaporate slowly. The yellow acicular crystals that separated were identified as ferrocene by infrared spectrum and melting point. A yield of about 4% was thus obtained. Variation of the base— $(C_2H_5)_3NH$, C_5H_5N , $NaOCH_3$ —also gave similar yields. The use of ferrous acetate in place of the chloride with the above bases gave ferrocene but did not improve the yield.

(2) A benzene solution of $TiCl_4$ was added slowly with vigorous stirring to an equimolar mixture of $(C_2H_5)_3N$ and C_5H_6 . The mixture was stirred overnight. Removal of the solvent from the red reaction mixture, extraction of the resulting residue with chloroform, and slow evaporation of the extracts yielded red crystals. Recrystallization from toluene gave pure $(C_5H_5)_2TiCl_2$, identified by its infrared spectrum. Yields of about 3% were obtained with triethylamine, diethylamine or pyridine. Again, serious competing reactions were the formation of insoluble $TiCl_4$ -amine complexes and polymerization of the cyclopentadiene.

(9) G. Wilkinson and J. M. Birmingham, *THIS JOURNAL*, **76**, in press (1954).

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

The Pyrolysis of Methyl Ethyl Ketone Cyanohydrin Acetate

By EARL C. CHAPIN AND RICHARD F. SMITH

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The pyrolysis of unsymmetrical aliphatic acetates has been reported¹ to yield the olefin with the least number of alkyl groups attached to it.

(1) W. J. Bailey and C. King, Abstracts of the 122nd Meeting of the American Chemical Society, 1952 p. 3M.

Although the dehydration of methyl ethyl ketone cyanohydrin has been reported² to yield a mixture of isomers, it was believed that the pyrolysis of the acetate might afford a single product, α -ethacrylonitrile. However, pyrolysis of the acetate on pulverized clay plate at 420–480° afforded a mixture of the desired α -ethacrylonitrile and its isomer, α -methylcrotononitrile.³

The infrared spectrum of the main fraction of the pyrolysis product possessed bands at 11.90 and 9.60 μ . These bands were not present in the spectrum of a sample of α -ethacrylonitrile which was prepared by the dehydration of α -ethacrolein oxime.⁴ Absorption near 11.90 μ has been attributed⁵ to 1,1,2-trisubstituted ethylenes, hence the presence of α -methylcrotononitrile was indicated. Refractionation afforded a poor yield of pure α -ethacrylonitrile which was devoid of infrared absorption at 11.90 and 9.60 μ .

The α -methylcrotononitrile was not isolated, but its presence was also indicated by the isolation of tiglic acid from basic hydrolysis of a higher boiling fraction of the pyrolysate.

Only red viscous oils were obtained when attempts were made to polymerize the α -ethacrylonitrile by conventional procedures.⁶

Experimental

Methyl Ethyl Ketone Cyanohydrin.—This compound was obtained in 76% yield by the procedure described in "Organic Syntheses"⁷ for the preparation of acetone cyanohydrin, b.p. 87–88° (17 mm.), n_D^{20} 1.4119.

Methyl Ethyl Ketone Cyanohydrin Acetate.—The cyanohydrin was acetylated by the slow addition (with stirring) to an equimolar quantity of acetic anhydride which contained a few drops of sulfuric acid. It was found necessary to neutralize the sulfuric acid with a few pellets of sodium hydroxide and distill the reaction mixture at reduced pressure as soon as the heat of reaction had subsided. The acetate was obtained in an 83% yield as a colorless oily liquid, b.p. 90–91° (16 mm.), n_D^{20} 1.4111.

Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.6; H, 7.9; N, 9.9. Found: C, 59.5; H, 7.9; N, 10.3.

Pyrolysis of Methyl Ethyl Ketone Cyanohydrin Acetate.—The pyrolysis chamber was constructed essentially as that described by J. Dvorak.⁸ Pulverized clay plate was used as the packing and the temperature was measured by an iron-constantan thermocouple.

A slow stream of nitrogen was passed through the chamber and the acetate (800 g.) was pyrolyzed at 420–480° over a 12-hr. period. The pyrolysate was washed with excess aqueous sodium carbonate and distilled through a 30-cm. helix-packed column to obtain 321 g. (70%) of a mixture of α -ethacrylonitrile and α -methylcrotononitrile (b.p. 110–

130°). This mixture was fractionally distilled through an electrically heated column (120 cm. \times 20 mm.) which was packed with glass helices. Thirteen fractions were cut with a 7–1 reflux ratio and a constant rise in boiling point and refractive indices was observed. Infrared analyses of the main three cuts (total of 159.8 g., b.p. 111–114°) indicated contamination with α -methylcrotononitrile. This material (140 g.) was redistilled through an electrically heated, helix-packed column (120 cm. \times 15 mm.). Employing a 15–1 reflux ratio, 68.0 g. of pure α -ethacrylonitrile was obtained, b.p. 111.9–112.9°, n_D^{20} 1.4118.

Anal. Calcd. for C_5H_7N : C, 74.0; H, 8.7; N, 17.3. Found: C, 73.9; H, 8.7; N, 17.3.

Hydrolysis of a 128–139° Pyrolysis Fraction.—The mixture (10 g.) was treated with a solution of 15 g. of sodium hydroxide, 20 cc. of water and 40 cc. of ethanol. Methanol was added to form a homogeneous solution and the reaction mixture was refluxed for 24 hr. The alcohol was removed by distillation and the residue was cautiously acidified with 50% sulfuric acid to yield a sharp smelling yellow liquid. The organic material was separated and the aqueous solution was extracted with 50 cc. of chloroform in small portions. Combination of the organic material and distillation of the chloroform yielded a yellow liquid which was dissolved in 250 cc. of boiling water. Ice cooling and scratching yielded 0.80 g. of tiglic acid, as white needles, m.p. 63–64° (uncor.), reported⁹ m.p. 64.5°, neut. equiv. calcd. 100, found 103.

α -Ethacrylic acid is reported¹⁰ as a liquid, m.p. –16°.

(9) A. Michael and J. Ross, *THIS JOURNAL*, **55**, 3612 (1933).

(10) W. G. Young, R. T. Dillon and H. J. Lucas, **51**, 2532 (1929).

MONSANTO CHEMICAL COMPANY
PLASTICS DIVISION
SPRINGFIELD, MASS.

Preparation of Amines by Low Pressure Hydrogenation of Oximes

BY DON C. IFFLAND AND TEH-FU YEN

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Although the oximino group is reported to react with Raney nickel catalyst under milder conditions than most other groups,¹ the generality and usefulness of this conversion at low hydrogen pressures have not been established. Hydrogenation over Raney nickel at hydrogen pressures of 60 to 100 atmospheres has been widely employed^{2–5} with numerous aliphatic and aromatic aldoximes and ketoximes. On the other hand, low pressure hydrogenation of oximes has been infrequently reported and limited to the hydrogenation of isobutyraldoxime and butanone oxime at 4 atmospheres by Campbell and co-workers⁶ and 5-heptanone and 5-decanone oximes at one atmosphere by Buckley.⁴

In order to prepare authentic samples of aliphatic amines and to determine the general usefulness of low pressure hydrogenation, ten aliphatic ketoximes have been treated with hydrogen at two to three atmospheres pressure over Raney nickel catalyst. Primary amines were obtained in 43 to 85% yields and secondary amines were not encountered. In most cases, however, a neutral fraction was isolated and found to be the related ketone resulting from partial hydrolysis of the oxime.

(1) C. F. Winans and H. Adkins, *THIS JOURNAL*, **5**, 2051 (1933).

(2) R. Paul, *Bull. soc. chim.*, [5] **4**, 1121 (1937).

(3) M. Harispe and J. Pernin, *ibid.*, 660 (1950).

(4) G. D. Buckley, *J. Chem. Soc.*, 1494 (1947).

(5) E. Rohrmann and H. A. Shonle, *THIS JOURNAL*, **66**, 1519 (1944).

(6) K. N. Campbell, A. R. Sommers, J. F. Kerwin and B. K. Campbell, *ibid.*, **68**, 1557 (1946).

(2) P. Bruylants, *et al.*, *Bull. sci. acad. roy. Belg.*, [5] **16**, 721 (1930).

(3) NOTE ADDED IN PROOF.—The referee has informed us that pyrolysis of this ester on glass helices affords a single pure product, α -ethacrylonitrile in 73% yield and has suggested that the formation of the two isomers which we have observed may be due to the acidic character of the clay plate. The selective pyrolysis is described in the Ph.D. thesis submitted in 1953 to the Graduate School of Wayne University by J. J. Hewitt.

(4) C. S. Marvel, W. Miller and L. Chou, *THIS JOURNAL*, **72**, 5408 (1950).

(5) R. Rasmussen and R. Brattain, *J. Chem. Phys.*, **15**, 120, 130, 135 (1947).

(6) NOTE ADDED IN PROOF.—Since the receipt of this publication, our observation of the reluctance of α -ethacrylonitrile to readily homopolymerize has been corroborated by others who mention that this monomer would not readily polymerize with free radical or ionic initiators. This work is described by C. S. Marvel, *et al.*, *Ind. Eng. Chem.*, **46**, 804 (1954).

(7) "Organic Syntheses." Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 7.

(8) J. Dvorak, *Collection Czech. Chem. Commun.*, **15**, 909 (1951).