glycoprotein like that isolated from the plasma of tumor bearing mice is completely absent in the plasma of normal mice, and it seems probable that it is one of the constituents of α-globulin which increases in concentration during the tumor growth.

The observation that the addition of sulfate ester containing polysaccharides to normal human plasma gives the illusion of an increased α-globulin[26] made it necessary to analyze our α-globulins for sulfate esters. Both globulins were found to contain only very small amounts of sulfate sulfur, and the phenomenon of the increase of α-globulin during tumor growth appears to be unrelated to the interaction of polysulfates with normal plasma proteins.

**Biological Properties.**—The growth of transplanted Sarcoma 180 in mice of the strain C57BL/6 was affected neither by injection of the host with α-globulin from tumor bearing mice (simultaneously or prior to the transplantation), nor by addition of this α-globulin to the tumor cell suspension before implantation.

On the other hand, the α-globulin, isolated from tumor bearing mice, did not induce progressive growth of a transplantable tumor (Sarcoma I) in a host otherwise resistant to this tumor (mice of the C57BL/6 strain), *i.e.*, the α-globulin obtained from Sarcoma 180 bearing mice was not identical with or did not contain the "enhancing" or "XYZ" factor.[27,28]

**Acknowledgment.**—We wish to thank Professor Blix for his generous gift of crystalline sialic acid.

(26) P. Bernfeld, *Federation Proc.*, **13**, 183 (1954); **14**, 182 (1955).

(27) S. Flexner and J. W. Jobling, *Proc. Soc. Exper. Biol. Med.*, **4**, 156 (1907).

(28) G. D. Snell, A. M. Cloudman, E. Failor and P. Douglass, *J. Nat. Cancer Inst.*, **6**, 303 (1946).

BOSTON, MASSACHUSETTS

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# COMMUNICATIONS TO THE EDITOR

## THE SODIUM-DIBORANE REACTION

*Sir:*

Stock[1] by direct reaction between sodium and diborane obtained $Na_2B_2H_6$. More recent investigators[2] obtained $NaB_2H_6$ and showed by X-ray analysis that it contained sodium borohydride. Studies in this laboratory have clarified the nature of the sodium–diborane reaction and have established the identity of another product, the new compound $NaB_3H_8$.

Early in the present investigation it was discovered that ethers promote the reaction of sodium and diborane. In ethyl ether sodium, as amalgam, and diborane reacted completely in two days at room temperature, forming a product of composition $NaB_2H_6$. Rate studies indicated that the reaction in the initial stages involved two gram atoms of sodium per mole of diborane and that $Na_2B_2H_6$ was an intermediate. X-Ray and infrared analysis of $NaB_2H_6$ confirmed the presence of sodium borohydride and revealed an unidentified constituent, soluble in ethyl ether. Upon evaporation of ether solutions, white solids of composition $NaB_3H_8$ remained. Calcd. for $NaB_3H_8$: Na, 36.1; B, 51.1; hydrolyzable hydrogen, 141 mmole/g. Found: Na, 34.5 and 35.6; B, 52.6 and 51.5; hydrolyzable hydrogen, 137 and 142 mmole/g. The X-ray pattern of $NaB_3H_8$ was unique and well-defined. Further instrumental and chemical analyses of $NaB_2H_6$ gave no evidence of constituents other than sodium borohydride and $NaB_3H_8$. The experimental facts quite satisfactorily support the relationship

$$2Na + 2B_2H_6 \longrightarrow NaBH_4 + NaB_3H_8$$

On this basis, an 80% yield of $NaB_3H_8$ was obtained in one experiment. The relatively small quantity of product compared to reactor volume and quantity of amalgam made quantitative isolation difficult.

The compound $NaB_3H_8$ is quite soluble in water and in ammonia and is more resistant toward hydrolysis than is sodium borohydride. The solid is thermally stable at least to 200°. Solution of $NaB_3H_8$ in ethyl ether is accompanied by solvation; at 0° a hemi- and a mono-etherate were identified.

The sodium–diborane reaction is undoubtedly of greater complexity than that indicated by the equation, which does not specify probable reaction intermediates. However, the new compound, $NaB_3H_8$, may be expected as a product of reactions employing a variety of conditions. It is suggested that $NaB_3H_8$ be designated as sodium triborohydride. A detailed description of this and related investigations of the reaction of sodium with diborane will be submitted at a later date.

CALLERY CHEMICAL COMPANY
CALLERY, PENNSYLVANIA
WILLIAM V. HOUGH
LAWRENCE J. EDWARDS
ALBERT D. MCELROY

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(1) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(2) J. S. Kasper, L. V. McCarty and A. E. Newkirk, THIS JOURNAL, **71**, 2583 (1949).

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## LIGHT CATALYZED ORGANIC REACTIONS. IV.[1] THE OXIDATION OF OLEFINS WITH NITROBENZENE

*Sir:*

As a consequence of the previously reported synthesis of oxetanes by light induced addition of carbonyl compounds to substituted olefins,[2] we have investigated the reaction of nitrobenzene with

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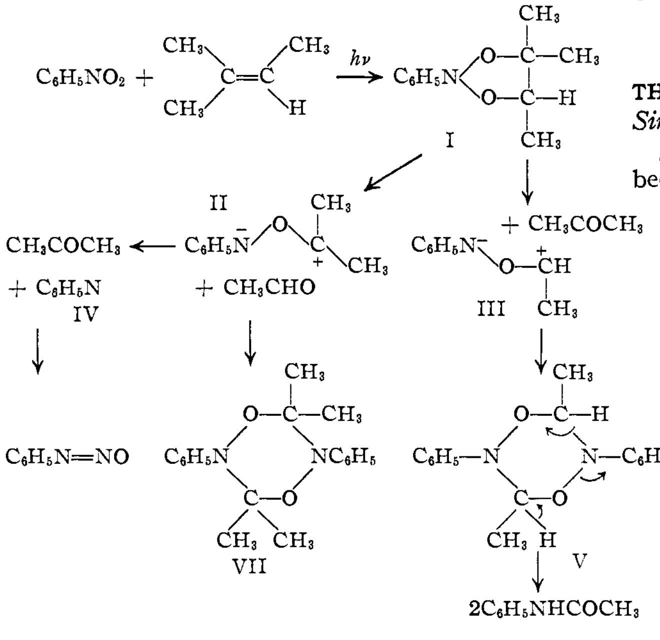
(1) Part of a program of research supported by a grant from the Godfrey L. Cabot Fund, Publication No. 61, M.I.T. Solar Energy Conversion Project.

(2) E. Paterno and G. Chieffi, *Gazz. chim. ital.*, **39**, 341 (1909); G. Büchi, C. G. Inman and E. S. Lipinsky, THIS JOURNAL, **76**, 4327 (1954).

olefins as a possible synthetic route to the unknown 1,3,2-dioxazolidines (I). The reactions outlined below demonstrate that addition of nitrobenzene does indeed occur, but that the expected primary products decompose mainly to carbonyl compounds and azobenzene.

A 1:4-mixture of nitrobenzene and 2-methyl-2-butene was irradiated at room temperature with a mercury resonance arc.[3] From the volatile portion of the reaction products, acetone (2,4-DNP, m.p. 124.5–125°) and acetaldehyde (dimedone derivative, m.p. 142–143°) were isolated (12%). After removal of starting material the following compounds were isolated by chromatography of the residue: N-phenylacetamide (VI), m.p. 114–115°; azobenzene, m.p. 66° and a neutral material (VII), m.p. 169–170°, $\lambda_{max.}$ 246 mμ (ε 10,600) infrared, no OH, no C=O, no C=N (*Anal.* Calcd. for $C_{18}H_{22}O_2N_2$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.40; H, 7.41; N, 9.37); mol. wt. calcd. 298, found 308. Refluxing VII with hydrochloric acid led to *p*-chloroaniline (m.p. 70–71°) and acetone (semicarbazone, m.p. 185–186°).[4]



When a 1:3-mixture of nitrobenzene and cyclohexene was irradiated, azobenzene (m.p. 66°) and adipaldehyde (dioxime, m.p. 170–172°; adipic acid, m.p. 150–152°) were formed in about 10% yield.

We wish to propose the following, mainly speculative, sequence of events to rationalize the formation of the products observed: (a) light catalyzed addition of nitrobenzene to the olefin to give intermediate I (similar to the one proposed by Splitter and Calvin, ref. 6); (b) fragmentation of I (possibly by a dark reaction) into two zwitterions (II and III) and the respective carbonyl compound, followed by (i), further decomposition to the carbonyl compounds and IV, which dimerizes to azobenzene, and (ii) dimerization of the zwitterions to the previously unreported heterocyclic derivatives (VII and V). Compound VII had no activated hydrogen atoms and might therefore be stable; V, however, decomposes into two molecules of N-phenylacetamide (VI).

The photolysis of nitrobenzene in the vapor phase has been studied and the products isolated were nitrosobenzene and *p*-nitrophenol.[5] Intramolecular, light induced oxygen transfer from nitro groups to double bonds, has been observed before.[6] The above, however, seems to be the first intermolecular change of this type reported. In conclusion we would like to point out the striking similarities between the products obtained in this oxidation and in the ozonization reaction.

[3] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

[4] The hydrolysis of O,N-substituted hydroxylamines has been investigated by J. Meisenheimer, *Chem. Ber.*, **52**, 1667 (1919), and by R. F. Kleinschmidt and A. C. Cope, THIS JOURNAL, **66**, 1929 (1944).

[5] S. H. Hastings and F. A. Matsen, THIS JOURNAL, **70**, 3514 (1948).

[6] *E.g.*, the light catalyzed conversion of *o*-nitrostilbenes to isatogens, J. S. Splitter and M. Calvin, *J. Org. Chem.*, **20**, 1086 (1955), and earlier literature cited therein.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY G. BUCHI
CAMBRIDGE, MASSACHUSETTS D. E. AYER

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## THE POLYMERIZATION OF *l*-PROPYLENE OXIDE

*Sir:*

*l*-Propylene oxide,[1] $[\alpha]^{21}_D$ +14.75° (ether), has been polymerized by shaking at 25° with powdered potassium hydroxide catalysis to produce a solid crystalline polymer, 88% yield, m.p. 55.5–56.5°, $\eta_{sp}/c$ = 0.141 (0.7%, benzene, 25°), $[\alpha]^{20}_D$ +25° ($CHCl_3$). *Anal.* Calcd. for $C_3H_6O$: C, 62.04; H, 10.41. Found: C, 62.19; H, 10.34. This is in contrast to the liquid polymer of about the same molecular weight ($\eta_{sp}/c$ = 0.129) produced from racemic oxide under the same conditions.[2]

The polymerization of *l*-propylene oxide in an equal volume of ether in a sealed tube at 80° for ten days, using 1–2% of a recently disclosed ferric chloride-propylene oxide complex catalyst,[3] produced a mixture of amorphous intermediate molecular weight optically inactive polymer (30%, $\eta_{sp}/c$ = 2.23) and crystalline high-molecular weight polymer (20%), m.p. 70–75°, $\eta_{sp}/c$ = 10.60, $[\alpha]^{20}_D$ + 23° ($CHCl_3$). The crystalline material separated from a 1–2% solution of mixed polymer in acetone on cooling to −30°.

From racemic monomer with this same iron catalyst under the same conditions, a 60% yield of amorphous and 30% yield of crystalline polymer were obtained. The latter had the same melting point, reduced viscosity, and X-ray diffraction spacings as the crystalline polymer from *l*-monomer but was optically inactive. This must mean that the racemic crystalline polymer consists of a mixture of all *d*- and all *l*-polymer molecules. The racemization involved in formation of the

[1] P. A. Levene and A. Walti, *J. Biol. Chem.*, **73**, 263; **75**, 325 (1927).

[2] C. C. Price and L. E. St. Pierre, 128th Meeting, Am. Chem. Soc., Minneapolis, Minn., Sept. 12, 1955.

[3] M. E. Pruitt and J. M. Baggett, U. S. Patent 2,706,181, April 12, 1955.