proton splittings is greater in the case of the deuterated compound. This fact is accounted for in the model we have presented by attributing a slightly larger ΔE (about 200 calories larger according to the present best estimate) to the deuterated system.

We are at present in the process of modifying our Strand Lab Model 601 X-band spectrometer so that we may follow the temperature variations in hyperfine splittings more precisely to get information about unpaired spin distribution in both ground and excited states. We point out that such an analysis would in many cases provide both the magnitude and the sign of coupling constants.

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RECEIVED MARCH 7, 1962

A NEW SYNTHESIS OF MONO- AND POLYCARBODIIMIDES

Sir:

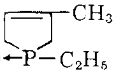
There are many simple, well-known condensation reactions which can be carried out on difunctional monomers with the production of linear polymers. However, those which can give polymers with sufficiently high molecular weight to be useful are quite limited in number.

We wish to call attention to a unique catalyzed condensation reaction in which an isocyanate is converted quantitatively to a carbodiimide

$$2RNCO \longrightarrow R{-}N{=}C{=}N{-}R + CO_2$$

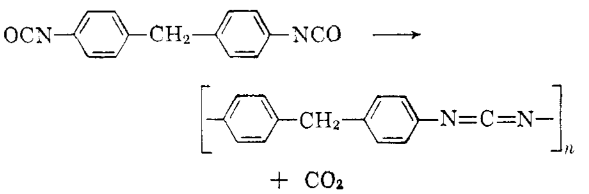
This reaction not only is suitable for the preparation in very high yield of a wide variety of mono-carbodiimides but, surprisingly, can be used to produce a new type of tough, high molecular weight condensation polymer in which the recurring unit is the —N=C=N— link.

The most active catalyst for this reaction, 1-ethyl-3-methyl-3-phospholine-1-oxide



was prepared according to McCormack.[1] An example of its use is the preparation of 4,4′-dinitrodiphenyl carbodiimide, a hitherto unreported compound. *p*-Nitrophenyl isocyanate (21.0 g., 0.128 mole) was melted and treated with 0.03 g. of catalyst at about 60°. Carbon dioxide was evolved almost explosively and in a matter of 1-2 min. the mixture had set to a crystalline mass. The last traces of carbon dioxide were removed *in vacuo* and 18 g. (100%) of a yellow crystalline solid melting at 165–170° was obtained. One recrystallization from petroleum ether–chloroform gave an analytical sample, m.p. 164–166°. *Anal.* Calcd. for $C_{13}H_8N_4O_4$: C, 54.9; H, 2.81; N, 19.7. Found: C, 54.8, 54.7; H, 2.88, 3.02; N, 19.9, 20.0.

To produce a polymer, the following procedure is typical. To a solution of about 20 g. of a diisocyanate in 150 ml. of a suitable solvent, such as benzene, xylene, carbon disulfide, was added about 0.03 g. of the catalyst. The polymerization proceeded smoothly in all cases studied at temperatures from 25 to 250°. At 250° the evolution of carbon dioxide was extremely fast, while at room temperature 24 hr. or more was required for completion of the polymerization. For example, polymerization of methylene bis-(4-phenyl isocyanate) in boiling xylene gave a tough, Nylon-like lump of polymer in four hours.



This was pressed at 250° to a clear, crystalline, orientable film with a tenacity of about 50,000 p.s.i. an initial modulus of 410,000 p.s.i. and an elongation of 20% at 25°.

The proposed structure of the polymers is based on (1) method of formation, (2) ultimate analyses, and (3) infrared analysis which in all cases showed the very characteristic N=C=N band at 4.76 microns.[2] In view of the reactivity of the carbodiimide link,[3] the polymers are remarkably inert to boiling acid, alkali and amines. This presumably is because of lack of penetration of the reagent.

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[1] W. C. McCormack, U. S. Patents 2,663,736-9 (Dec. 22, 1953).

[2] G. D. Meakins and R. J. Moss, *J. Chem. Soc.*, 993 (1957).

[3] H. G. Khorana, *Chem. Revs.*, **53**, 145 (1953).

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RECEIVED FEBRUARY 14, 1962

NEW, HIGHLY ACTIVE METAL CATALYSTS FOR THE HYDROLYSIS OF BOROHYDRIDE

Sir:

We wish to report that the treatment of aqueous solutions of platinum, ruthenium and rhodium salts with aqueous sodium borohydride produces finely-divided black precipitates which are exceedingly active catalysts for the hydrolysis of the borohydride ion.

It has been known since the original discovery of sodium borohydride[1] that aqueous solutions of the salt exhibit a remarkable stability to hydrolysis. The hydrolysis can be facilitated by acids, or by certain metal ions.[2] Among the metals investigated, iron, cobalt and nickel salts appeared to be most effective, with cobalt being superior to the other two. This discovery led to the development of sodium borohydride pellets containing a small quantity of cobalt chloride. Such pellets, placed in contact with water, rapidly liberated hydrogen, and thereby provided an easily portable source of the gas.[2]

In the course of examining the interaction of sodium borohydride with a number of heavy metals,

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[1] H. I. Schlesinger, H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **75**, 186 (1953).

[2] H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hocekstra and E. K. Hyde, *ibid.*, **75**, 215 (1953).