solids is plotted against the optical density at 440 mμ (Fig. 3) it is clear that far more carbon dioxide is produced per unit optical density at 100° than at 56.5°. The carbon dioxide-producing reaction therefore may not follow the same course at the two different temperatures, though the color-producing parts of the two reactions appear to be similar. This suggests the carbon dioxide liberation in amino acid–sugar reactions may not be essential for color production, which is substantiated by the fact that brown pigments retained after dialysis[6] contain less carboxyl carbon when browning occurs at 100° than when it takes place at 56.5°. It is significant that considerable amounts of carboxyl carbon from glycine become associated with the brown pigment produced.[5] CO_2 liberation may therefore take place subsequent to pigment formation.

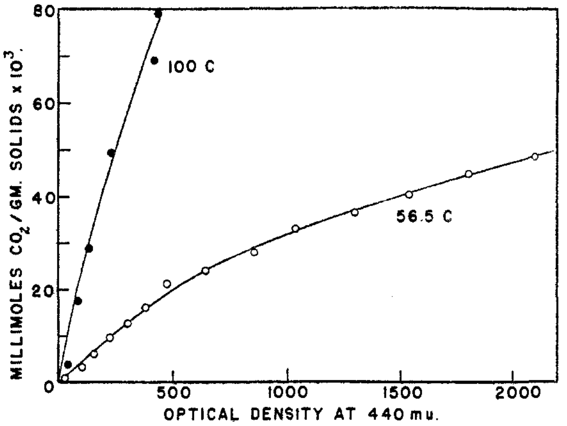

Fig. 3.—Carbon dioxide production in relation to pigment production at the two temperatures.

The results obtained with C^{14}-labeled glucose show that some CO_2 is derived from the sugar as well as the amino acid, Fig. 4. The major portion, well over 80%, is derived from the carboxyl group of the amino acid, as Maillard suggested, and somewhat less than 10% comes from the sugar. The rather unlikely possibility that the methyl carbon of the glycine contributes to the CO_2 will be checked, and the fate of the amino acid residue will be determined, through the use of methyl-labeled glycine.

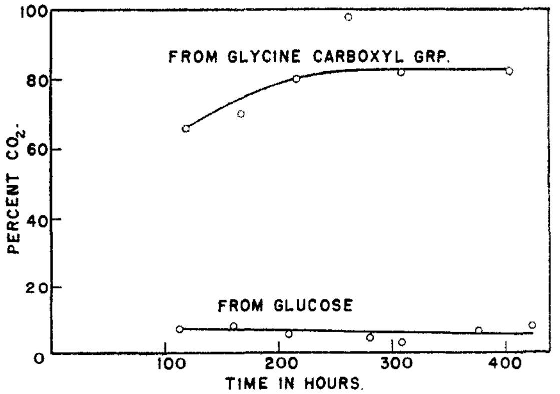

Fig. 4.—The percentages of carbon dioxide derived from glucose and glycine as a function of time.

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[6] C. O. Chichester, F. H. Stadtman and G. Mackinney, This Journal, **74**, in press (1952).

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N-Methyl-6,7,8-trimethoxy-1,2,3,4-tetrahydroisoquinoline

BY E. P. TAYLOR

RECEIVED MARCH 11, 1952

In an attempt to synthesize trichocereine, *i.e.*, N-dimethylmescaline, by methylation of mescaline with formic acid–formaldehyde, Reti and Castrillón[1] found that the product was a tetrahydroisoquinoline base. This has now been identified by Castrillón[2] as N-methyl-6,7,8-trimethoxy-1,2,3,4-tetrahydroisoquinoline. Oxidation of the hydrochloride to the known N-methyl-3,4,5-trimethoxyphthalimide confirms the structure of the base, which is claimed as a new compound. May I point out that this substance has already been prepared and described[3]: its constitution has been established by a Bischler–Napieralski reaction upon N-formylmescaline, followed by reduction of the methiodide of the resultant 6,7,8-trimethoxy-3,4-dihydroisoquinoline. In addition, reduction of the ethiodide of this base yielded the corresponding N-ethyl-1,2,3,4-tetrahydroisoquinoline.

(1) L. Reti and J. A. Castrillón, This Journal, **73**, 1767 (1951).

(2) J. A. Castrillón, *ibid.*, **74**, 558 (1952).

(3) E. P. Taylor, *J. Chem. Soc.*, 1153 (1951).

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The Reaction of Silyl Bromide with Magnesium

BY E. R. VAN ARTSDALEN[1] AND JEROME GAVIS

RECEIVED FEBRUARY 5, 1952

The preparation of compounds of the type SiH_3MgX, analogous to organic Grignard reagents, should offer many interesting new possibilities for syntheses of compounds containing the silyl group. Emeleus, Maddock and Reid[2] in conjunction with their studies on the synthesis and properties of silyl iodide, SiH_3I, describe a reaction between SiH_3I and magnesium in diisoamyl ether. The reaction yielded hydrogen, silane and silicon but no stable addition compound. Complete reaction took place. These results were attributed to the formation of an unstable Grignard-type compound.

This note describes an attempt to prepare a Grignard compound using silyl bromide. It was hoped that use of the bromide would impart greater stability to the desired product, which was then to be used in synthesis of other silyl compounds.

We were unable to obtain any stable Grignard compound, nor did any easy reaction of the type found by Emeleus, Maddock and Reid take place. Indeed, no reaction occurred between Mg and

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[1] Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[2] H. J. Emeleus, A. G. Maddock and C. Reid, *Nature*, **144**, 328 (1939); *J. Chem. Soc.*, 353 (1941).

SiH_3Br beyond the evolution of small amounts of silane and a non-condensable gas, presumably hydrogen, and the deposition of a small amount of silicon. Eighty-five to 90% of the SiH_3Br could be recovered after the reaction, while the amounts of SiH_4 produced varied between 4 and 6% of the SiH_3Br originally present in the reaction mixture. These results are consistent with the interpretation that between 8 and 12% of the original amount of SiH_3Br reacted with Mg according to the over-all equation

$$2SiH_3Br + Mg \longrightarrow SiH_4 + H_2 + Si + MgBr_2$$

Thus our work, as well as that of Emeleus, Maddock and Reid,[2] suggests that reaction between silyl radicals leads to drastic disproportionation rather than recombination. Presumably this means that the free energy of formation of SiH_4 (−9.4 kcal./mole[3]) is more favorable than that of Si_2H_6.

A possible explanation for the great difference between the bromide and iodide in their ease of reaction with magnesium may be had by a consideration of bond strengths (dissociation energies). In carbon systems Grignard reagents are in general more difficult to prepare with chlorides than with the corresponding bromides which latter have lower bond strengths. While data are not available from which to compute the silicon–halogen bond strengths in SiH_3Br and SiH_3I, one can estimate from data tabulated by the Bureau of Standards[3] that the average Si–Br bond strength in $SiBr_4$ is 70.2 kcal. while the corresponding Si–I bond strength is 51.4 kcal., a difference of 19 kcal. Although these values are not directly applicable, we would certainly predict on their basis a much lessened reactivity in the case of SiH_3Br compared with SiH_3I.

Experimental

All experimental work was carried out in a high vacuum apparatus, using glass stopcocks greased with Apiezon N which was stable toward SiH_3Br at moderately low pressures.

Preparation of Silane.—Although the greater part of the SiH_4 used was supplied through the courtesy of the General Electric Company, supplementary amounts were prepared by the method of Finholt, Bond, Wilzbach and Schlesinger[4] which employs reduction of $SiCl_4$ by $LiAlH_4$ in ethyl ether solution. Purity was controlled by checking vapor pressures at two different temperatures and comparing with the values given by Stokland.[5]

Preparation of SiH_3Br.—The method used was essentially that of Stock and Somieski.[6] Silane was heated for two hours at 100–110° with a 15% excess of dry HBr in the presence of $AlBr_3$ in a previously evacuated flask immersed in an oil-bath. Purification was accomplished, after removal of non-condensable gases, by a distillation at −126° to remove unreacted SiH_4 and then several distillations at −96° to separate the SiH_3Br from higher bromides. When the vapor pressures checked at two temperatures with those reported by Stock and Somieski,[6] the SiH_3Br was considered pure.

Since SiH_3Br tends to disproportionate readily, it was kept at Dry Ice temperatures till needed, closed off by a stopcock. There was no detectable deterioration for periods of several weeks as verified by vapor pressure measurements.

Reaction of SiH_3Br with Mg.—A small shaving of Mg, burnished with a knife and washed with ether, was placed in a 0.6 × 5 cm. tube which was sealed into the vacuum apparatus, evacuated, and well flamed to remove surface adsorbed water. C.P. dibutyl ether was distilled over sodium into the tube. The SiH_3Br was then distilled into the tube and frozen with liquid nitrogen. The ratio of bromide to ether was varied in the different runs. The amounts of SiH_3Br varied from about 0.0005 mole (0.055 g.) to about 0.001 mole (0.11 g.) in quantities of ether ranging from about 0.1 to 0.5 ml. No correlation was evident between the ratio of halide to ether and extent of reaction.

The mixture was allowed to warm to room temperature, whereupon the SiH_3Br dissolved in the ether to form a clear solution. Loss of volatile SiH_3Br to the vapor state was minimized by using short lengths of small bore tubing, and closing the reaction tube with a stopcock. Gradually, over a period of 3 or 4 hours a dark deposit began to form on the Mg. Except for a small amount of bubbling, which could have been caused by vaporization into the vacuum above, there was no other evidence of reaction. In a few trials the mixture was allowed to stand overnight, but no further reaction could be observed.

To separate the products, the mixture was frozen with liquid nitrogen, and the non-condensable gas (H_2) removed. Distillation at −126° removed SiH_4, and the unreacted SiH_3Br was recovered by distilling at −63° and later purified by redistillation at -96°. There was no evidence of disilane. Four to 6% of SiH_4 was found on the basis of the original SiH_3Br and 85–90% of the SiH_3Br was recovered.

Acknowledgment.—We are indebted to Dr. A. E. Newkirk, of the General Electric Company, Schenectady, New York, for his advice and for generously providing the silane with which most of this investigation was carried out.

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(3) Natl. Bur. Standards, "Selected Values of Chemical Thermodynamic Properties," Series I, 1949.

(4) A. E. Finholt, A. C. Bond, K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **69**, 2692 (1947).

(5) K. Stokland, *Kgl. Norske Videnskab. Selskabs, Forh.*, **12**, 122 (1939).

(6) A. Stock and C. Somieski, *Ber.*, **50**, 1739 (1917).

Fluorene Analog of Trypan Blue[1] (2,7-Bis-(8'-amino-3',6'-disulfo-1'-hydroxy-2'naphthylazo)-fluorene)

BY SIEGFRIED WOISLAWSKI

RECEIVED NOVEMBER 5, 1951

In continuation of previous work[2] on compounds useful in cancer research, 2,7-diaminofluorene dihydrochloride has been tetrazotized coupled with H-acid to form an analog of Trypan Blue. Novelli[3] reported the preparation of this compound but gave no details of yield or purity. When prepared by his method the compound was not homogenous. Both Trypan Blue and the fluorene analog have an absorption maximum at 590 $m\mu$, Fig. 1.

Experimental

To a solution of 5.38 g. (0.02 mole) of 2,7-diaminofluorene dihydrochloride in 100 ml. of water was added 4.5 ml. (0.06 mole) of concentrated hydrochloric acid (sp. gr. 1.18) and 50 g. of ice. After cooling to 2°, agitation was started and 90% of 2.8 g. (0.04 mole) of sodium nitrite (95%) in 40 ml. of water was added rapidly, and the balance dropwise until a distinct test for nitrous acid was obtained. This excess was maintained for 0.5 hour. Throughout the tetrazotization tests were made for an excess of acid by means of congo red paper. When the tetrazotization was completed, excess nitrous acid was eliminated by adding 0.3 g. of urea. The brown tetrazonium chloride may form an emulsion that can easily be broken up by adding ice or a few drops of capryl alcohol. The temperature during the tetrazotization was kept at 0–5°.

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(1) Supported by Grant C-1356 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

(2) H. S. Block and F. E. Ray, *J. Nat. Cancer Inst.*, **7**, 61 (1946).

(3) A. Novelli, *Anales Soc. espan. fis. quim.*, **28**, 362 (1930).