

in fact effect under appropriate conditions saturation of several, randomly chosen model olefins.

In general the reductions were carried out by stirring a solution of the unsaturated compound in an organic solvent with an azodicarboxylate salt and added carboxylic acid (two equivalents with respect to the azodicarboxylate to effect its decomposition) under nitrogen for three to twelve hours at room temperature. Reductions which were carried out in methanol with sodium azodicarboxylate (100% excess) and acetic acid gave the following results: elaidic acid to stearic acid (62% by infrared analysis and titration with iodine monobromide); oleic acid to stearic acid (51% by infrared spectra and titration), and quinine to dihydroquinine (78% by quantitative hydrogenation). Reduction of allyl alcohol in β -ethoxyethanol with potassium azodicarboxylate (20% excess) and octanoic acid catalyst gave 1-propanol (78% by gas chromatography and infrared spectra of the products, and similarly cyclohexene gave cyclohexane (10% by gas chromatography). Finally, a reduction of azobenzene in methanol with potassium azodicarboxylate (20% excess) and acetic acid catalyst gave a quantitative yield of hydrazobenzene, m.p. 125–126°, mixed m.p. 125–126.5° (less than 1% azobenzene by ultraviolet spectroscopy).

Although several mechanistic interpretations for these reductions present themselves, diimide is implicated. The utility of this substance as a reagent in the field of organic chemistry has not been recognized heretofore, but the potential for liberation of elemental nitrogen suggests that its reducing power should be substantial. Through the agency of azodicarboxylic acid salts, the reactivity with other types of materials is currently under investigation in this Laboratory.

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RECEIVED JULY 1, 1961

1-METHYL- π -ALLYLIRONTRICARBONYL CHLORIDE Sir:

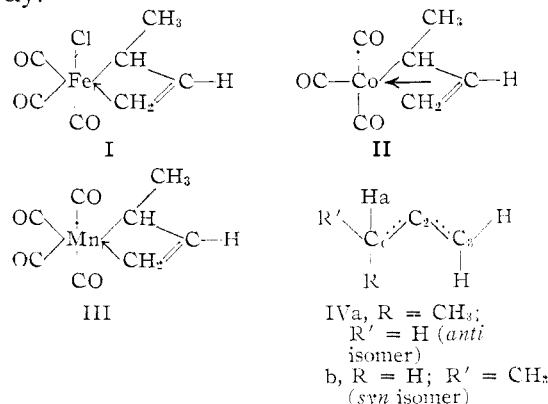
During the course of an earlier investigation, butadiene irontricarboxyl was found to react with anhydrous hydrogen chloride in room temperature to yield compound I as the only isolable organometallic. Yields ranged from 30 to 45%. Compound I was obtained as a yellow-brown solid, m.p. 58–60°, which decomposed rapidly at temperatures above the melting point, although it was relatively stable at room temperature. Purification could be effected by low temperature recrystallization from hydrocarbon solvents, or sublimation at room temperature and 0.05 mm. pressure. Elemental analysis showed I to be a 1:1 adduct of butadiene irontricarboxyl and hydrogen chloride. Magnetic susceptibility measurements showed the complex to be diamagnetic.¹ It was insoluble in,

(1) We wish to thank Professor S. Kirschner of Wayne State University, Detroit, Michigan, for these measurements.

and unaffected by, water and soluble in a broad variety of organic solvents.

Anal. Calcd. for $C_7H_7O_3ClFe$: C, 36.5; H, 3.14; Cl, 15.4; Fe, 24.3. Found: C, 36.8; H, 3.28; Cl, 15.6; Fe, 24.3.

The spectral characteristics of I are in complete accord with the proposed π -allyl structure, being basically the same as those exhibited by the cobalt² and manganese³ compounds, II and III, respectively.



The infrared spectrum of I has four metal carbonyl bands at 2041, 2000, 1961, and 1923 cm^{-1} . The band at 1520 cm^{-1} was assigned to the π -allyl C=C vibration. Absorptions are also present at 1385 cm^{-1} for the methyl group, and at 3086 and 3012 cm^{-1} for the =CH stretch.

The nuclear magnetic resonance spectrum of I in carbon tetrachloride (60 mc.) possesses four general bands whose integrated intensities are in the ratio of 1:2:1:3. The group of lines centered at 5.08 τ represents Ha⁴ (see structures IV). The pair of doublets centered at 5.83 and 7.10 τ represent the *syn* and *anti* hydrogens on C₃. Furthermore, the relative intensity of the doublet centered at 5.83 τ , plus an unsymmetrical broadening of the base on the high field side, indicate a masking of the lines predicted for the hydrogen on C₁. The doublet centered at 7.93 τ is from the methyl group hydrogens.

Among other products, a mixture of butenes is formed on thermal decomposition of I. This precise behavior is exhibited by the above mentioned cobalt compounds.⁵ When a solution of I in benzene is refluxed, ferrous chloride is precipitated and carbon monoxide is evolved smoothly until 50% of the theoretical amount has been given off. Gas evolution stops abruptly at this point. Butenes were evolved and trapped out. They were identified by mass spectrometry, vapor phase chromatography, and comparison of the bromination products with authentic samples. The reaction mixture was shown by vapor phase chromatography to contain only butadiene irontricarboxyl. The products formed suggest that the decomposi-

(2) H. B. Jonassen, R. I. Stearns, J. Kenttämä a, D. W. Moore and A. G. Whittaker, *J. Am. Chem. Soc.*, **80**, 2586 (1958).

(3) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. I. Muettterties and R. W. Howk, *ibid.*, **83**, 1601 (1961).

(4) The nomenclature used in this paper is that proposed by McClellan, *et al.*, in reference 3.

(5) C. L. Aldridge, H. B. Jonassen, and E. Pulkkinen, *Chem. and Ind.* 374 (1960).

tion of I occurs by disproportionation, half being dehydrohalogenated to butadiene irontricarbyl by the other half, which in turn decomposes to ferrous chloride, carbon monoxide, and but-2-enes. Such a mechanism is in accord with the stability of I in the melt or in solution.

It is interesting to note that the spectral data indicate that I is not a mixture of isomers, as was found to be the case with the cobalt complex.^{3,5} While such evidence is not definitely conclusive, it seems reasonable, from the mode of formation of I, that the geometry of the C₄ moiety in butadiene irontricarbyl might be maintained on conversion to the π -allyl complex. On this basis, it is suggested that I isolated as described above is the *anti* isomer (IVa).

An X-ray study of the structure of I is currently under way.⁶ Alternate synthetic routes for the preparation of I also are being investigated.

We are indebted to Dr. T. H. Coffield for suggestions leading to the carrying out of the initial reaction.

(6) X-Ray studies are being carried out by Professor L. L. Dahl of the University of Wisconsin.

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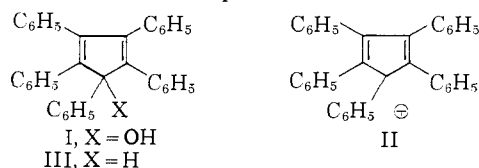
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RECEIVED JULY 17, 1961

THE REARRANGEMENT OF THE PENTAPHENYLCYCLOPENTADIENYL CATION¹

Sir:

Some time ago Ziegler² reported that the solution of pentaphenylcyclopentadienol (I) in concentrated sulfuric acid contains a purple species which he considered to be the pentaphenylcyclopentadienyl cation (II). He reported that this solution, poured into water, afforded a material which was "evidently the dimeric ether" of I. On the basis of spectroscopic studies Bloom and Krapcho³ concluded that the colored species was indeed II, but they did not further investigate the supposed dimeric ether. Because II is a derivative of the cyclopentadienyl cation in which the five-fold symmetry (D_{5h}) is retained it is of particular interest, since it is also predicted to have a (possible) triplet ground state. The stability and nature of such species is still an open question.⁴ Accordingly we have examined the sulfuric acid solution of I in some detail, and find that after a few seconds none of the cation II is present.



When the solution is poured into water a mixture of products is obtained whose exact composition varies with the strength of the acid and the

(1) This work was supported by a grant from the National Science Foundation, which is gratefully acknowledged.

(2) K. Ziegler and B. Schnell, *Ann.*, **445**, 266 (1925).

(3) S. M. Bloom and A. P. Krapcho, *Chem. and Ind.*, **882** (1959).

(4) For evidence on the possibility that tetraphenylcyclobutadiene has a triplet ground state, cf. H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2195 (1961).

time of standing, but in a typical run (96% H₂SO₄ for 2 min.) the products are pentaphenylcyclopentadiene (III), 25%, 1,2,3-triphenyl-1H-cyclopenta[1]phenanthrene (IV), 48%, 2,2,3,4,5-pentaphenyl-3-cyclopentene-1-one (V), 5%, and an amorphous oxygen-containing material which has not yet been identified, 21%. This latter does not form pentaphenylcyclopentadienyl chloride with hydrogen chloride in acetic acid under conditions in which I is quantitatively converted to the chloride,² and it gives a brown solution in sulfuric acid.

Compound IV, m.p. 220–221°, has mass 444,⁵ C₃₅H₂₄ (C, 94.26; H, 5.52). In the n.m.r. it has a one-proton singlet at 4.73 τ , a two-proton multiplet at 1.48 τ which is characteristic of the 4,5 hydrogens of a phenanthrene,⁶ and a twenty-proton multiplet at 2.85 τ . All together these data established the structure IV (or, less likely, IV'); the structure was confirmed by synthesis. Phenylcyclohexane with phenyllithium yielded VI, m.p. 222–223°,⁷ (C, 90.28; H, 5.31), which with thionyl chloride and pyridine yielded VII, m.p. 253–254°, (C, 87.47; H, 5.01). Treatment of VII with zinc in acetic acid afforded IV, identical with the previously obtained material. Structure IV' and an analogous one for the chloride VII, are ruled out by the ultraviolet spectra; λ_{max} (ϵ): VI, 251 (34,000), 281 (30,000), 415 (3,600); VII 250 (37,000), 352 (4,000); IV, 253 (40,000), 345 (12,000) m μ .⁸ The structure of the ketone (V), m.p. 194–195°, (C, 90.67; H, 5.69), is indicated by the fact that its formation is reversible, since on standing in sulfuric acid it affords III and IV, and by spectroscopic data indicating an unconjugated cyclopentenone⁹: infrared, 5.76 μ , ultraviolet, 261 m μ (13,000); in the n.m.r. it has one proton at 5.25 τ and twenty-five protons in a multiplet at 2.85 τ . Compound III was identified by comparison with an authentic sample.²

The spectrum previously assigned to II is simply the composite spectrum of III and IV in sulfuric acid. Thus III in sulfuric acid forms a bright orange solution, λ_{max} 502 (32,400) and 445 m μ (18,700) from which III is recovered quantitatively on dilution. The solution of IV in sulfuric acid has λ_{max} 520 (26,500) and 376 m μ (13,000). The spectrum of I in sulfuric acid, λ_{max} 516 m μ (20,500), can be reproduced quantitatively by an appropriate mixture of III and IV. The spectra are ascribable to one or the other of two possible processes:¹⁰ (a) protonation of III and IV to car-

(5) The mass spectrum was obtained through the courtesy of Dr. B. Dudenbostel of Esso Research Laboratories.

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, p. 248 ff.

(7) The compound of m.p. 255–257°, prepared by V. Abramov and P. Malskii, *J. Gen. Chem. U.S.S.R.*, **9**, 1533 (1939) by the reaction of phenylcyclohexane with phenylmagnesium bromide, is a ketone resulting from conjugate addition, and does not have the structure (VI) which they assigned.

(8) This slight change when the chloride is converted to a hydrocarbon is mirrored in the pentaphenylcyclopentadiene series; the ultraviolet spectrum of pentaphenylcyclopentadienol resembles that of the corresponding chloride and hydrocarbon.

(9) Cf. C. F. Allen, J. A. VanAllen and J. F. Tinker, *J. Org. Chem.*, **20**, 1387 (1955).

(10) S. I. Weissman, E. deBoer and J. Conradi, *J. Chem. Phys.*, **26**, 963 (1957); W. Aalbersberg, G. Hoijtink, E. Mackor and W.