

A minor side-reaction observed is dissociation of the intermediate II to the thioamide derived from I and the nitrile (or presumably iminochloride when $R^1 \neq H$) derived from the initially-added thioamide.¹⁸ This side-reaction can be utilized to advantage in the synthesis of 2-unsubstituted 4-mercaptopyrimidines from *o*-aminonitriles and thioformanilide by employing dimethylformamide-hydrogen chloride as the reaction medium. The thioamide derived from I by the exchange reaction is formylated by the dimethylformamide-hydrogen chloride mixture (a variant of the Vilsmeier-Haack procedure) and the resulting *o*-formylaminothioamide then cyclizes under the reaction conditions to the same 4-mercaptopyrimidine obtained *via* the *m*-thiazine pathway pictured above. Improved yields are thus generally obtained.

(16) C. J. Cavallito, C. M. Martini and F. C. Nachod, *THIS JOURNAL*, **73**, 2544 (1951).

(17) M. R. Atkinson, G. Shaw, K. Schaffner and R. N. Warrener, *J. Chem. Soc.*, 3847 (1956).

(18) E. C. Taylor and J. A. Zoltewicz, *THIS JOURNAL*, **82**, 2656 (1960).

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CATALYSIS OF THE DIELS-ALDER REACTION

Sir:

The recent report¹ that certain Diels-Alder reactions are accelerated by aluminum chloride prompts us to outline the results of our own investigations, which are the subject of a patent.² We found that in the presence of catalysts of the Friedel Crafts type, for example aluminum chloride, stannic chloride, boron trifluoride, ferric chloride, titanium tetrachloride, *etc.*, a number of Diels-Alder additions could be effected under much milder conditions than those required in the absence of such catalyst.

A good example of this catalytic effect was shown in the reaction of butadiene with methyl vinyl ketone to afford 4-acetylcyclohexene. This reaction was originally investigated by Petrov,³ who reported yields of 75-80% on heating the reactants at 140° in a sealed tube for 8-10 hours. We found that similar yields of the adduct could be obtained by adding methyl vinyl ketone at room temperature to an excess of butadiene in benzene (or similar solvent) in the presence of the above-mentioned catalysts. Less than one molar proportion of catalyst could be used; thus with 0.18 mol. equiv. of stannic chloride, a 73% yield of the adduct was obtained after reaction during 1 hour. In the absence of catalyst no adduct was formed under otherwise similar conditions.

The results of our investigations with a range of dienes and dienophiles may be summarized: Of the dienophiles which were studied in conjunction with butadiene, only acrolein, methyl vinyl ketone, and acrylic acid gave useful yields of the Diels-Alder

adducts under the above conditions. The general utility of the catalysts was obviously subjected to a further limitation by the readiness with which many dienes polymerize. In comparative experiments with methyl vinyl ketone and titanium tetrachloride, 2,3-dimethylbutadiene and cyclopentadiene yielded only polymer and dimer, respectively,⁴ whereas butadiene afforded 4-acetylcyclohexene in 63% yield, and anthracene⁵ gave a 46% yield of 9,10-(acetyleno)-9,10-dihydroanthracene,⁶ m.p. 151° (2,4-dinitrophenylhydrazones, m.p. 194-195°).

(4) With 2,3-dimethylbutadiene, the use of a milder catalyst, *vis.*, zinc chloride, enabled the adduct to be obtained in 16% yield.

(5) At 40-45°.

(6) Satisfactory analyses were obtained.

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CHEMISTRY OF THE METAL CARBONYLS. VII. PERFLUOROALKYL IRON COMPOUNDS¹

Sir:

A new class of transition metal compound is represented by perfluoroalkyl derivatives of iron. These perfluoroalkyl transition metal compounds have properties significantly different from those of perfluoroalkyl derivatives of main group metals, or alkyl compounds of transition metals.

Iron pentacarbonyl (29 g., 150 mmoles) and *n*-perfluoropropyl iodide (25 g., 85 mmoles) were heated under nitrogen at 45° for 21 hr. in benzene (50 ml.). The mixture then was cooled and evaporated to dryness. Sublimation (25° at 10⁻¹ mm.) of the solid residue onto a probe cooled to 0° gave 11.0 g. (28% yield) of red crystalline *n*-C₃F₇Fe(CO)₄I (m.p. 69-70° (dec.)), soluble in organic solvents. *Anal.* Calcd. for C₃F₇O₄IFe: C, 18.1; F, 28.7; I, 27.4; Fe, 12.1; mol. wt., 464. Found: C, 18.2; F, 28.5; I, 27.3; Fe, 12.5; mol. wt. (isopiestic), 480.

The perfluoropropyliron compound reacts with iodine at 150° with quantitative release of four moles of carbon monoxide per mole of complex. Perfluoropropyliron tetracarbonyl iodide, however, is not attacked by water or concentrated hydrochloric acid, and is much more stable than alkyl iron compounds such as C₅H₅Fe(CO)₂CH₃.²

Whereas perfluoroalkyl derivatives of main group metals react rapidly with base at moderate temperatures with quantitative release of their perfluoroalkyl groups as C_nF_{2n+1}H,³ perfluoroalkyl derivatives of transition metals studied are much less affected by base. A sample (0.722 g., 1.56 mmoles) of perfluoropropyliron tetracarbonyl iodide heated (100° for 65 hr.) with concentrated sodium hydroxide solution (2 ml.) gave carbon monoxide and only 14.7 cc. (S.T.P.) of heptafluoropropane (42% of theor.), identified by its infrared spectrum. Moreover, certain perfluoroalkyl transition metal compounds do not give the

(1) Previous article in this series, T. A. Manuel and F. G. A. Stone, *THIS JOURNAL*, **82**, 6240 (1960).

(2) T. S. Piper and G. Wilkinson, *J. Inorg. & Nuclear Chem.*, **3**, 104 (1956).

(3) H. C. Clark and C. J. Willis, *THIS JOURNAL*, **82**, 1888 (1960); H. D. Kaesz, J. R. Phillips, and F. G. A. Stone, *ibid.*, **82**, 6228 (1960).

(1) P. Yates and P. Eaton, *THIS JOURNAL*, **82**, 4436 (1960).

(2) Sir Robert Robinson and G. I. Fray, British Patent 835,840 (1960).

(3) A. A. Petrov, *J. Gen. Chem. U.S.S.R.*, **11**, 309 (1941).