

curred at  $x = 0.443$ . Substitution in the appropriate equation (ref. 5b, equation 7) gives 0.1 for  $K = ([Ni^{++}][N_2H_4])/([Ni(N_2H_4)^{++}]$ ). The stability constant of the dihydrazinate could not be determined because of the interfering absorption of the first complex in the same region. In addition precipitation prevented sufficiently high concentrations. The evidence is therefore only quantitative for the existence of the monohydrazine nickel(II) ion in solution.

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### Perfluorinated Grignard Derivatives

BY ALBERT L. HENNE AND WILLIAM C. FRANCIS

Since the recent disclosure by Haszeldine<sup>1</sup> that we had obtained perfluorinated Grignard derivatives, we have received repeated requests for experimental directions. The following general procedure, while not yet optimum, will permit others to proceed with practical results.

We have made our Grignard derivatives from iodides,  $C_nF_{2n+1}I$ , and most of the work was done with  $C_3F_7I$ . Contrary to a general impression, the formation of  $C_3F_7MgI$  is exceedingly easy; its stability is, however, so poor that complete decomposition occurs promptly at room temperature.

A clue to this behavior was obtained when the Grignard was prepared in an atmosphere of dry carbon dioxide. Under these conditions  $C_3F_7CO_2H$  resulted in 6 to 10% yield. When the reaction was carried out in a nitrogen atmosphere and later carbonated, little or no acid was obtained. At 0°, the Grignard is still unstable, but it is possible to form it in ether solution at this temperature, drop it promptly into water or a slurry of Dry Ice in ether<sup>2</sup> and isolate  $C_3F_7H$  or  $C_3F_7CO_2H$ , respectively, in 5 to 7% yields. These experiments show that perfluorinated Grignard reagents exist as such, and appear to react normally.

If Grignard formation is carried out at about -80° in an ether solution of  $C_3F_7I$  containing a suspension of magnesium and Dry Ice, a 45% yield of  $C_3F_7CO_2H$  is easily obtained, presumably improvable by refining the mechanical handling.

Reaction in a carbon dioxide atmosphere using the "extreme dilution" procedure usually applied to allylic halides appears promising, but at the present time the recommended procedure is the low-temperature reaction just described.

Pilot tests have shown that these procedures can be extended to reaction with the carbonyl function, and acetone gives the expected carbinol. More detailed information will be presented later.<sup>3</sup>

(1) R. N. Haszeldine, *Nature*, **167**, 139 (1951).

(2) A. S. Hussey, *THIS JOURNAL*, **73**, 1364 (1951).

(3) In a preprinted abstract for the New York Meeting of the A.C.S., September, 1951, Haszeldine states that perfluorinated Grignard Reagents appear to condense normally with a series of conventional functions (private communication).

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### The Synthesis of 4-Chloro-3-indoleacetic Acid

BY CORWIN HANSCH AND JOHN C. GODFREY

4-Chloro-3-indoleacetic acid has been synthesized by the procedure of Snyder and Pilgrim<sup>1</sup> for assess-

(1) H. R. Snyder and F. J. Pilgrim, *THIS JOURNAL*, **70**, 3770 (1948).

ment as a plant growth-regulator. This substance has been tested by the avena test as part of a program<sup>2</sup> to correlate plant growth activity with chemical structure. The compound was found by Dr. Robert Muir of the State University of Iowa to be active in promoting plant growth; his complete results will be published elsewhere. The starting point for the synthesis of the 4-substituted acid was 4-chloroindole<sup>3</sup> a generous sample of which was supplied by Dr. F. C. Uhle of Harvard University.

### Experimental

**4-Chloro-gramine.**—To 1.42 ml. of 25% aqueous dimethylamine cooled in an ice-bath was added 1 g. of cold acetic acid and 0.58 g. of cold 40% formalin. This solution was then poured onto 1.12 g. of 4-chloroindole, the beaker being rinsed with 1/3 ml. of water. The mixture was allowed to come to room temperature and after some shaking all of the chloroindole dissolved. This solution was allowed to stand overnight and then heated to 30–40° for 2 hours after which 1.35 g. of KOH in 10 ml. of water was added. The oil which separated crystallized quickly and after standing in an ice-bath 2 hours, the crystals were separated and dried. Dilution of the filtrate with the wash water caused more crystals to separate. Yield of crude chloro-gramine was 1.4 g., m.p. 135–143°. After crystallization from acetone the m.p. was 147.6–148.4°.

*Anal.*<sup>4</sup> Calcd. for  $C_{11}H_{13}N_2Cl$ : C, 63.31; H, 6.24. Found: C, 63.40; H, 6.50.

The picrate was prepared in ethanol solution and recrystallized from the same solvent; m.p. 157.4–158.6°.

*Anal.* Calcd. for  $C_{17}H_{16}N_2O_7Cl$ : C, 46.63; H, 3.66. Found: C, 46.60; H, 4.10.

**4-Chloro-3-indoleacetic Acid.**—To 0.91 g. of potassium cyanide dissolved in 1.7 ml. of water and 5.4 ml. of 95% ethanol was added 0.57 g. of 4-chloro-gramine. This mixture was heated under reflux for 98 hours and then diluted with 12 ml. of water. The resulting precipitate (presumably amide of 4-chloroindoleacetic acid) was removed by filtration (no free 4-chloroindoleacetic acid was obtained from this filtrate on acidification) and hydrolyzed by boiling with 2 *N* KOH for 4 hours. Acidification of the KOH solution caused a considerable precipitate of silicic acid and chloroindoleacetic acid. This precipitate and solution was evaporated to dryness and the residue extracted with ether. After evaporation of the ether the residue was crystallized from alcohol and ethylene chloride; yield 0.1 g., m.p. 179–180°.

*Anal.* Calcd. for  $C_{10}H_8O_2NCl$ : C, 57.28; H, 3.82. Found: C, 56.90; H, 4.30.

(2) C. Hansch and R. M. Muir, *Plant Physiol.*, **25**, 389 (1950).

(3) F. C. Uhle, *THIS JOURNAL*, **71**, 761 (1949).

(4) All analyses were made by C. F. Geiger of Chaffey College, Ontario, California.

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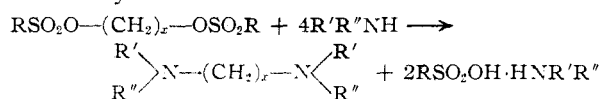
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### Preparation of N,N,N',N'-Tetrasubstituted Diamines

BY THOMAS M. LAAKSO AND DELBERT D. REYNOLDS

Recent investigations in our laboratory required the use of certain N,N,N',N'-tetrasubstituted diamines. A general method for their preparation is not described in the literature.

The method described here involves the reaction of glycol disulfonates with secondary amines as indicated by



R may be alkyl, aryl, and so forth; R' and R'' may