# NOTES

## A Polarographic Examination of Diazotized Amines. II. Additional Coulometric Data

By Edward R. Atkinson,[1] Charles E. Garland and Arthur F. Butler

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Our interpretation of the polarographic behavior of benzenediazonium salts[2] was aided by coulometric analyses carried out at *p*H 7. This study has been extended to include data obtained at *p*H 4.1 and *p*H 1.1 with benzenediazonium chloride and at *p*H 7 with *o*-carboxybenzenediazonium chloride. We have observed that in the *p*H range studied there is no change in the electron consumption at a particular potential, as was indicated earlier by the small change in $i_d/C$ for the total second wave.

We have continued to observe that the electron consumption at −0.6 v. *vs.* S.C.E. was 1 electron/mole $RN_2X$, but in contrast to our earlier observation we now find that the electron consumption at −1.2 v. *vs.* S.C.E. is 2 electrons/mole $RN_2X$. This new value has been observed not only at the *p*H values studied for the first time in our present work but also at *p*H 7 used previously.

In seeking an explanation for this serious discrepancy at the more negative potential we discovered that when a typical coulometric analysis of millimolar benzenediazonum chloride was interrupted after but 1 electron/mole $RN_2X$ was consumed the solution in the cell had no polarographic activity. It was this criterion which led us to conclude in our earlier work that the electrolysis was complete.[3] This criterion was false, for when the solution was removed from the cell and allowed to stand in the cold polarographic activity returned slowly. This same phenomenon was observed with partially electrolyzed solutions at −0.6 v. also. This return of polarographic activity was not noted after the consumption of 1 electron/mole $RN_2X$ at −0.6 v. or of 2 electrons/mole $RN_2X$ at −1.2 v. The complete disappearance of polarographic activity from partially electrolyzed solutions of diazotized anthranilic acid was not observed and the electron consumption at the more negative potential was 2 electrons/mole $RN_2X$.

It is apparent that in the case of diazotized aniline the solution must contain a reservoir of material in equilibrium with the substances responsible for the two polarographic waves but not itself reducible at the potentials available to us. Our interpretation of the polarographic results[2] ascribed the second wave to the undissociated diazohydroxide. It is reasonable to continue to apply the classical hypothesis and ascribe the second wave to the *syn*-diazohydroxide while the reservoir substance becomes the less reactive *anti*-diazohydroxide. Our results demonstrate that such a reservoir substance is not an important part of diazotized anthranilic acid.

Throughout our current work we have continued to observe the mobile equilibrium between the substances responsible for the first and second polarographic waves; these waves invariably appear with diffusion currents in the same proportion and diffusion currents decrease according to the Ilkovic equation as drop times are increased from 2.6 to 4.5 seconds.

Since we now know that 2 electrons/mole $RN_2X$ are involved in the second polarographic wave our original equation (C)[2] becomes (C′).

$$\text{(C)}\quad \mathrm{R{-}N{=}N{-}OH + H^+ + e \longrightarrow R\cdot + N_2 + H_2O}$$

$$\text{(C}'\text{)}\quad \mathrm{R{-}N{=}N{-}OH + 2H^+ + 2e \longrightarrow 2RH + N_2 + H_2O}$$

Alternate expressions for (C′) to indicate a free radical intermediate may be written; disintegration of the mercury cathode and the formation of tarry products was observed in coulometric work at the more negative potential as well as at −0.6 v. where a 1 electron process occurs.[4]

Our coulometric work does not support the assertion of Elofson, Edsberg and Mecherly[5] that a four electron process leading to the hydrazine is responsible for the total polarographic activity of diazo compounds.[6] Our earlier work has shown that the second wave represents the reduction of a substance entirely different from that responsible for the first wave but in equilibrium with it.

Since it is unlikely that we shall be able to continue our work in this field we wish to take this opportunity to call attention to the work of Rheaume[7] who carried out a detailed study of the polarographic behavior of diazotized aniline in the range +0.1 to −0.1 v. *vs.* S.C.E. At high galvanometer sensitivities it was possible to detect a small wave which occurred just prior to the first major wave. The diffusion current of this small wave was proportional to concentration in the case of the chloride salt and much smaller and not proportional to concentration in the case of the bisulfate salt. Many hypotheses were examined experimentally but no conclusions were reached.

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[1] Dewey and Almy Chemical Co., Cambridge 40, Mass.

[2] E. R. Atkinson, H. H. Warren, P. I. Abell and R. E. Wing, This Journal, **72**, 915 (1950).

[3] A less satisfactory criterion was a decrease in the current flowing through the cell to the pre-electrolysis value of 1 ma. or less. This appears to have been because of poor stirring.

[4] A sequence suggested by the referee is

$$\mathrm{R{-}N{=}N{-}OH + H^+ + e \longrightarrow R\cdot + N_2 + H_2O}$$
$$\mathrm{R\cdot + Hg \longrightarrow RHg\cdot}$$
$$\mathrm{RHg\cdot + H^+ + e \longrightarrow RH + Hg}$$
$$\mathrm{2RHg\cdot \longrightarrow R_2Hg + Hg}$$

[5] R. M. Elofson, R. L. Edsberg and P. A. Mecherly, *J. Electrochem. Soc.*, **97**, 166 (1950).

[6] S. Wawzonek (*Anal. Chem.*, **24**, 36 (1952)) accepts the four electron process of the above authors and believes that our observed electron consumption of 1 (now 2) electrons/mole $RN_2X$ can be attributed to the stirring in the coulometric cell which sweeps away the initial reduction products before all four electrons are absorbed.

[7] L. A. Rheaume, B.S. Thesis, University of New Hampshire, 1950.

This small wave was not observed in the case of other diazo compounds studied in this Laboratory.

This work was made possible by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

### Experimental

*o*-Carboxybenzenediazonium chloride was prepared from anthranilic acid by a method similar to that used for benzenediazonium chloride.[2] Other materials and apparatus were the same as those used earlier.[2] Our coulometric cell had a capacity about twice that of the original model and this required very careful deaeration to avoid interference from hydrogen peroxide waves which were encountered at *p*H 4.1 and *p*H 1.1. At these *p*H values (in contrast to *p*H 7 where it was negligible) the non-electrolytic decomposition of diazotized aniline in the presence of the large stirred mercury cathode became noticeable. The extent of decomposition during the 40–90 min. required for a typical coulometric analysis was measured by noting the decrease in the diffusion currents of either wave. It was observed that, for example, the actual electron consumption at −0.6 v. (0.90 electron/mole $RN_2X$) was raised to the integral value by correction for the non-electrolytic decomposition. In cases where the electrolysis was interrupted at an intermediate stage it was necessary to remove the solution from contact with the cathode since the non-electrolytic decomposition of the diazo compound was still more rapid in the presence of the mercury dust which accumulated on the cathode during electrolysis. It was only our good fortune in removing a partially electrolyzed solution from the cell which permitted us to observe the increase in polarographic activity which occurred on standing. The increase in diffusion currents was observed by recording polarograms of fresh portions of the solution at 15-minute intervals. It was observed that the return of polarographic activity continued for about one hour.

No difficulty from non-electrolytic decomposition was experienced with diazotized anthranilic acid.

Coulometric analyses performed during the present work showed a precision of 2%.

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## Acrylates of Difficultly Esterified Alcohols

BY ARTHUR H. AHLBRECHT AND DONALD W. CODDING

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The use of trifluoroacetic acid anhydride as an esterification agent has been extended to the preparation of acrylate esters of alcohols which normally need to be treated with acrylyl chloride or acrylic anhydride.

The procedure is essentially that of Bourne, Stacey, Tatlow and Tedder[1] who used trifluoroacetic acid anhydride in the esterification of alcohols and phenols. In this process, the alcohol is added to a mixture of acrylic acid and trifluoroacetic acid anhydride. The resulting acrylate ester is easily recovered in very good yield by washing and distilling.

This procedure was developed primarily for the production of acrylate and methacrylate esters of 1,1-dihydroperfluoroalkyl alcohols, but it also worked very well when applied to the preparation of phenyl acrylate. As noted by previous workers[1,2] the only ester formed is the one resulting from esterification with the non-fluorinated carboxylic acid.

### Experimental

**Preparation of Phenyl Acrylate.**—To a 2-liter 3-necked flask immersed in an ice-bath and equipped with reflux condenser, stirrer, dropping funnel and thermometer is added 288 g. (4 moles) of hydroquinone inhibited glacial acrylic acid. Trifluoroacetic acid anhydride (840 g., 4 moles) is then added through the dropping funnel at such a rate that the temperature of the stirred solution does not exceed 15°. Stirring is continued 15 minutes after the addition of the anhydride and during the addition of the phenol (376 g., 4 moles), which is added at such a rate that the temperature of the cooled mixture does not exceed 25°. After 90 minutes additional stirring, the reaction mixture is transferred to a separatory funnel and water is added until two layers separate. The top ester layer is washed with water, 5% NaOH and again with water. Using hydroquinone and copper flake as inhibitors, two distillations through an efficient column packed with glass helices produced 332 g. (56%) of pure phenyl acrylate,[3] b.p. 65° (1 mm.), $n^{20}$D 1.5210. The bottom layer consists of trifluoroacetic acid and water from which the $CF_3COOH$ can be recovered as the sodium salt by neutralization with sodium hydroxide and evaporation to dryness on the steam-bath.

**Preparation of 1,1-Dihydroperfluorobutyl Acrylate.**—Using almost the same procedure, 1,1-dihydroperfluorobutyl alcohol was esterified with glacial acrylic acid in yields of 85–90%. The 1,1-dihydroperfluorobutyl acrylate had the following physical properties, b.p. 51° (50 mm.), $n^{20}$D 1.3317, $d^{20}_4$ 1.409. *Anal.* Calcd. for $C_7H_5O_2F_7$: C, 33.1; F, 52.4. Found: C, 33.1; F, 52.4.

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[1] E. J. Bourne, M. Stacey, J. C. Tatlow and J. M. Tedder, *J. Chem. Soc.*, 2976 (1949).

[2] P. W. Morgan, THIS JOURNAL, **73**, 860 (1951).

[3] E. M. Filachione, J. H. Lengel and C. H. Fisher, *ibid.*, **66**, 494 (1944).

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## The Preparation of Tris-acetylacetone–Rhodium(III) and -Iridium(III)

BY F. P. DWYER AND A. M. SARGESON

RECEIVED SEPTEMBER 17, 1952

No acetylacetone complexes of rhodium or iridium in any valency state appear to have been described. The tervalent complexes have been prepared in connection with the study of the optical properties of non-electrolytic complexes. Rhodium(III) hydroxide or sodium rhodate(III) failed to react with acetylacetone. Small amounts of the compound were obtained by refluxing sodium hexachlorhodate(III) with sodium acetylacetonate but the best results by heating a mixture of rhodium(III) nitrate with acetylacetone at *p*H 4. The iridium compound was obtained in small yield from iridium(III) hydroxide. An unstable reddish water-soluble substance of unknown composition also resulted. This was possibly the acid $H[Ir(OH)_2(Aca)_2]$.

**Tris-acetylacetone–rhodium(III).**—Rhodium(III) nitrate solution (0.1 g. Rh) in 0.2 *N* nitric acid (10 ml.) was neutralized with sodium bicarbonate solution (10%) to *p*H 4. At this acidity the light yellow hydroxide (or basic nitrate) just commenced to separate. Acetylacetone (5 ml.) was added and the mixture refluxed. After a few minutes orange-yellow crystals started to separate, the *p*H of the mixture falling. After 30 minutes the *p*H was readjusted and the refluxing continued for a further 15 minutes. The substance after crystallization from aqueous methanol gave orange-yellow monoclinic plates, m.p. 260°, yield 0.3 g., 75%) sublimed at 240° at 1.0 mm. pressure, and decomposed at 280° forming a rhodium mirror. The substance was insoluble in water, slightly soluble in alcohol and petroleum ether, but easily soluble in benzene and chloroform. It was stable to boiling dilute acids and 10% aqueous caustic soda.

*Anal.* Calcd. for $C_{15}H_{21}O_6Rh$: Rh, 25.75; C, 45.01; H, 5.29; mol. wt., 400. Found: Rh, 25.5; C, 45.2; H, 5.35; mol. wt. (Rast in camphor), 390.

**Tris-acetylacetone–iridium(III).**—Freshly precipitated iridium dioxide, from potassium hexachloriridate(IV) (1.0 g.) was dissolved by heating with sulfuric acid (1 *N*, 25 ml.) and a few crystals of sodium sulfate, and evaporated until the acid started to fume. The cooled solution was diluted to the original volume, and the undissolved iridium dioxide removed by centrifuging. The light green solution was treated with 10% caustic soda solution until the green iridium(III) hydroxide precipitate was just redissolved. The substance was reprecipitated quickly in order to avoid oxidation, the solution adjusted to *p*H 6, and the mixture heated at 60° with acetylacetone (2 ml.) for an hour. The solution became red, depositing a yellow crystalline precipitate, which crystallized from aqueous methanol in orthorhombic plates, m.p. 269° (yield 0.1 g., 10%). The substance sublimed at 260° under 1 mm. pressure and decomposed at 290° depositing an iridium mirror. The solubility in solvents was similar to the rhodium compound.

*Anal.* Calcd. for $C_{15}H_{21}O_6Ir$: Ir, 39.37; C, 36.73; H, 4.32; mol. wt., 490. Found: Ir, 39.3; C, 36.9; H, 4.4; mol. wt. (Rast in camphor), 400.

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## Extension of the Leuckart Synthesis of Tertiary Amines, Including its Application to α,β-Unsaturated Carbonyl Compounds[1]

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RECEIVED JULY 16, 1952

In 1949, we reported[3] the preparation of a number of tertiary amines by the reaction of ketones with dialkylformamides in the presence of formic acid and magnesium chloride; conversions[4] in the range 20 to 55% and adjusted yields[4] in the range 40 to 60% were obtained. We now report the application of an improved variation of this technique to a number of additional carbonyl compounds; our results are summarized in Table I.

TABLE I

TERTIARY AMINES SYNTHESIZED BY THE LEUCKART REACTION

| Tertiary amine product[a] | Conversion,[4] % | Adjusted yield,[4] % | B.p. °C. | Mm. | Picrate m.p., °C. | Hydrochloride m.p., °C. | Refractive index $n_D^t$ | $t$, °C. |
|---|---|---|---|---|---|---|---|---|
| N,N-Dimethyl-α-ethylbenzylamine (I) | 30 | 79 | 105–106 | 25 | 165.5–166.6 | | 1.5002 | 25 |
| α-Ethylbenzylpiperidine (II) | 65 | 77 | 155–157 | 25 | | 187–188 | 1.5210 | 25 |
| N,N,1-Trimethyl-3-phenylpropylamine (III) | 43 | 60 | 118–121 | 14 | 113.5–114 | | 1.4985 | 23 |
| 1-Methyl-3-phenylpropylpiperidine (IV) | 57 | 57 | 176–177 | 25 | | 164.5–165.5 | 1.5140 | 25 |
| N,N,1-Trimethyl-3-(*p*-methoxyphenyl)-propylamine (V) | 30 | 55 | 152–154 | 14 | 129.5–130.5 | 169–170 | 1.5060 | 24 |
| N,N-Dimethyl-3-phenylallylamine (VI) | 55 | 55 | 125–132 | 25 | 123.5–124.5 | 187.5–188.5 | | |
| N,N,1-Trimethyl-3-phenylallylamine (VII) | 23 | 44 | 139–140 | 25 | 138–139 | | 1.5350 | 25 |
| 1-Methyl-3-phenylallylpiperidine (VIII) | 15 | 15 | 180–187 | 25 | 142.5–143.5 | | | |

[a] Experimental details and data supporting structures are given in the Experimental section.

It will be noted that in general the yields reported here range higher than those reported previously. This improvement is due in part to the use of a longer reaction time (eight hours instead of three or four hours) and in part to a modified technique for removing the low-boiling constituents (principally water and formic acid) of the original reaction mixture. This technique involves distilling the reaction mixture rapidly until the pot temperature approximates the boiling point of the formamide being used, and then allowing the system to reflux. Efforts to improve the yield by the use of excess formic acid or by the use of nickel catalyst[5] (from pyrolysis of nickel formate) were not fruitful. It is of parenthetical interest that when the magnesium chloride and formic acid of a typical reaction mixture were replaced by phosphoric acid (making the molar ratio phosphoric acid:propiophenone:formpiperidide = 1:1:4), the conversion[4] to α-ethylbenzylpiperidine was 30% compared to 65% by our best procedure.

Shortly after the appearance of our earlier paper,[3] Staple and Wagner[6] published a careful study of factors influencing the rate of formation of tertiary amines from piperidine formate or formpiperidide and benzaldehyde or cyclohexanone. Using these particularly reactive carbonyl compounds, they found that a faster reaction and better yields were obtained when the amine formate was used rather than formpiperidide. On the basis of this experience, they suggested that the amine formate would in general prove to be the better reagent for tertiary amine synthesis. We attempted to prepare amines from 4-(*p*-methoxyphenyl)-butanone-2 and dimethylamine formate, and from propiophenone and piperidine formate by their recommended procedure, but in neither case were we able to obtain any measurable amount of the expected tertiary amine. Since the successful preparation of both these tertiary amines is recorded in Table I, we believe that our procedure is more suitable for the preparation of tertiary amines from carbonyl compounds in general.

Our success in obtaining unsaturated tertiary amines (the last three amines in Table I) from α,β-unsaturated carbonyl compounds contrasts with the

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[1] Based in part on the B.A. Thesis of Henry Moe, June, 1952. Presented at The Northwest Regional Meeting of The American Chemical Society, Corvallis, Oregon, June 20, 1952.

[2] Dept. of Chemistry, Univ. of North Carolina, Chapel Hill, N. C.

[3] J. F. Bunnett and J. L. Marks, THIS JOURNAL, **71**, 1587 (1949).

[4] In this paper, "conversion" means yield based on the amount of ketone introduced, and "adjusted yield" means yield based on the amount of ketone consumed, that is, on the amount introduced less the amount recovered.

[5] A. N. Kost, A. P. Terent'ev and G. A. Shvekhgeimer, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 150 (1951) [*C. A.*, **45**, 10194 (1951)], reported catalysis of the Leuckart synthesis of primary and secondary amines by nickel metal and other hydrogenation catalysts.

[6] E. Staple and E. C. Wagner, *J. Org. Chem.*, **14**, 559 (1949).

failure of others[7–9] to obtain unsaturated primary amines by the Leuckart reaction. From carvone and ammonium formate, Wallach[9] obtained dihydrocarvylamine in which the double bond α,β- to the carbonyl group has been reduced. Irwin[8] allowed formamide to act upon a number of α,β-unsaturated ketones; in general, mixtures were formed from which, in two cases, the saturated primary amines were isolated and identified. However, he adduced no evidence that any unsaturated amines were formed.

With these considerations in mind, we made special efforts to confirm the identity of our unsaturated amine products. The structure assigned to VII (obtained from benzalacetone and dimethylformamide) is confirmed by analyses on the amine and its picrate, by the fact that it differs from the saturated amine (III), by the fact that it absorbs bromine rapidly, and by its conversion by catalytic hydrogenation (palladium-on-carbon catalyst, ethanol solution) into III. In the case of VI, the physical constants we obtained agree with those reported by King and Holmes[10] for VI prepared by another method. The structure assigned to VIII is supported by analyses and by the fact that it differs from the saturated amine IV.

Whereas the saturated amines I–V were obtained in a condition of high purity from the initial vacuum distillation, the unsaturated amines VI–VIII were obviously contaminated by impurities at this stage of purification. The nature of the impurities is perhaps indicated by the fact that the saturated amine III was isolated, as its picrate, from the liquors from recrystallization of crude VII picrate. It is suspected that crude VI and VIII were also contaminated with the corresponding saturated amines, but in these cases efforts to isolate the saturated amines as by-products were not successful.

Several efforts to prepare the *p*-methoxy derivative of VII by the reaction of *p*-methoxybenzalacetone with dimethylformamide were rewarded very meagerly. In each run a very small amount of amine was obtained; the substance was not investigated further.

The action of hydrobromic acid on V produced N,N,1-trimethyl-3-(*p*-hydroxyphenyl)-propylamine; our melting points for this product and its hydrochloride were in each case nine degrees higher than those reported elsewhere.[11]

## Experimental[12]

**Materials.**—Dimethylformamide was generously donated by the Grasselli Chemicals Department, E. I. du Pont de Nemours and Co. Other starting materials were commercial products repurified, or were synthesized by standard methods. Our 4-phenyl-2-butanone, prepared both from ethyl α-benzylacetoacetate and by hydrogenation of benzalacetone, followed by purification through its bisulfite addition product, had $n^{25}D$ 1.5100, a value different from that reported by Briggs, De Ath and Ellis,[13] but in approximate agreement with the value given by Klages.[14] The melting point of the semicarbazone of our product, 142°, agrees with the generally accepted value. The melting point of its 2,4-dinitrophenylhydrazone was 125–126.3°, in comparison to 131–132° reported by Briggs, De Ath and Ellis.[13]

**Preparations Summarized in Table I.**—In most cases, 0.13 mole of carbonyl compound was used, though the preparations of III, V and VII were run on a scale approximating 0.5 mole. The ketone or aldehyde, the formamide (dimethylformamide or formpiperidide, 4 moles per mole of carbonyl compound), magnesium chloride hexahydrate ($^1/_6$ mole per mole of carbonyl compound) and 85% formic acid (one mole per mole of carbonyl compound) were mixed in a three-neck flask equipped with a stirrer, thermometer and condenser set for downward distillation. The mixture was heated and volatile constituents were removed until the pot temperature approximated the boiling point of the formamide being used. A reflux condenser was then installed in place of the condenser set for downward distillation, and the mixture was refluxed with stirring for eight hours. After the mixture had been poured into dilute mineral acid, unreacted ketone was removed by steam distillation and purified by standard procedures. The mixture was then made basic and the amine was distilled off with steam. The steam distillate was saturated with sodium chloride and extracted with ether. The ether extract, after drying over solid sodium hydroxide, was distilled, the amine finally being distilled at reduced pressure. Saturated amines were obtained from this distillation in a state of considerable purity, but unsaturated amines were, to judge from the refractive indices and boiling points of distillation fractions, not pure, and were further purified by recrystallization of their picrate or hydrochloride salts. Picrates were recrystallized from ethanol and hydrochlorides from acetone.

The following data support the structures assigned to the products:

I.—Dunn and Stevens[15] reported for I b.p. 100–105° (22 mm.), picrate m.p. 161–164°.

II.—Calcd. for $C_{14}H_{21}N$ (amine): C, 82.70; H, 10.41. Found: C, 83.02; H, 10.43. Calcd. for $C_{14}H_{22}ClN$ (hydrochloride): C, 70.12; H, 9.25; Cl, 14.79. Found: C, 70.26; H, 9.00; Cl, 14.68.

III.—Calcd. for $C_{12}H_{19}N$: C, 81.29; H, 10.80; N, 7.93. Found: C, 81.38; H, 10.38; N, 8.21.

IV.—Calcd. for $C_{15}H_{24}ClN$ (hydrochloride): C, 70.98; H, 9.53; Cl, 13.97. Found: C, 71.40; H, 9.59; Cl, 13.92.

V.—Davies, Haworth, Jones and Lamberton[11] reported for V b.p. 155° (14 mm.), picrate m.p. 129°, hydrochloride m.p. 166°.

VI.—King and Holmes[10] reported for VI: picrate m.p. 124–125°, hydrochloride m.p. 190.5–191°.

VII.—Calcd. for $C_{12}H_{17}N$ (amine): C, 82.22; H, 9.78. Found: C, 82.24; H, 9.84. Calcd. for $C_{18}H_{20}N_4O_7$ (picrate): C, 53.46; H, 4.98. Found: C, 54.05; H, 4.77. From the liquors from recrystallization of the picrate, a small amount of yellow material, m.p. 113–113.5°, was recovered. It did not depress the m.p. of III picrate.

VIII.—Calcd. for $C_{21}H_{24}N_4O_7$ (picrate): C, 56.75; H, 5.44. Found: C, 56.55; H, 5.62.

**N,N,1-Trimethyl-3-(*p*-hydroxyphenyl)-propylamine.**—A solution of 30 g. of V in 150 cc. of 48% hydrobromic acid was refluxed five hours. The mixture was made alkaline by adding sodium carbonate and extracted with ether. The ether extracts were dried and evaporated, and the residue distilled at reduced pressure, furnishing 13.2 g. (47.3%) of the phenolic amine, b.p. 192–195° (14 mm.), m.p. 73.5–76°.

*Anal.* Calcd. for $C_{12}H_{19}NO$: C, 74.56; H, 9.91. Found: C, 74.96; H, 9.58.

The hydrochloride was recrystallized from absolute ethanol, m.p. 161–162°; a mixed melting point with V hydrochloride was depressed (154–157°).

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(7) A. W. Ingersoll, J. H. Brown, C. K. Kim, W. D. Beauchamp and G. Jennings, THIS JOURNAL, **58**, 1808 (1936).

(8) O. R. Irwin, Ph.D. Thesis, University of Missouri, 1950; Univ. Microfilms, pub. No. 1785; *C. A.*, **45**, 6204 (1951).

(9) O. Wallach, *Ber.*, **24**, 3984 (1891).

(10) F. E. King and D. Holmes, *J. Chem. Soc.*, 168 (1947).

(11) R. E. Davies, R. D. Haworth, B. Jones and A. H. Lamberton, *ibid.*, 191 (1947).

(12) Melting points are uncorrected. Analyses for carbon and hydrogen by Clark Microanalytical Laboratories, Urbana, Ill.; Dr. Adalbert Elek, Los Angeles, Calif.; and Dr. Carl Tiedcke, New York, N. Y.

(13) L. H. Briggs, G. C. De Ath and S. R. Ellis, *J. Chem. Soc.*, 61 (1942), reported for 4-phenyl-2-butanone: $n^{25}D$ 1.5140.

(14) A. Klages, *Ber.*, **37**, 2313 (1904), reported for 4-phenyl-2-butanone: $n^{21.7}D$ 1.511.

(15) J. L. Dunn and T. S. Stevens, *J. Chem. Soc.*, 281 (1934).

*Anal.* Calcd. for $C_{12}H_{20}ClNO$: Cl, 15.43. Found: Cl, 15.50.

Davies, Haworth, Jones and Lamberton[11] have reported melting points for this phenolic amine and its hydrochloride in each case about nine degrees lower than our values.

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# *t*-Alkyl-*n*-alkyl Orthosilicates

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Mixed alkyl orthosilicates are produced by the interaction of ethyl orthosilicate and an alcohol in the presence of a basic catalyst, provided that the ethanol formed is continuously removed.

$$(EtO)_4Si + x\,ROH \xrightarrow{NaOR} (RO)_xSi(OEt)_{4-x} + x\,EtOH$$

Furthermore, this reaction is applicable to the synthesis of mixed alkyl orthosilicates containing tertiary alkoxy groups.[1,2] We have applied this method of synthesis to the preparation of six mixed alkyl orthosilicates. The pertinent data on synthesis and properties are summarized in Table I.

TABLE I

| | | Unreacted $(EtO)_4$-Si, % | Yield,[a] % | B.p., uncorr.[b] °C. | B.p., uncorr.[b] Mm. | $n^{20}_{\mathrm{D}}$[b] | $d^{20}$[b] | $R_{\mathrm{D}}$[c] Calcd. | $R_{\mathrm{D}}$[c] Obsd. | Analyses, % Carbon Calcd. | Carbon Obsd. | Hydrogen Calcd. | Hydrogen Obsd. | Mol. wt.[d] Calcd. | Mol. wt.[d] Obsd. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | *n*-$BuOSi(OEt)_3$[e] | | 49 | 128 | 77 | 1.3939 | 0.919 | 0.2585 | 0.2602 | 50.8 | 50.7 | 10.2 | 11.1 | ... | ... |
| II | (*n*-$BuO)_2Si(OEt)_2$[e] | 27 | 24 | 155 | 78 | 1.4019 | .912 | .2661 | .2669 | 54.5 | 54.4 | 10.7 | 10.9 | ... | ... |
| III | *t*-$BuOSi(OEt)_3$ | | 54 | 95 | 40 | 1.3872 | .905 | .2585 | .2602 | 50.8 | 51.3 | 10.2 | 10.4 | 236 | 231 |
| IV | (*t*-$BuO)_2Si(OEt)_2$ | 32 | 11 | 101 | 34 | 1.3899 | .887 | .2661 | .2675 | 54.5 | 55.7 | 10.7 | 11.1 | 264 | 266 |
| V | *t*-$AmOSi(OEt)_3$[f] | | 53 | 116 | 55 | 1.3859 | .910 | .2625 | .2640 | 52.8 | 53.3 | 10.5 | 10.8 | 250 | 242 |
| VI | (*t*-$AmO)_2Si(OEt)_2$ | 24 | 19 | 141 | 59 | 1.4052 | .900 | .2722 | .2724 | 57.5 | 57.7 | 11.0 | 11.1 | 278 | 290 |

[a] Based on unrecovered ethyl orthosilicate and calculated from distillation curves. [b] These physical properties are those of a center fraction of the particular distillation flat. [c] The calculated values were obtained by use of bond refractions given by K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940), and by E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946). Similar results may be obtained by use of the method of R. O. Sauer, *ibid.*, **68**, 954 (1946). [d] Determined cryoscopically in cyclohexane. [e] H. W. Post and C. H. Hofrichter, *J. Org. Chem.*, **5**, 576 (1940), reported the synthesis of these two compounds in 22 and 30% yields, respectively, by prolonged heating of ethyl orthosilicate with *n*-butyl orthosilicate. These workers found that the *n*-butylethyl orthosilicates disproportionate on heating at their atmospheric boiling points. [f] G. W. Pedlow and C. S. Miner, Jr., U. S. Patent 2,566,365 (September 4, 1951), reported the synthesis of this compound by the reaction of *t*-amoxytrichlorosilane with ethanol in the presence of pyridine.

In general, the experimental procedure was as follows. The reaction mixture, consisting of several small pieces of sodium and equimolar amounts of ethyl orthosilicate and the appropriate alcohol, was heated, and the resulting reflux was rectified through an efficient column. Distillate was removed slowly at the boiling point of ethyl alcohol until the refluxing slowed and the weight of distillate approximately equalled the theoretical amount of ethyl alcohol. The reaction mixture was allowed to cool, washed thoroughly with water, dried and fractionally distilled. The mixed-alkyl silicates thus obtained were water-white mobile liquids having an odor similar to the alcohol from which they were prepared. Yields ranged from 10% to 50%. Table I summarizes physical properties and analyses.

## Experimental

**Intermediates.**—The ethyl orthosilicate was purchased from Carbide and Carbon Chemicals Company and used as received. Distillation of other samples had indicated that this material is of high quality. The *n*-butyl alcohol, *t*-butyl alcohol and *t*-amyl alcohol were the ordinary materials of commerce used without further purification.

**Synthesis of *t*-Alkyl-*n*-alkyl Orthosilicates.**—All six compounds were prepared in essentially the same manner. The following detailed description of the synthesis of *t*-amyltriethyl silicate (V) and di-*t*-amyldiethyl silicate (VI) is illustrative of the method used. Yields, properties and analyses of the six compounds prepared may be found in Table I.

In a round-bottom flask was placed 1040 g., 5.0 moles, of ethyl orthosilicate and 440 g., 5.0 moles, of *t*-amyl alcohol. Several pea-sized chunks of sodium were added and the reaction flask was attached to a glass helix-packed rectification column having an estimated efficiency of twenty theoretical plates. As heat was applied to the reaction vessel, the sodium went into solution and reflux appeared at the head of the column. The reaction was stopped after 233 g. of distillate had been taken off at 78° over a period of six hours; the theoretical yield of ethanol was 230 g.

The crude reaction product was washed thoroughly with four 300-ml. portions of distilled water and dried for several days over Drierite. Fractional distillation was carried out at reduced pressure in a glass helix-packed column having an estimated efficiency of thirty theoretical plates. Graphical analysis of the distillation data revealed three plateaus identified as ethyl orthosilicate (physical properties and molecular weight), *t*-amyltriethyl silicate (V) and di-*t*-amyldiethyl silicate (VI).

Other compounds prepared by this method were: *n*-butyltriethyl silicate (I), di-*n*-butyldiethyl silicate (II), *t*-butyltriethyl silicate (III) and di-*t*-butyldiethyl silicate (IV).

In the case of the *t*-butyl compounds the proximity of the boiling points of ethanol and *t*-butyl alcohol necessitated a slightly modified procedure. The distillate consisted of a mixture of the two alcohols whose composition was determined by refractive index. More *t*-butyl alcohol was added to the reaction mixture and distillation was continued until one mole of ethanol had been removed for each mole of ethyl orthosilicate used.

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(1) We learned of this reaction through a private communication from Dr. C. S. Miner, Jr., and co-workers of the Miner Laboratories of Chicago, Illinois.

(2) (a) D. F. Peppard, W. G. Brown and W. C. Johnson, THIS JOURNAL, **68**, 73 (1946), reported that acid-catalyzed alcoholysis of ethyl orthosilicate did not occur with *t*-butyl alcohol; while *t*-amyl alcohol did react to give ethyl alcohol, these workers did not report any *t* amyl silicate. (b) D. Ridge and M. Todd, *J. Chem. Soc.*, 2637 (1949), reported that uncatalyzed alcoholysis of ethyl orthosilicate occurred to a slight extent with *n*-butyl alcohol but not at all with *t*-butyl alcohol or with *t*-amyl alcohol.

**Acknowledgment.**—The authors wish to thank Mr. E. M. Hadsell and Miss J. N. Whiteman for the fractional distillations reported herein. The authors are also grateful to Dr. E. W. Balis and Mrs. Miriam Lennig for the carbon and hydrogen determinations, and to Mr. L. B. Bronk and Mrs. Grace Poellmitz for molecular weight and density determinations.

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## Dimethylvinylethoxysilane and Methylvinyldiethoxysilane

BY M. COHEN AND J. R. LADD

RECEIVED NOVEMBER 12, 1952

A mixture of magnesium (2.63 moles) and absolute ether (800 ml.) was placed in a two-liter, three-necked, round-bottom flask equipped with a mercury-sealed stirrer, Dry Ice condenser and a gas inlet tube. A stopcock had been previously sealed to the bottom of the reaction flask. Methyl bromide was bubbled into the stirred mixture until all the magnesium had dissolved.

After excess methyl bromide had been allowed to evaporate from the solution, the methylmagnesium bromide solution was added to a stirred solution of 500 g. (2.63 moles) of vinyltriethoxysilane[1] and 960 ml. of ether in a three-liter, three-necked, round-bottom flask equipped with a mercury-sealed stirrer and a water condenser. All outlets were protected with calcium chloride tubes. The rate of addition was such that the ether refluxed gently.

The mixture was stirred under reflux one hour, and the ether distilled off. The distillation was continued at atmospheric pressure until the temperature of the distillate reached 100°. The remainder of the silanes was separated from the residue of magnesium salts at reduced pressure (40 mm.). On fractionation of the combined silanes there was obtained 19 g. (5.6% yield) of vinyldimethylethoxysilane, b.p. 99°, $n^{20}{}_D$ 1.3983, $d^{20}{}_4$ 0.790; *MR* calcd.[2] 39.8, obsd. 39.8; and 241 g. (57.4% yield) of vinylmethyldiethoxysilane, b.p. 133 to 134°, $n^{20}{}_D$ 1.4000, $d^{20}{}_4$ 0.858; *MR* calcd.[2] 45.2, obsd. 45.3.

*Anal.* Calcd. for $C_6H_{14}OSi$: C, 55.3; H, 10.8; Si, 21.5. Found: C, 55.4; H, 11.1; Si, 21.0. Calcd. for $C_7H_{16}O_2Si$: C, 52.5; H, 10.1; Si, 17.5. Found: C, 52.5; H, 10.2; Si, 17.2.

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(1) Linde Air Products, New York, N. Y.

(2) E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946).

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## Thiosemicarbazones of Thiophene Derivatives[1]

BY E. CAMPAIGNE, P. A. MONROE, B. ARNWINE AND W. L. ARCHER

RECEIVED JULY 31, 1952

Due to the effectiveness of *p*-acetaminobenzaldehyde thiosemicarbazone (Tibione)[2] as an antituberculous agent, a number of thiosemicarbazones have been prepared for biological testing. Among these have been a number of heterocyclic derivatives, including several of the thiophene series. 2-Thenaldehyde thiosemicarbazone has been reported to have a relatively high order of activity against the tubercle bacillus *in vitro*.[3,4] In addition, Anderson, *et al.*,[4] reported *in vitro* tests on the thiosemicarbazones of 2-acetothienone, 2-propiothienone, 2-butyrothienone and 2,5-dimethyl-3-acetothienone. Of these, 2-propiothienone thiosemicarbazone afforded the best protection. A later report[5] indicated that 2-thenaldehyde thiosemicarbazone gave weak protection to mice infected with tuberculosis.

In recent papers[6,7] Hamre, *et al.*, reported that *p*-aminobenzaldehyde thiosemicarbazone caused a significant delay in death of chick embryos and mice infected with vaccinia virus. This observation was confirmed by Thompson, Price and Minton[8] who reported that benzaldehyde thiosemicarbazone prevents multiplication of vaccinia virus in check embryonic tissue, but that substitution in the *p*-position of the benzene nucleus reduced virostatic activity.

In pursuing a program of virus chemotherapy, we have synthesized a number of heterocyclic thiosemicarbazones, and report here a group of thiophene derivatives. All of the carbonyl compounds used in preparing the thiosemicarbazones have been reported previously, either from these laboratories, or from other sources. The compounds prepared, their melting points and analyses are presented in the table. The biological testing data have been reported elsewhere by Dr. R. L. Thompson.[9]

TABLE I

THIOSEMICARBAZONES OF THIOPHENE DERIVATIVES

| Cmpd. No. | 3-Thenaldehydes | M.p., °C.[a] | Formula | Nitrogen, % Calcd. | Nitrogen, % Found |
|---|---|---|---|---|---|
| 1 | Unsubstituted | 151–152 | $C_6H_7N_3S_2$ | 22.78 | 22.70 |
| 2 | 2-Chloro- | 196–198 dec. | $C_6H_6N_3S_2Cl$ | 19.15 | 19.06 |
| 3 | 2-Bromo- | 192–194 dec. | $C_6H_6N_3S_2Br$ | 15.91 | 15.64 |
| 4 | 2,5-Dichloro- | 232–233 dec. | $C_6H_5N_3S_2Cl_2$ | ...[b] | ...[b] |
| | 2-Thenaldehydes | | | | |
| 5 | 5-Chloro- | 164–165 | $C_6H_6N_3S_2Cl$[c] | 19.15 | 19.27 |
| 6 | 5-Bromo- | 182–184 | $C_6H_6N_3S_2Br$ | 15.91 | 15.97 |
| 7 | 5-Nitro- | 252–255 dec. | $C_6H_6N_4O_2S_2$ | 24.36 | 24.05[d] |
| 8 | 5-Acetamido- | 231–233 | $C_8H_{10}N_4OS_2$ | 23.15 | 23.05[d] |
| 9 | 5-Methyl- | 160–161 | $C_7H_9N_3S_2$ | 21.08 | 21.02[d] |
| 10 | 3-Methyl- | 185–187 | $C_7H_9N_3S_2$ | 21.08 | 21.40[d] |
| 11 | 5-*t*-Butyl- | 182–183 | $C_{10}H_{15}N_3S_2$ | 17.42 | 17.40 |
| | 2-Acetothienones | | | | |
| 12 | Unsubstituted[e] | 147–148 | $C_7H_9N_3S_2$ | 21.08 | 21.12[d] |
| 13 | 5-Bromo- | 200–201 | $C_7H_8N_3S_2Br$ | 15.11 | 14.99[d] |
| 14 | 5-Methyl- | 161–163 | $C_8H_{11}N_3S_2$ | 19.73 | 19.72[d] |
| 15 | 4-Nitro-5-methyl- | 232–235 dec. | $C_8H_{10}N_4O_2S_2$ | 21.72 | 21.48[d] |

[a] All melting points uncorrected. [b] Calcd.: S, 25.2; Cl, 28.0. Found: S, 25.2; Cl, 27.9. [c] Calcd.: S, 29.16. Found: 29.06. [d] Analyses by H. L. Clark, Urbana, Ill. [e] Previously reported by F. E. Anderson, C. J. Duca and J. V. Scudi, THIS JOURNAL, **73**, 4967 (1951), m.p. 148–149° uncor.

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(1) Contribution No. 571 from the Chemistry Laboratory of Indiana University. This work was supported by a contract between the Office of Naval Research, Department of the Navy, and Indiana University.

(2) R. Behnisch, F. Mietzsch and H. Schmidt, *Am. Rev. Tuberc.*, **61**, 1 (1950).

(3) R. Donovick, F. Pansy, G. Stryker and J. Bernstein, *J. Bact.*, **59**, 667 (1950).

(4) F. E. Anderson, C. J. Duca and J. V. Scudi, THIS JOURNAL, **73**, 4967 (1951).

(5) C. J. Duca, M. V. Rothlauf and J. V. Scudi, *Antibiotics and Chemo.*, **2**, 16 (1952).

(6) D. Hamre, J. Bernstein and R. Donovick, *Proc. Soc. Exp. Biol. Med.*, **73**, 275 (1950).

(7) K. A. Brownlee and D. Hamre, *J. Bact.*, **61**, 127 (1951).

(8) R. L. Thompson, M. L. Price and S. A. Minton, Jr., *Proc. Soc. Exp. Biol. Med.*, **78**, 11 (1951).

(9) R. L. Thompson, S. A. Minton, Jr., and J. E. Officer, *J. Immunology*, in press.

The following points about the chemical work are worthy of comment. 1. The addition of a small amount of acetic acid facilitated the reaction of thiosemicarbazide with the carbonyl compounds, so that it was essentially complete in one-half to one hour. Anderson, *et al.*,[4] reported the reaction time to vary from 8 to 80 hours when no acetic acid was added. 2. The synthesis of 5-chloro-2-thenaldehyde in 50–55% yield by formylation of thiophene with N-methylformanilide was recently reported.[10] It was therefore interesting to carry out the synthesis of this compound by the Sommelet procedure, in order to compare the yields by the two methods. When 5-chloro-2-methylthiophene was converted to the thenyl bromide with N-bromosuccinimide, and thence to the aldehyde, a 33% yield was obtained. When 2-chlorothiophene was chloromethylated by the procedure of Cairns and McKusick[11] and the thenyl chloride converted to the aldehyde, a 25% yield was obtained. Thus neither process is as efficient as the formylation procedure.[10]

### Experimental

**Thiosemicarbazones.**—The general procedure for the preparation of all the thiosemicarbazones was as follows: 0.1 mole of the carbonyl compound was dissolved in 100 ml. of 50% ethanol (95% ethanol was used for the less soluble compounds) and approximately 2 ml. of glacial acetic acid and 9.1 g. (0.10 mole) of thiosemicarbazide added. The solution was warmed with occasional swirling until the thiosemicarbazide dissolved and then refluxed for approximately one hour. After cooling, the crystalline thiosemicarbazone was collected and recrystallized from 50% ethanol or methanol. The crude yields ranged from 90–96%. The thiosemicarbazones are all yellow crystalline compounds, but occasionally on fresh crystallization, some of them appear almost white. After drying and exposure to air, however, they assume a yellow tinge.

**Intermediate Carbonyl Compounds.**—Although all of the thenaldehydes and acetothienones have been previously reported, some of them were prepared by methods not previously applied to these compounds and these are briefly described. 3-Thenaldehyde was prepared by the Sommelet procedure, as previously described,[12] as were 2-chloro-, 2-bromo-, and 2,5-dichloro-3-thenaldehyde.[13] In the latter case, 54 g. (59%) of crude 2,5-dichloro-3-thenaldehyde was obtained from 108 g. (0.65 mole) of 2,5-dichloro-3-methylthiophene and 0.6 mole of N-bromosuccinimide, which is a considerable improvement over the yield previously reported, although no changes were made in the procedure.

5-Nitro-2-thenaldehyde was prepared by the method of Patrick and Emerson.[14] The observation of Dullaghan, *et al.*,[15] that this compound could not be obtained by application of the Sommelet procedure to the product obtained on treatment of 5-nitro-2-methylthiophene with N-bromosuccinimide was confirmed.

5-Methyl-, 3-methyl-, 5-*t*-butyl- and 5-acetamido-2-thenaldehyde were obtained by the dimethylformamide formylation procedure described by Campaigne and Archer.[16] The various 2-acetothienones were samples previously prepared in this Laboratory.[17]

**5-Chloro-2-thenaldehyde.**—A mixture of 125 g. (0.94 mole) of 5-chloro-2-methylthiophene[18] and 1 g. of benzoyl peroxide was refluxed in 250 ml. of dry benzene, and 160 g. (0.9 mole) of N-bromosuccinimide mixed with 1 g. of benzoyl peroxide was added portionwise at such a rate as to maintain vigorous refluxing of the benzene. When addition was complete, the mixture was refluxed vigorously for about 5 minutes, then cooled and filtered with suction. Most of the benzene was removed by distillation at water-pump vacuum, and the crude 5-chloro-2-thenyl bromide was added dropwise to a refluxing stirred solution of 132 g. (0.94 mole) of hexamethylenetetramine in 200 ml. of chloroform. The heavy crystalline precipitate was collected, washed repeatedly with chloroform and dried *in vacuo*, yielding 220 g. (0.62 mole) of hexamine salt of 5-chloro-2-thenyl bromide. Without further purification, this salt was dissolved in 1 l. of 50% acetic acid and the solution rapidly steam distilled. Extraction of the distillate with ether yielded 43.9 g. (33.4% over-all yield) of 5-chloro-2-thenaldehyde, b.p. 85–88° (5–6 mm.). Oxidation of a small sample with silver oxide gave an acid melting at 147–148°.[19]

**5-Bromo-2-thenaldehyde.**—5-Bromo-2-thenyl chloride[20] was converted to the hexamine salt by refluxing with hexamine in chloroform and the crude salt steam-distilled in 1 l. of 50% acetic acid. After working up by the usual procedure, a 32% yield of 5-bromo-2-thenaldehyde, b.p. 81–84° (4 mm.), was obtained. Oxidation gave an acid which melted at 141–142°.[21] This process does not afford as good yields of this aldehyde as the phosphorus oxybromide formylation reported by King and Nord.[22]

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[10] W. J. King and F. F. Nord, *J. Org. Chem.*, **13**, 635 (1948).

[11] T. L. Cairns and B. C. McKusick, *ibid.*, **15**, 790 (1950).

[12] E. Campaigne and W. M. LeSuer, This Journal, **70**, 1555 (1948).

[13] E. Campaigne and W. M. LeSuer, *ibid.*, **71**, 333 (1949).

[14] T. M. Patrick and W. S. Emerson, *ibid.*, **74**, 1356 (1952).

[15] M. E. Dullaghan, L. J. Owen and F. F. Nord, *ibid.*, **74**, 2676 (1952).

[16] E. Campaigne and W. L. Archer, *ibid.*, **75**, 989 (1953).

[17] E. Campaigne and J. L. Diedrich, *ibid.*, **73**, 5240 (1951).

[18] E. Campaigne and W. M. LeSuer, *ibid.*, **70**, 415 (1948).

[19] J. F. Bunnett, D. M. Bachman, L. P. Snipper and J. H. Maloney, *ibid.*, **71**, 1493 (1949).

[20] R. C. Clapp, *et al.*, *ibid.*, **69**, 1549 (1947).

[21] H. D. Hartough and L. G. Conley, *ibid.*, **69**, 3096 (1947).

[22] W. J. King and F. F. Nord, *J. Org. Chem.*, **14**, 405 (1949).

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## The Use of Dimethylformamide as a Formylation Reagent[1]

By E. Campaigne and Wesley L. Archer[2]

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The direct formylation of the thiophene nucleus by N-methylformanilide and phosphorus oxychloride has been recently reported.[3,4] Dimethylformamide has been reported in the patent literature as an effective substitute for N-methylformanilide in formylation of aromatic tertiary amines.[5] Tyson and Shaw[6] obtained a 72% yield of 3-indolecarboxaldehyde upon formylation of indole with dimethylformamide, and the application of this formylating agent to thiophenes has been patented.[7]

This formylation agent has two strong advantages despite the somewhat lower yields of aldehydes as compared to the N-methylformanilide procedure. Firstly, dimethylformamide is commercially an inexpensive reagent as compared to N-methylformanilide and therefore can be used in liberal excess as solvent, and secondly the weight of formyl group per mole of dimethylformamide is approximately twice the available formyl weight afforded by N-methylformanilide.

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[1] Contribution No. 570 from the Chemistry Laboratory of Indiana University. This work was supported by a Contract between the Office of Naval Research, Department of the Navy, and Indiana University.

[2] Abstracted from the thesis of Wesley L. Archer, to be submitted to Indiana University in partial fulfillment for the Degree of Doctor of Philosophy.

[3] W. J. King and F. F. Nord, *J. Org. Chem.*, **13**, 635 (1948).

[4] A. W. Weston and R. J. Michaels, Jr., This Journal, **72**, 1422 (1950).

[5] C. D. Wilson, U. S. Patents 2,437,370 (1948), 2,558,285 (1951).

[6] F. T. Tyson and J. T. Shaw, This Journal, **74**, 2273 (1952).

[7] W. S. Emerson and T. M. Patrick, U. S. Patent 2,581,009 (1952).

In order to compare the two methods, several thiophenes and two other aromatic compounds were formylated with dimethylformamide. Table I records the constants of the aldehydes prepared and compares the yields with those previously reported by the N-methylformanilide procedure.[4] In three instances, thiophene, 3-methylthiophene and 2-*t*-butylthiophene, the aldehydes were obtained in yields approximately equal to those obtained by the N-methylformanilide method, while dimethylaniline gave *p*-dimethylaminobenzaldehyde in yields that exceeded the previously reported yield with N-methylformanilide.[8]

TABLE I

ALDEHYDES PREPARED BY DMF PROCEDURE

| | B.p.,[a] | | Yield, % using | | |
|---|---|---|---|---|---|
| Aldehyde | °C. | Mm. | D-MF[b] | M-FA[b] | Acid, m.p., °C. |
| 2-Thenaldehyde | 44–45 | 1.1 | 72 | 77[d] | 129–130[e,f] |
| 5-Chloro-[g] | 52–53 | 0.5 | 43 | 59[d] | 152–152.5[e,f] |
| 5-Methyl-[g] | 84–85 | 3.5 | 66 | 81[d] | 136–137[e,f] |
| 3-Methyl-[g] | 84–85 | 3.5 | 80 | 83[d] | 147–148[e,f] |
| 5-*t*-Butyl-[g] | 107–108 | 3.6 | 76 | 76[d] | 126.5–127[e,f] |
| 5-Acetamido-[g] | 183.5–184[c] | | 47 | ... | 271–272[e,h] |
| 4-Dimethylaminobenzaldehyde | 71–71.5[c,i] | | 71 | 50[j] | ...[k] |
| 9-Anthraldehyde[l] | 103.5–104[c,i] | | 63 | 84 | ...[m] |

[a] See ref. 1 and 2 for other b.p. values. [b] DMF is dimethylformamide, MFA is N-methylformanilide. [c] Melting point (all melting points are uncorrected). [d] See ref. 3. [e] Thiosemicarbazone derivatives of the 2-thenaldehyde compounds correspond to the derivatives described by E. Campaigne, *et al.*, THIS JOURNAL, **75**, 988 (1953). [f] These values agree with those given by Weston and Michaels, ref. 4. [g] Substituted 2-thenaldehyde derivatives. [h] M.p. 272–273°, ref. 13. [i] R. Adams, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 214, reports m.p. 73°. [j] Ref. 6. [k] Thiosemicarbazone of this aldehyde melted at 208–209° (dec.) which agrees with the reported m.p. given by Bernstein, *et al.*, THIS JOURNAL **73**, 906 (1951). [l] L. F. Fieser, *Org. Syntheses*. **20**, 11 (1940), reports m.p. 104.5–105°. [m] Thiosemicarbazone melts at 194–195°. Calcd. for $C_{16}H_{13}N_3S$: N, 15.05. Found: N, 15.09.

A previously unreported compound, 5-acetamido-2-thenaldehyde, has been synthesized by means of dimethylformamide. Repeated attempts to formylate 2-acetamidothiophene using the more active N-methylformanilide in benzene gave only tars, but when no solvent was used a very low yield of the desired aldehyde was obtained. Possibly the active hydrogen on the nitrogen atom of the acetamido group is competing with the $\alpha$-hydrogen of the thiophene nucleus in the formylation reaction and as a result of this competition tars are the principal products. In the case of dimethylformamide a 47% yield of the 5-acetamido-2-thenaldehyde, which melted at 183.5–184°, was obtained.

It is interesting to note that Weston[4] reported that unsubstituted formamide gave only traces of aldehyde. In the case of dimethylformamide it was found that the best yields were obtained when the reaction mixture was heated on a steam-bath for a period of one to two hours. The strong exothermic reaction at the first heating sometimes became violent unless properly suppressed by cooling in an ice-bath. In all cases phosphorus oxychloride was used as the condensing agent and often an excess of the dimethylformamide was necessary in order to give a homogeneous mixture. In most cases a slight excess of dimethylformamide and phosphorus oxychloride gave maximum yields.

In an attempt to use the modification of Weston,[4] in which the reactants were allowed to stand at room temperature for 16 hours, only 28% of 2-thenaldehyde was obtained when thiophene, dimethylformamide and phosphorus oxychloride were mixed and allowed to stand at room temperature for 72 hours. This indicates that the dimethylformamide is somewhat less reactive than the N-methylformanilide.

For purposes of identification the thiophene aldehydes were converted to the corresponding acids by oxidation with silver oxide, except in the case of the 5-acetamido-2-thenaldehyde, which was oxidized quantitatively with aqueous Fehling solution.

**Acknowledgment.**—We are indebted to the Socony–Vacuum Laboratories for samples of 2-methylthiophene and 2-*t*-butylthiophene, and to the Sterling–Winthrop Research Institute for a sample of 3-methylthiophene. We are also indebted to the E. I. du Pont de Nemours Company for the DMF used in these experiments.

## Experimental

**Substituted 2-Thenaldehydes.**—The various 2-thenaldehydes were all prepared by the same method, and the boiling points and yields are reported in the table. Examples of the method are given in the following specific preparations.

**2-Thenaldehyde.**—To a solution of 42.0 g. (0.5 mole) of thiophene and 46.0 g. (0.64 mole) of dimethylformamide[9] which was cooled and shaken in a 500-ml. flask equipped with a reflux condenser and calcium chloride drying tube was added slowly 96.0 g. (0.62 mole) of phosphorus oxychloride. The flask was carefully heated on a steam-bath until a strong exothermic reaction commenced, after which the reaction was modified by cooling in an ice-bath until the rapid evolution of hydrogen chloride ceased. The mixture was finally heated on a steam-bath for one hour with occasional shaking, and then cooled and poured with stirring into a beaker containing 500 g. of cracked ice, after which the acidic solution was neutralized with a saturated solution of sodium acetate. The oily layer was separated and combined with the ether extracts of the aqueous solution. The ether solution was washed free of all traces of acid with dilute sodium bicarbonate solution, dried over anhydrous sodium sulfate and finally concentrated. Vacuum distillation of the resulting red oil gave 40.7 g. (72.7%) of 2-thenaldehyde, b.p. 44–45° (1.1 mm.). A forerun of unreacted thiophene was also obtained.

**5-Acetamido-2-thenaldehyde.**—Fourteen grams (0.1 mole) of 2-acetamidothiophene, prepared in 33% yield from 2-nitrothiophene[10] by the method of Steinkopf,[11] was dissolved in 54.0 g. (0.75 mole) of dimethylformamide contained in a 500-ml. flask equipped with a reflux condenser and calcium chloride drying tube. This solution was shaken and cooled while 18.5 g. (0.12 mole) of phosphorus oxychloride was added slowly. The flask was then heated on a steam-bath with occasional shaking for a period of one hour. A green suspension developed after 15 minutes of heating. The contents of the flask were added to 500 g. of cracked ice and neutralized by the slow addition of a saturated solution of sodium acetate. Solid sodium acetate was then added until the solution was saturated and the ruby-red solution was stirred with a mechanical stirrer for one or two hours until the aldehyde began to crystallize. At this point the mixture was allowed to stand in a refrigerator overnight and then filtered to give 14.0 g. of dark tan

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(8) A. Vilsmeier and A. Haack, *Ber.*, **60**, 119 (1927).

(9) The dimethylformamide was technical DMF obtained from Grasselli Chemicals Dept., E. I. du Pont de Nemours and Company, Wilmington, Delaware.

(10) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, 1943, p. 466.

(11) W. Steinkopf, *Ann.*, **403**, 17 (1914).

crystals. Recrystallization from the minimum amount of water gave 8.0 g. of white crystals (47.5%), which melted at 183.5–184°. The loss encountered in the recrystallization was due to the inclusion of excess sodium acetate in the crude precipitate.

*Anal.* Calcd. for $C_7H_7ON_2S$: N, 8.28. Found: N, 8.23.

**5-Acetamido-2-thenaldoxime.**—This aldehyde gives an immediate deep violet precipitate with 2,4-dinitrophenylhydrazine in alcohol, but the melting point of this derivative was above 300° and it was too insoluble to be readily crystallized. The oxime was readily formed by the usual procedure and crystallized in glistening white needles which, even after repeated crystallization from water, had a broad melting range, 198–202°. This may be due to the presence of *syn* and *anti* isomers, since the analysis was satisfactory.

*Anal.* Calcd. for $C_7H_8O_2N_2S$: N, 15.21. Found: N, 15.35.

**5-Acetamido-2-thenoic Acid.**—Three-tenths of a gram of 5-acetamido-2-thenaldehyde (0.00177 mole) was dissolved in 60 ml. of stock Fehling solution[12] (30 ml. of solution I and 30 ml. of solution II) and 100 ml. of water and the blue solution allowed to stand at room temperature for three days. The red precipitate of cuprous oxide was then filtered off, the aqueous solution concentrated to approximately 50 ml. and cooled to give 0.32 g. (quantitative yield) of white crystalline 5-acetamido-2-thenoic acid, which when recrystallized from hot water melted at 271–272°, as previously reported.[13]

*Anal.* Calcd. for $C_7H_7NO_3S$: neut. equiv., 185. Found: neut. equiv., 182.

***p*-Dimethylaminobenzaldehyde.**[14]—Fifty-one grams (0.34 mole) of phosphorus oxychloride was added dropwise with stirring and cooling to 88.0 g. (1.2 moles) of dimethylformamide contained in a 500-ml. three-necked flask equipped with a reflux condenser, drying tube, stirrer, and dropping funnel. To this mixture was added dropwise with stirring 40.0 g. (0.34 mole) of technical dimethylaniline, after which the solution was heated with stirring on a steam-bath for two hours. The mixture was poured over ice and neutralized by dropwise addition of aqueous sodium acetate with vigorous stirring. Any excessive increase in temperature of the aqueous solution during neutralization led to the formation of greenish-blue dyestuffs which could not be removed from the product by recrystallization or acidification and reprecipitation by alkali. White crystalline *p*-dimethylaminobenzaldehyde which weighed 34.8 g. (70.5%), was obtained from the neutral solution after standing overnight in a refrigerator. The product was essentially pure as it precipitated from the reaction mixture.

**9-Anthraldehyde.**—In a 1-l. three-necked flask equipped with a reflux condenser, drying tube and stirrer was placed 18.0 g. (0.104 mole) of anthracene (m.p. > 215°), 16.0 g. (0.22 mole) of technical dimethylformamide, 28.0 g. (0.118 mole) of phosphorus oxychloride and 20 cc. of *o*-dichlorobenzene. The suspension was stirred and heated on a steam-bath for 30 minutes to complete solution, after which the heating was continued for an additional 90 minutes. The cool reaction solution was then neutralized with aqueous sodium acetate and diluted with water to a volume of 2 liters. After standing overnight in a refrigerator the yellow precipitate was filtered from the mother liquor and recrystallized from 50 ml. of glacial acetic acid. Washing the acetic acid from the resulting crystals with a small amount of cold methanol gave 13.0 g. (62.5%) of beautiful yellow needles of 9-anthraldehyde. An attempt to use excess dimethylformamide to replace the *o*-dichlorobenzene solvent resulted in a lower yield of aldehyde which was more difficult to purify. The *o*-dichlorobenzene held the unreacted anthracene in solution at the point of neutralization and prevented contamination of the product.

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[12] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 86.

[13] H. D. Hartough, "Thiophene and its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 380.

[14] The preparation of this compound by the DMF procedure is not original (British Patent 607,920 (1948); *C. A.*, **43**, 2232 (1949)) but is repeated for convenience.

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# Acidity and Infrared Absorption of Fluorinated Alcohols

BY ALBERT L. HENNE AND WILLIAM C. FRANCIS

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It is now firmly established that the ionization constant of alcohols perfluorinated in the $\alpha$-position is of the order of magnitude of $K_i = 10^{-12}$. Specifically, we have reported $4.0 \times 10^{-12}$ for $CF_3CH_2OH$,[1] and $1.2 \times 10^{-11}$ and $4.1 \times 10^{-12}$ for the first and second constants of $HOCH_2CF_2CF_2CH_2OH$,[2] in good agreement with similar results reported from other laboratories.[3] Perfluorinated primary alcohols are thus about $10^6$ times more acid than their unfluorinated analogs, and we have wondered whether this increase might be about doubled in secondary alcohols, and perhaps almost tripled in tertiary alcohols. This was found not to be the case. Specifically, ionization constants were measured as $4.3 \times 10^{-12}$ for $C_3F_7CH_2OH$, $4.3 \times 10^{-12}$ for $C_3F_7CH(OH)C_3H_7$ and $2.2 \times 10^{-11}$ for $C_3F_7CH(OH)C_3F_7$. The bulk of the inductive effect is thus exercised by the first fluorinated group, and we can now predict that perfluorinated tertiary alcohols will prove comparable to phenol in acidity, at best.[4]

The three alcohols were prepared as follows: $C_3F_7CH_2OH$ by reduction of the acid with lithium aluminum hydride, $C_3F_7CH(OH)C_3F_7$ by reduction of the ketone with the same reagent, and $C_3F_7CH(OH)C_3H_7$ by condensation of $C_3F_7MgI$ with butyraldehyde; the preparations of $C_3F_7MgI$, $C_3F_7COC_3F_7$ and $C_3F_7CH(OH)C_3H_7$ are given in an accompanying paper.[5]

The ionization constants were determined by glass electrode measurements of the *p*H at the half-equivalence point in 50% aqueous methanol, using tenth normal sodium hydroxide in the same solvent.

Perfluorinated secondary heptanol, $C_3F_7CH(OH)C_3F_7$, boils at 58° under 78 mm., and has $d^{20}{}_4$ 1.6735; its refractive index at 20° is well below the scale of an Abbe refractometer (1.30); a sample sent to Minnesota Mining Co. was reported back as $n^{25}{}_D$ 1.2911; its 3,5-dinitrobenzoate, melting at 84.0–84.2°, was analyzed. Calcd.: C, 29.9; H, 0.7; N, 5.0. Found: C, 30.2; H, 0.9; N, 5.6.

$C_3F_7CH(OH)C_3H_7$ boils at 63.5° under 45 mm., $n^{20}{}_D$ 1.3391, was analyzed. Calcd.: C, 34.71; H, 3.72. Found: C, 34.18; H, 3.05. Its 3,5-dinitrobenzoate melts at 63.5–63.8°, and calcd.: N, 6.42. Found: N, 6.91.

The infrared spectra of the three alcohols were taken on the pure liquids at a cell thickness of 0.025 mm. with a Baird spectrophotometer. Each shows carbon–fluorine stretching in the range 7.1 to 10.0 $\mu$. The carbon–hydrogen absorption at about 3.4 to 3.5 $\mu$ is in agreement with the assigned structures. For instance, in the case of $C_3F_7CH$-

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[1] A. L. Henne and R. L. Pelley, THIS JOURNAL, **74**, 1426 (1952).

[2] A. L. Henne and S. Richter, *ibid.*, **74**, 5420 (1952).

[3] E. T. McBee, W. F. Marzluff and O. R. Pierce, *ibid.*, **74**, 444 (1952).

[4] In agreement, Dr. R. N. Haszeldine reported at the September, 1952, Meeting of the A.C.S., the following values for perfluorinated alcohols: primary alcohols, $4 \times 10^{-12}$; secondary alcohols, $3 \times 10^{-11}$; tertiary alcohols, $3 \times 10^{-10}$ for $(CF_3)_3COH$, $1 \times 10^{-10}$ for $(C_3F_7)_3COH$.

[5] A. L. Henne and W. C. Francis, THIS JOURNAL, **75**, 992 (1953).

(OH)$C_3H_7$ there is a strong, sharply defined band in this region with a transmittance of only 9%, while for the hydrogen-poorer $C_3F_7CH_2OH$ there is a much weaker absorption (42% transmittance) and the peaks of the band are less sharp; for $C_3F_7CH$(OH)$C_3F_7$ the carbon–hydrogen absorption is very weak, with 74% transmittance.

For $C_3F_7CH_2OH$ the strong, broad band for associated –OH is at 3 μ with 6% transmittance; it differs very little from that of 1-butanol. The unassociated –OH band appears only as a break in the curve at 2.8 μ with 69% transmittance.

For $C_3F_7CH(OH)C_3H_7$, the associated –OH band is very similar to that of $C_3F_7CH_2OH$, but with a slight shift toward shorter wave lengths at 2.97 μ with 10% transmittance. The reason for such a shift is not apparent, but might perhaps be attributed to steric factors. The non-associated –OH is still overlapped, and appears only as a break at 2.8 μ with 70% transmittance.

For $C_3F_7CH(OH)C_3F_7$ there is a strong difference. The non-associated –OH is now quite prominent at 2.8 μ with 39% transmittance; the associated –OH band is much less intense than in the previous cases, with 36% transmittance, and there is a shift to a shorter wave length at 2.9 μ. All this denotes a weaker hydrogen bonding, attributable to the reduced basicity of the hydroxylic oxygen atom.

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## Reactions of Perfluorinated Propylmagnesium Iodide

BY ALBERT L. HENNE AND WILLIAM C. FRANCIS

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Pilot information on perfluorinated Grignard reagents, $C_nF_{2n+1}MgX$ has appeared recently,[1,2,3] and in a preliminary communication[1] we have shown that $n$-$C_3F_7MgI$ could be formed and combined at low temperature with carbon dioxide or acetone in workable syntheses. The present paper reports further details and observed limitations in the formation and reactions of perfluorinated $n$-propylmagnesium iodide, $C_3F_7MgI$. The yields reported are not the best possible, but are either minimal yields or else clear indications that the reactions do not occur to any appreciable extent.

At room temperature, $n$-$C_3F_7I$ reacts readily with magnesium in ethyl ether or tetrahydrofuran, but the main products are $CF_3CF{=}CF_2$ and fluorinated tars. Hydrolysis to $C_3F_7H$ and titration with aqueous acids agree to show the presence of about 5% of $C_3F_7MgI$, and this order of magnitude can be confirmed by carbonation or condensation with acetone. The instability of $n$-$C_3F_7MgI$ at this temperature is such that it is completely decomposed in a few hours.

At lowered temperatures, down to −80°, the stability of $n$-$C_3F_7MgI$ improves progressively, but its rate of formation is much slower. As these two factors oppose each other, the problem of devising practical applications is not solved by a mere lowering of the temperature. As previously reported,[1] the best results were obtained by forming the Grignard reagent at low temperature in the presence of the compound with which it should condense. This procedure has now been applied to several derivatives with a carbonyl or carboxyl group.

The following results were noted when $C_3F_7MgI$ was prepared at temperatures lower than −40° and in the presence of the condensing agent which should consume it as made, except where otherwise stated: (1) Acetone gave a 10% yield of $C_3F_7C(OH)(CH_3)_2$, which was identified and measured as its dehydration product, $C_3F_7C(CH_3){=}CH_2$. Mesityl oxide appeared as side-product, in quantities which varied with experimental conditions. (2) Butyraldehyde gave a 16% yield of the expected secondary alcohol, $C_3H_7CH(OH)C_3F_7$ and by-products attributed to aldol-type condensation of the aldehyde. (3) Perfluorinated butyraldehyde failed to give more than traces of the expected secondary alcohol, $C_3F_7CH(OH)C_3F_7$, and was recovered as aldehyde hydrate (38%), aldehyde polymer (48%) and perfluorobutyric acid (6%). (4) Ethyl formate gave a 24% yield of perfluorobutyraldehyde isolated as its hydrate, $C_3F_7CH(OH)_2$, but no secondary alcohol even when a large excess of the Grignard reagent was supplied. (5) Ethyl perfluorobutyrate gave 20% of perfluorinated ketone, $C_3F_7COC_3F_7$, but no tertiary alcohol. (6) Perfluorinated butyryl chloride, $C_3F_7COCl$, stopped the formation of the Grignard derivative. The condensation was therefore carried out in a separate step, which gave a 4% yield of ketone, $C_3F_7COC_3F_7$.

The reaction with a perfluorinated aldehyde, $C_3F_7CHO$, which could not suffer from competing aldolization but gave, nevertheless, practically no condensation with the Grignard reagent is consistent with the poor yields reported for its condensations with ordinary Grignard reagents.[4,5] With ethyl formate, the formation of $C_3F_7CHO$ only agrees with the observed indifference of this aldehyde to $C_3F_7MgI$. With derivatives of the perfluorinated acids, the preferential formation of ketones is consistent with the action of ordinary Grignard reagents on these derivatives.[6]

The most practical result is the preparation of perfluorinated ketones from perfluorinated acids which are now commercially available.[7]

To illustrate, $C_3F_7COC_3F_7$ was synthesized from two moles of $C_3F_7CO_2H$, one mole of which was transformed into $C_3F_7MgI$ by the sequence $C_3F_7CO_2H$ to $C_3F_7CO_2Ag$ to $C_3F_7I$ to $C_3F_7MgI$, and

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[1] A. L. Henne and W. C. Francis, THIS JOURNAL, **73**, 3518 (1951).

[2] R. N. Haszeldine, *Nature*, **167**, 139 (1951); **168**, 1028 (1951).

[3] R. N. Haszeldine, 120th and 122nd A.C.S. Meetings, September, 1951 and 1952.

[4] E. T. McBee, J. F. Higgins and O. R. Pierce, THIS JOURNAL, **74**, 1387 (1952).

[5] E. T. McBee, O. R. Pierce and J. F. Higgins, *ibid.*, **74**, 1737 (1952).

[6] K. N. Campbell, J. O. Knobloch and B. C. Campbell, *ibid.*, **72**, 4380 (1950).

[7] Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.

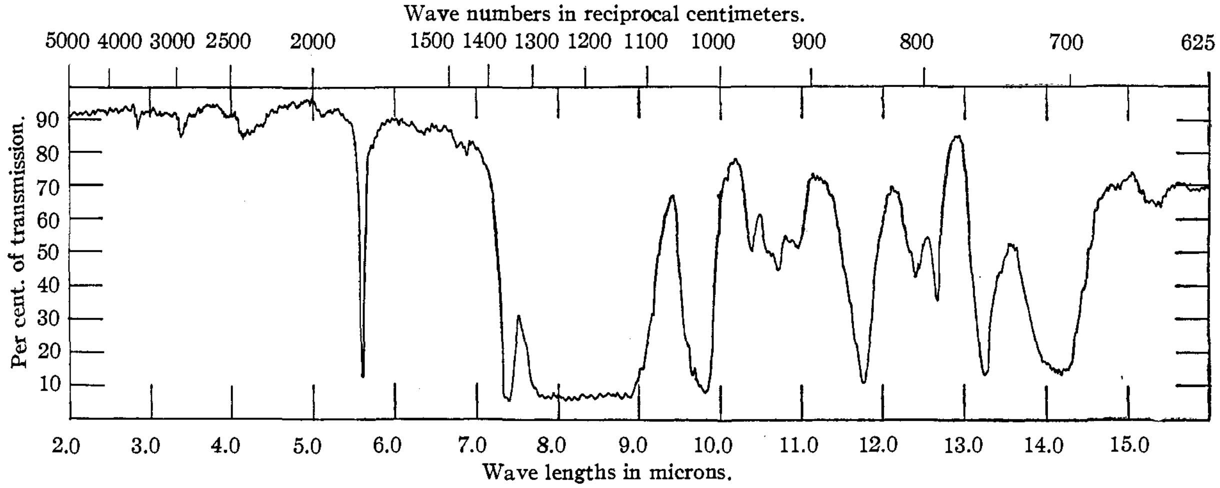

Fig. 1.—$C_3F_7COC_3F_7$.

condensed with an ester of the second mole. Unsymmetrical ketones are similarly obtainable from two different acids.

The perfluorinated ketones are so sensitive to nucleophilic attack that they are split by a reagent as weakly basic as the bicarbonate ion. The perfluorinated secondary alcohol made by reduction of such a ketone has acidity and infrared absorption characteristics which are described in an accompanying paper.[8]

On the basis of all our observations in the forming and utilization of $n$-$C_3F_7MgI$, the following general recommendations are made: (1) Where its boiling point (65°) does not interfere with the isolation and purification of the final product, tetrahydrofuran appears to be a more satisfactory solvent than ethyl ether in rate of reaction, amount of magnesium consumed and yield of condensation product. (2) A solvent ratio of about 1300 ml. of ether per mole of iodide appears best; with tetrahydrofuran, a slightly greater dilution is expedient. (3) Condensation reagents not subject to aldolization give better yields when the Grignard reagent is formed in their presence. Acyl halides, which practically prevent Grignard formation, are exceptions. (4) After initiation of the reaction at room temperature, if needed, a reaction temperature of about $-80°$ should be maintained for at least 24 hours before completing the consumption of the magnesium at temperatures raised progressively from $-60$ to $-30°$. Acyl halides, or aliphatic aldehydes and ketones, are best added after the initial low temperature period, but before the temperature rises above $-50°$.

## Experimental

**Preparation of $C_3F_7I$.**—This was prepared in 87% yield from silver perfluorobutyrate by the previously described procedure,[9,10] and with no more than 3% of perfluoropropylene as by-product. The observed physical constants agreed with the literature.

**Reaction with Magnesium.**—At room temperature, $C_3F_7I$ reacts very readily with magnesium in ether or tetrahydrofuran, but not in perfluorinated butyl ether (b.p. 101°) or perfluorinated triethylamine (b.p. 70°). A basic solvent is thus needed. Addition of ethyl ether to one of the perfluorinated solvents causes the reaction to start. Darkening and tar precipitation occurs promptly and hampers conventional[11] titration of the Grignard. When a delay of one day is allowed before titration, the Grignard reagent is completely absent.

During the attack of the magnesium, 15 to 20% of low-boiling material ($-30$ to $-20°$) is formed, the infrared spectrum of which shows it to be a mixture of perfluoropropylene and heptafluoropropane, with the olefin predominant. Addition of bromine gives the known $CF_3CFBrCF_2Br$, b.p. 71°, $n^{28}\text{D}$ 1.3579, and the unbrominated material is shown by its infrared spectrum to be $C_3F_7H$ free of $C_3F_6$.

Subsequent carbonation by the usual procedures gives no better than traces of $C_3F_7CO_2H$, but when the reaction of $C_3F_7I$ on magnesium is performed in an atmosphere of carbon dioxide, the acid is obtained in 4 to 10% yields. For conveniency in handling, this acid was collected as its crystalline amide, m.p. 105°, after esterification and treatment with dry ammonia. This procedure was first tested on known solutions of similar dilution and composition; it was found to supply 60% of the theoretical amount of amide, and such a correcting factor was then applied to the above measurements.

Attack of the magnesium in the presence of a slight excess of acetone gives 8% of crude carbinol $C_3F_7C(OH)(CH_3)_2$, characterized as its product of dehydration over $P_2O_5$, $C_3F_7C(CH_3){=}CH_2$, b.p. 54–55°, $n^{25}\text{D}$ 1.2997, in fair agreement with the literature constants.[12]

In the presence of ethyl perfluorobutyrate, about 8% of crude $C_3F_7COC_3F_7$ (see below) was formed, but no perfluorinated tertiary carbinol could be traced.

**Low Temperature Reactions. (a) Grignard Formation.**—$C_3F_7I$ can attack magnesium at $-80°$, and the Grignard reagent has sufficient stability at this low temperature to permit the use of fairly high concentrations, and to allow delay before subsequent condensations. But when the magnesium attack was carried out at $-40°$ over a period of 48 hours, and was followed by carbonation the only product isolated was $C_3F_6$, obtained in 13% yield, and no $C_3F_7CO_2H$.

**(b) Carbonation.**—After initiation at room temperature, a solution of $C_3F_7I$ (38 g. or 0.128 mole) in 60 ml. of dry ether (equivalent to 470 ml. of solvent per mole of iodide), was stirred for 24 hours with magnesium (17 g. or 0.7 g. atom) at $-80°$, in the presence of powdered Dry Ice in constant excess. Filtration of the remaining metal indicated a 63% consumption of the theoretical amount of magnesium, and working up of the filtrate gave a 41% yield of $C_3F_7CO_2H$ isolated as such, on the basis of the consumed magnesium. The use of a more dilute solution (660 ml. per mole) slowed down the reaction to 48% of magnesium consumption in 67 hours, but did not appreciably affect the yield of $C_3F_7CO_2H$, 38%. With much greater dilutions (5,000 ml. per

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[8] A. L. Henne and W. C. Francis, This Journal, **75**, 991 (1953).

[9] A. L. Henne and W. G. Finnegan, *ibid.*, **72**, 3806 (1950).

[10] M. Hauptschein and A. V. Grosse, *ibid.*, **73**, 2461 (1951).

[11] H. Gilman, *et al.*, *ibid.*, **45**, 150 (1923).

[12] Minnesota Mining and Manufacturing Co. technical literature: Heptafluorobutyric Acid, 1949.

mole), the attack of the magnesium could not be maintained below −30°. The use of tetrahydrofuran instead of ether (470 ml. per mole) gave a 54% consumption of magnesium in 48 hours, and a yield of $C_3F_7CO_2H$ of 51%.

(c) **Condensation with Acetone.**—An equimolecular solution of 1/3 mole of $C_3F_7I$ and 1/3 mole of acetone in 125 ml. of ether (370 ml. per mole) was stirred at −80° with an excess of magnesium for 58 hours, after initiation at room temperature. When allowed to warm up, the reaction mixture suddenly boiled over into the traps, from which it was returned. Working up gave a 10% yield of impure tertiary carbinol $C_3F_7C(OH)(CH_3)_2$, b.p. 100–110°, $n^{20}$D 1.3355, better characterized by dehydration to $C_3F_7C(CH_3){=}CH_2$; see above. This reaction was then repeated at a progressively raised temperature: 18 hours at −40°, 19 hours at −25° and 5 hours at −15°. Even then, only 48% of the theoretical magnesium had been consumed. The working up of this reaction did not give any fluorinated tertiary carbinol, but only mesityl oxide in 31% yield, and high-boiling condensation products. Remembering the results obtained at room temperature, it was concluded that the carbonyl group of acetone interferes with Grignard formation, and that at intermediate temperatures the Grignard reagent causes ketolization instead of condensing with the keto group.

(d) **Condensation with Butyraldehyde.**—After initiating the attack of the magnesium at room temperature with a small amount of iodide, *n*-butyraldehyde (0.5 mole) was added at −40° to a stirred solution of $C_3F_7I$ (0.4 mole) in 370 ml. of ethyl ether (923 ml. per mole of iodide) containing an equivalent quantity of magnesium. The mixture was stirred for 39 hours in the −50 to −40° range, then for .72 hours at about −30° and 17 hours at −20°. Much magnesium remained unconsumed, but was finally taken up during a 36-hour period of stirring at room temperature. In this time, 25.5 g. of low-boiling material was collected. After hydrolysis, working up gave first a mixture of recovered iodide and aldehyde, then a 16% yield of secondary alcohol, $C_3F_7CH(OH)C_3H_7$, b.p. 63.5° (45 mm.), $n^{20}$D 1.3391. Calcd.: C, 34.71; H, 3.72. Found: C, 34.18; N, 3.75. Dinitrobenzoate, m.p. 63.5–63.8°; Found: N, 6.91. Calcd.: N, 6.42. Analyses by Elek microanalytical laboratories, Los Angeles. The acidity and infrared characteristics of this alcohol are discussed in an accompanying paper.[8] The above conditions were an effort to avoid excessive interference with Grignard formation, and yet avoid aldolization at the expense of condensation.

(e) **Condensation with $C_3F_7CHO$.**—So little condensation occurred that only traces of the desired $C_3F_7CH(OH)C_3F_7$ were observed; this alcohol, prepared by reduction of $C_3F_7COC_3F_7$ is described in another paper.[8] Simultaneous Grignard formation and condensation was tried on 1/4 mole amounts of reagents in 313 ml. of ether (1250 ml. per mole) in the −50 to −40° temperature range. Even at that low temperature, $C_3H_7CHO$ polymerized partly and, by coating, interfered with but did not prevent the progressive consumption of the magnesium in a 22-hour period. Working up recovered 86% of the aldehyde (48% as polymer and 38% as hydrate) and 6% of $C_3H_7CO_2H$, which accounted for 92% of the reagent. The failure to obtain much secondary alcohol can thus be attributed to the sluggishness of the perfluorinated aldehyde.

(f) **Condensation with Ethyl Formate.**—The experiment was started by initiating the magnesium attack with 5 ml. of $C_3F_7I$ in 25 ml. of tetrahydrofuran at room temperature, quickly cooling to −80° by immersion in a Dry Ice-bath, then rapidly adding the remainder of the iodide (0.17 mole total) in 200 ml. of solvent. Immediately following, a solution of 0.41 mole of formate in 275 ml. of tetrahydrofuran was dripped in over a 90-minute period. The concentration was thus 2850 ml. of solvent per mole of iodide. The mixture was stirred under nitrogen for 23 hours at −80°, then 20 hours at −30°, when it appeared chocolate brown and practically free of magnesium. After hydrolysis and treatment with ferrous sulfate to destroy peroxides, distillation up to 65° removed unreacted reagents and the solvent. The remaining aqueous solution was continuously extracted with ether. After removal of the ether by distillation, the aldehyde hydrate $C_3F_7CH(OH)_2$ distilled at 92–98° (9.2 g.), then the azeotrope of formic acid and water came over at 102–104° (7.0 g.); the residue distilled at 125–130° (20 mm.) (7 g. of wet material) and after drying proved to be 1,4-diiodobutane, b.p. 130° (20 mm.), $n^{15}$D 1.6201, % iodine 79.02, obtained at the expense of the solvent. The aldehyde hydrate was thus obtained in 24% yield; its 2,4-dinitrophenylhydrazone, m.p. 102–104°, was made in 6 *N* sulfuric acid, and its free aldehyde, b.p. 28°, in agreement with the literature,[12] was obtained by distillation from $P_2O_5$.

(g) **Condensation with $C_3F_7CO_2Et$.**—Pure ethyl perfluorobutyrate was prepared in 91% yield[13] by mixing one mole of acid and 2 moles of absolute alcohol in a flask equipped with a reflux condenser, pouring 1.5 moles of concentrated sulfuric acid in small portions through the condenser as fast as the exothermic reaction would permit, cooling, decanting the top layer of nearly pure ester and rectifying from a small amount of $P_2O_5$; observed b.p. 95°, $n^{20}$D 1.3011, literature values[12] b.p. 95°, $n^{20}$D 1.3032.

After initiation of the magnesium attack, a mixture of 0.3 mole of iodide and 0.3 mole of ester in 390 ml. of ether (1300 ml. of ether per mole of iodide) was stirred with magnesium for 18 hours at −50°, 24 hours at −40° and 12 hours at −30°, and practically all the magnesium was consumed. After hydrolysis, the mixture was continuously extracted with ether. The ether solution was dried, its ether removed by distillation, and most of the residue rapidly brought over at 27–40° (100 mm.) to a Dry Ice cooled receiver. Redistillation at one atmosphere gave a fraction of crude ketone contaminated with alcohol at 63–85°, then recovered ester at 93–95°, after which a residue was left in the flask. Rectification of the first fraction from $P_2O_5$ to destroy the alcohol gave the ketone at 74–78° and a small amount of ester at 94°. Rectification of the residue, diagnosed as mostly hemi-ketal was also done from $P_2O_5$ and gave a small additional amount of ketone. When an attempt was made to simplify the separation by distilling all of the first ether extract from $P_2O_5$, a considerable amount of ethyl iodide distilling as an azeotrope with the ketone at 54° complicated the procedure; this was due to the solubility of magnesium iodide in ether.

Final distillation from $P_2O_5$ gave, in 20% yield, pure $C_3F_7COC_3F_7$, b.p. 75° (740 mm.), $d^{20}_4$ 1.6250, with a refractive index too low to be read on an Abbe refractometer. *Anal.* Calcd.: C, 22.9; F, 72.7. Found: C, 22.6; F (cor.), 72.5. The carbon microanalysis was obtained from Dr. Robert N. Haszeldine, of Cambridge University. This ketone is very hygroscopic, and is easily split by 5% aqueous alkali into $C_3F_7CO_2H$ characterized by its odor and its amide m.p. 105° (mixed m.p.), and $C_3F_7H$ characterized by its infrared spectrum. Figure 1 shows the spectrum of the ketone $C_3F_7COC_3F_7$ with a strong absorption band (12% transmittance) at 5.8 μ characteristic of the carbonyl function, and with strong absorption for C–F stretching in the 7.1 to 10 μ region. Repeated attempts to prepare a 2,4-dinitrophenylhydrazone, a semicarbazone or an oxime were all unsuccessful. The ketone is insoluble in water or in concentrated sulfuric acid, which shows the non-basic character of its carbonyl oxygen atom.

(h) **Condensation with $C_3F_7COCl$.**—This is not recommended, as it has no advantage over a condensation with the ester in preparing a ketone. The condensation cannot be performed on nascent $C_3H_7MgI$, because the acyl chloride stops the reaction of the iodide on magnesium. In trying the condensation at −30° after completing the Grignard formation at low temperature, a 4% yield of ketone was obtained.

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[13] T. S. Reid, Minnesota Mining and Manufacturing Co., private communication.

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## Silico-alkylation of Sodio Esters with Trimethylchlorosilane to Form Silyl Esters[1]

BY CHARLES R. HANCE AND CHARLES R. HAUSER

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It has previously been shown in this Laboratory that ethyl isobutyrate and certain other esters may

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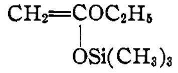
[1] Supported by the Office of Naval Research.

be alkylated with alkyl halides by means of sodium triphenylmethide.[2] We have now found that ethyl isobutyrate and even acetate, which underwent self-condensation instead of being alkylated by benzyl chloride, may be silico-alkylated by the more reactive trimethylchlorosilane.[3] The ester was first converted to its sodio derivative which was then condensed with the chlorosilane (equations 1 and 2).

$$\underset{}{CH_3COOC_2H_5} \xrightarrow[2,\ (CH_3)_3SiCl]{1,\ NaC(C_6H_5)_3} \underset{\mathrm{I}}{(CH_3)_3SiCH_2COOC_2H_5} \quad (1)$$

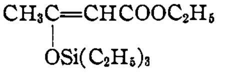
$$(CH_3)_2CHCOOC_2H_5 \xrightarrow[2,\ (CH_3)_3SiCl]{1,\ NaC(C_6H_5)_3} \underset{\mathrm{II}}{(CH_3)_3SiC(CH_3)_2COOC_2H_5} \quad (2)$$

These reactions are assumed to produce the C-derivatives, I and II, rather than the O-derivative, for example, III. The related reaction of sodioacetoacetic ester with triethylchlorosilane has been assumed to form such an O-derivative (IV)[4] but this structure has been questioned.[5]



$CH_2{=}C(OSi(CH_3)_3)OC_2H_5$

III



$CH_3C(OSi(C_2H_5)_3){=}CHCOOC_2H_5$

IV

Evidence that the reaction represented by equation 1 formed structure I is the fact that the product had physical properties practically identical with those reported previously[6] for the silyl ester obtained from the reaction represented by equation 3 which must produce structure I.

$$(CH_3)_3SiCH_2MgCl + ClCOOC_2H_5 \longrightarrow \underset{\mathrm{I}}{(CH_3)_3SiCH_2COOC_2H_5} + MgCl_2 \quad (3)$$

Similar to earlier observations with silyl ester I,[6] silyl ester II was found to undergo cleavage, on refluxing with ethanol, to form ethyl isobutyrate and trimethylethoxysilane. It should be pointed out that the silyl esters obtained in the present work were isolated in the absence of water or acid. When the reaction mixture from sodio ethyl isobutyrate and trimethylchlorosilane was acidified as in the alkylations of esters,[2] only cleavage products, ethyl isobutyrate and hexamethyldisiloxane, were obtained.

### Experimental

Trimethylchlorosilane, obtained from the General Electric Co., was used without further purification. Ethyl isobutyrate (Florasynth Laboratories) and ethyl acetate (Eastman Kodak Co.) were dried over Drierite and distilled prior to use.

Sodium triphenylmethide was prepared in ether solution from 3% sodium amalgam and triphenylchloromethane.[7] Triphenylchloromethane, obtained from Columbia Organic Chemicals Co., or prepared in this Laboratory,[8] was recrystallized from benzene; it then melted at 111–113°.

**Ethyl Trimethylsilylacetate** (I).—A solution of 0.16 mole of sodium triphenylmethide in 750 ml. of ether was transferred under nitrogen pressure[9] to a nitrogen flushed one-liter, three-necked, round-bottomed flask equipped with a sealed stirrer, a dropping funnel, and bulb-type reflux condenser topped with a drying tube. To the stirred dark red solution, cooled to 0° or below by means of an ice–salt-bath, was added rapidly 16.0 g. (0.18 mole) of ethyl acetate in 50 ml. of ether, followed immediately (red color being discharged) by the rapid addition of 20.2 g. (0.184 mole) of trimethylchlorosilane in 50 ml. of ether. After stirring 3 hours and standing 12 hours, the mixture was filtered and the gelatinous precipitate washed thoroughly with ether. The filtrate and washings were concentrated and the precipitate of triphenylmethane removed by filtration and washed with ether. The solvent was removed from the filtrate and washings and the residue distilled through a 15-cm. Vigreux column. The distillate was redistilled through a 21-cm. glass helices-packed column to give 8.2 g. (51%) of recovered ethyl acetate, b.p. 76–78° ($n^{20}$D 1.3735) and 6.9 g. (27%, 48% based on unrecovered ethyl acetate) of ethyl trimethylsilylacetate, b.p. 74.5° (41 mm.), $n^{20}$D 1.4150, $d^{20}{}_4$ 0.8761 (reported b.p. 75.5° (42 mm.), $n^{20}$D 1.4149, $d^{20}{}_4$ 0.8762).[6]

**Ethyl Trimethylsilylisobutyrate** (II).—This ester was prepared in a manner similar to that described for silyl ester I. To a stirred solution of 0.32 mole of sodium triphenylmethide in 700 ml. of ether at room temperature was added 43.8 g. (0.378 mole) of ethyl isobutyrate in 50 ml. of ether and, after 15 minutes, 40.8 g. (0.376 mole) of trimethylchlorosilane in 50 ml. of ether was added. After stirring one hour and standing 12 hours, the gelatinous precipitate was removed by centrifuging and washed thoroughly with ether. The ether solution was concentrated, the triphenylmethane removed, and the solvent distilled. The residue was distilled through a 30-cm. Vigreux column to give 23.0 g. (52%) of recovered ethyl isobutyrate, b.p. 100–110°, and 22.0 g. (38%, 65% based on unrecovered ethyl isobutyrate) of ethyl trimethylsilylisobutyrate, b.p. 50° (9 mm.), $n^{20}$D 1.4168, $d^{20}{}_4$ 0.8553; *MR*D calcd.[10] 55.20, found 55.32.

*Anal.*[11] Calcd. for $C_9H_{20}SiO_2$: C, 57.40; H, 10.70. Found: C, 57.20; H. 10.31.

Treatment of 7.3 g. (0.0388 mole) of silyl ester II with 50 ml. of absolute ethanol, refluxing 4 hours, gave 2.1 g. of material, b.p. 67–70°, which appeared to be an azeotrope of trimethylethoxysilane and ethanol (reported b.p. 66.4°)[12] and 1.2 g. of impure ethyl isobutyrate. None of the original silyl ester was recovered.

Silyl ester II decolorized bromine in carbon tetrachloride within a few minutes. The products were not determined.

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[2] B. E. Hudson and C. R. Hauser, This Journal, **62**, 2457 (1940).

[3] Trimethylchlorosilane is the silicon analog of *t*-butyl chloride but, unlike this alkyl halide which exhibits β-elimination with bases such as ester anions, the chlorosilane undergoes the displacement reaction.

[4] H. Gilman and R. N. Clark, This Journal, **69**, 967 (1947).

[5] F. C. Whitmore, L. H. Sommer, J. Gold and R. E. Van Strien, *ibid.*, **69**, 1551 (1947).

[6] J. R. Gold, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2874 (1948).

[7] W. B. Renfrow and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

[8] C. R. Hauser and B. E. Hudson, *Org. Syn.*, **23**, 102 (1947).

[9] E. Baumgarten and C. R. Hauser, This Journal, **66**, 1039 (1944).

[10] E. L. Warrick, *ibid.*, **68**, 2455 (1946).

[11] Analysis by Clark Microanalytical Laboratory, Urbana, Ill.

[12] R. O. Sauer, This Journal, **66**, 1707 (1944).

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## The Reaction of Diphenyldichlorosilane with Ammonia and Amines

By Erik Larsson and Lars Bjellerup

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As part of the investigation of the synthesis and the reactions of aminosilanes[1–7] the reactions of

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[1] E. Larsson and O. Mjörne, *Trans. Chalmers Univ. Technol., Gothenburg*, **87**, 29 (1949).

[2] E. Larsson, *Svensk Kem. Tid.*, **61**, 59 (1949).

[3] E. Larsson and B. Smith, *Acta Chem. Scand.*, **3**, 487 (1949).

[4] E. Larsson, *ibid.*, **4**, 45 (1950).

[5] E. Larsson and B. Smith, *Svensk Kem. Tid.*, **62**, 141 (1950).

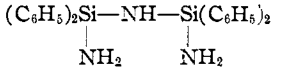
[6] O. Mjörne, *ibid.*, **62**, 120 (1950).

[7] E. Larsson and R. Mårin, *Acta Chem. Scand.*, **5**, 1173 (1951).

diphenyldichlorosilane with ammonia, methylamine, *n*-propylamine, *n*-hexylamine and benzylamine were studied. The following substances were prepared: hexaphenylcyclotrisilazane, diphenyldi-(methylamino)-silane, diphenyldi-(*n*-propylamino)-silane, diphenyldi-(*n*-hexylamino)-silane and diphenyldi-(benzylamino)-silane.

The starting material, diphenyldichlorosilane, was prepared from diphenyldiethoxysilane and benzoyl chloride. Pyridine was used as a catalyst[8] as quinoline was not satisfactory in this case.[9]

The reaction of diphenyldichlorosilane with ammonia was carried out under various conditions: a solution of diphenyldichlorosilane in dry ether was added to liquid ammonia; dry gaseous ammonia was bubbled into a solution of diphenyldichlorosilane in dry ether at 0°, into a boiling solution of diphenyldichlorosilane in dry carbon tetrachloride, and into a boiling solution of diphenyldichlorosilane in dry toluene. From the toluene solution hexaphenylcyclotrisilazane was obtained in good yield. Also from the carbon tetrachloride solution hexaphenylcyclotrisilazane was obtained but in poor yield. The reactions in ether at 0° and at $-33°$ gave no crystalline silicon compounds. However, liquid products were formed which evolved ammonia rapidly on heating and slowly on standing at room temperature. Minute amounts of crystals were deposited on standing at room temperature. The nitrogen content of the primary liquid product was between the values calculated for hexaphenylcyclotrisilazane and for *sym*-tetraphenyldiaminodisilazane



$$\underset{\displaystyle NH_2}{(C_6H_5)_2\text{Si}}\text{—NH—}\underset{\displaystyle NH_2}{\text{Si}(C_6H_5)_2}$$

These observations showed that the reaction of diphenyldichlorosilane with ammonia affords a mixture, the composition of which is determined largely by the reaction conditions. This was in accordance with the results obtained by Larsson and Smith[5] for the reaction between di-*t*-butoxydichlorosilane and ammonia. Analogous observations have been reported by Brewer and Haber[10] and by Schwarz and Weigel.[11]

The hexaphenylcyclotrisilazane was not affected by limited contact with water. It could be dissolved in moist acetone and precipitated with water without decomposition. The nitrogen content of the substance could be determined by dissolving a weighed sample in acetone, adding 0.1 *N* hydrochloric acid, digesting for 18 hours and back-titrating with standard base. Digesting for only a short time gave slightly low values of the nitrogen content. After digesting a weighed sample of hexaphenylcyclotrisilazane for three hours in the manner described, standard base equivalent to the introduced amount of hydrochloric acid was added. From the resulting solution no hexaphenylcyclotrisilazane was recovered. These experiments imply that the action of hydrogen ions on hexaphenylcyclotrisilazane involves an actual cleavage of the Si–N bonds and not only a formation of $-\text{Si}-\overset{+}{\text{N}}H_2-$ groups (*cf.* Larsson and Mårin[7]).

In accordance with the general exchange reaction

$$R_3\text{Si—NH—}R' + R''\text{—NH}_2 = R_3\text{Si—NH—}R'' + R'\text{—NH}_2$$

used by Larsson and co-workers,[2-7] hexaphenylcyclotrisilazane on refluxing with aniline gave diphenyldianilinosilane.

The reactions of diphenyldichlorosilane with methylamine, *n*-propylamine, *n*-hexylamine and benzylamine all gave products of the formula $(C_6H_5)_2\text{Si}(\text{NHR})_2$.

## Experimental

All experiments were performed with carefully dried solvents and reagents and precautions were taken to exclude moisture from the reaction vessels.

**Diphenyldichlorosilane.**—A mixture of 27 g. (0.10 mole) of diphenyldiethoxysilane, 84 g. (0.60 mole) of benzoyl chloride and 1 ml. of pyridine was refluxed for eight hours and then subjected to fractional distillation under reduced pressure. After removal of the benzoyl chloride and the ethyl benzoate 19 g. (0.075 mole) of diphenyldichlorosilane was collected at 135° (4 mm.). The chlorine content of the product was determined by dissolving a weighed sample in 96% alcohol and titrating with standard base.

*Anal.* Calcd. for $C_{12}H_{10}Cl_2Si$: Cl, 28.0. Found: Cl, 27.8.

An experiment performed exactly as above with quinoline instead of pyridine gave a product with a chlorine content of 14.5%. Without a catalyst the reaction gave a product with a chlorine content of only 1.6%.

**Hexaphenylcyclotrisilazane.**—Into a stirred, refluxing solution of 23 g. (0.091 mole) of diphenyldichlorosilane in 50 ml. of toluene gaseous ammonia was bubbled for five hours. Filtration of the hot mixture and washing with toluene left 10 g. of solid on the filter, which corresponds with the calculated amount of ammonium chloride. From the hot filtrate white crystals precipitated on cooling. They were removed by filtration to give 10 g. (62%) of crystals melting at 211–213°. Recrystallization from 45 ml. of toluene yielded 8.5 g. of hexaphenylcyclotrisilazane melting at 213.5° over a range of 0.3°.

*Anal.* Calcd. for $C_{36}H_{33}N_3Si_3$: H, 5.6; N, 7.1; Si, 14.2; mol. wt., 592. Found: H, 5.7; N, 7.0; Si, 14.2; mol. wt. (Rast), 610.

From carbon tetrachloride solution hexaphenylcyclotrisilazane crystallized with one mole of the solvent, which was only partly removed by storage in a vacuum desiccator.

**Reaction of Hexaphenylcyclotrisilazane with Aniline.**—A mixture of 3.0 g. (0.0051 mole) of hexaphenylcyclotrisilazane and 6.9 g. (0.074 mole) of freshly distilled aniline was refluxed for 18 hours. After cooling 5 ml. of benzene and 5 ml. of (30–50°) petroleum ether were added. During 24 hours in the ice-box crystals formed which were removed, washed with benzene and dried to give 1.3 g. of diphenyldianilinosilane melting sharply at 162°. Anderson reported[12] a melting point of 153° for this compound. We also prepared the substance from diphenyldichlorosilane and aniline in accordance with the directions in Anderson's report and obtained a product which on recrystallization from benzene gave crystals melting at 156–161°.

**Diphenyldi-(methylamino)-silane.**—To an ice-cooled, vigorously stirred solution of about 1.5 moles of methylamine in benzene a solution of 40 g. (0.16 mole) of diphenyldichlorosilane in 35 ml. of benzene was added dropwise. After all had been added the stirring was continued and the temperature was slowly raised by the removal of the ice-bath. Finally the stirred mixture was heated to refluxing temperature in order to remove all the excess of methylamine. Filtration of the hot mixture and washing with benzene left 22 g. of solid on the filter, which corresponds with the calculated amount of methylamine hydrochloride. From the filtrate benzene was removed by distillation under reduced pressure. The residue was distilled under reduced pressure. A center cut of 27 g. was taken and redistilled as above, giving 8 g. of diphenyldi-(methylamino)-silane

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[8] R. O. Sauer and W. Patnode, This Journal, **67**, 1548 (1945).

[9] R. O. Sauer, *ibid.*, **68**, 138 (1946).

[10] S. D. Brewer and C. P. Haber, *ibid.*, **70**, 3888 (1948).

[11] R. Schwarz and F. Weigel, *Z. anorg. allgem. Chem.*, **268**, 291 (1952).

[12] H. H. Anderson, This Journal, **73**, 5802 (1951).

collected at 155–156° (3 mm.). Another fraction of 8 g. collected at 157–167° (3 mm.) probably contained a high percentage of diphenyldi-(methylamino)-silane.

*Anal.* Calcd. for $C_{14}H_{18}N_2Si$: Si, 11.6. Found: Si, 11.5.

**Diphenyldi-(*n*-propylamino)-silane.**—To a stirred solution of 9.8 g. (0.166 mole) of *n*-propylamine in 50 ml. of toluene a solution of 9.0 g. (0.036 mole) of diphenyldichlorosilane in 15 ml. of toluene was added dropwise. After all had been added the stirring was continued for another 15 minutes and then the mixture was refluxed (with continued stirring) for 15 minutes. After cooling the mixture was filtered and the precipitate washed with toluene to give 6.1 g. of solid on the filter, which corresponds with the calculated amount of *n*-propylamine hydrochloride. After removal of the toluene from the filtrate by distillation under reduced pressure the liquid residue was distilled from a claisen flask giving a center fraction of 7.6 g. (70%) of diphenyldi-(*n*-propylamino)-silane boiling at 178–182° (2 mm.).

*Anal.* Calcd. for $C_{18}H_{26}N_2Si$: Si, 9.4. Found: Si, 9.6.

The substance could be distilled under atmospheric pressure without decomposition.

**Diphenyldi-(*n*-hexylamino)-silane.**—This substance was prepared exactly as described for diphenyldi-(*n*-propylamino)-silane from 21 g. (0.21 mole) of *n*-hexylamine and 12 g. (0.047 mole) of diphenyldichlorosilane giving a center fraction of 5.5 g. boiling at 215–230° (3 mm.). On redistillation 1.5 g. of diphenyldi-(*n*-hexylamino)-silane were collected at about 215° (2 mm.).

*Anal.* Calcd. for $C_{24}H_{38}N_2Si$: Si, 7.3. Found: Si, 7.5.

**Diphenyldi-(benzylamino)-silane.**—A solution of 13 g. (0.051 mole) of diphenyldichlorosilane in 15 ml. of toluene was run slowly during a period of 15 minutes into a stirred, refluxing solution of freshly distilled benzylamine in 50 ml. of toluene. The mixture was stirred and refluxed for 15 minutes longer. Filtration of the hot mixture and washing with toluene gave 14 g. of solid on the filter, corresponding with the calculated amount of benzylamine hydrochloride. From the filtrate toluene was removed by distillation under reduced pressure at about 30°. The liquid residue was cooled in the ice-box. On scratching with a glass rod crystallization started and proceeded till the whole mass had solidified to yield 20 g. of substance, which was the calculated amount of diphenyldi-(benzylamino)-silane. Recrystallization from 10 ml. of ether yielded 8.4 g. of white crystals, which slowly decomposed on standing in a closed vessel at room temperature. On account of this no defined melting point can be recorded.

*Anal.* Calcd. for $C_{26}H_{26}N_2Si$: Si, 7.1. Found: Si, 7.4.

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## Selenium Dithiocyanate

BY STANLEY M. OHLBERG[1] AND P. A. VANDER MEULEN

RECEIVED OCTOBER 1, 1952

Three investigators[2–4] have reported the reduction of selenious acid to elemental selenium by the reaction between selenious acid and thiocyanic acid. Selenic acid, also, is reduced by the latter reagent to elemental selenium. In a series of experiments designed to study this latter reaction, a yellow crystalline substance was obtained as an intermediate product. The same crystalline product is obtained by the reaction between selenious and thiocyanic acid under certain conditions of temperature, concentration and acidity of the solution.

A survey of the literature revealed that only two investigators have reported compounds containing selenium and a thiocyanogen radical, Baroni[5] has prepared thiocyanogen selenide, $Se_2(SCN)_2$, and thiocyanogen thioselenide, $SeS(SCN)_2$. Ivanov[4] describes thiocyanoselenious acid, $(HSCN)_2 \cdot H_2SeO_3$. An analysis of our crystalline product did not agree with any of the compounds described heretofore, but agreed very closely with the formula for selenium dithiocyanate, $Se(SCN)_2$. The preparation of this new compound, and its properties are described below.

### Experimental

1. **Preparation of Selenium Dithiocyanate.**—The best product was obtained by the reaction between selenious acid and thiocyanic acid. A 1.1-g. portion of selenium dioxide[6] was treated with 8.6 ml. of concentrated hydrochloric acid, the mixture was diluted to 50 ml. with water, and cooled to room temperature. Thiocyanic acid was prepared by the method of Gluud, Keller and Klempt[7] and diluted to produce a tenth molar solution. The thiocyanic acid solution was poured, with stirring, into the selenious acid solution, and the mixture was allowed to stand at room temperature for 30 minutes.

The crystals were then collected in a Gooch crucible, excess mother liquor was pressed out by tamping with a glass rod, and the product was washed, first with a little glacial acetic acid, then with anhydrous ether, and tamped again to remove the ether as completely as possible. Finally the product was transferred to a vacuum desiccator containing sodium hydroxide pellets and paraffin shavings. The desiccator was evacuated to 2 mm. and kept in a refrigerator at 5°. The yield was about 70%, based on the $SeO_2$ used in the preparation.

The compound can also be prepared by bringing together, at room temperature, 50 ml. of a solution containing 1.1 g. of selenium dioxide, 12.9 ml. of concentrated hydrochloric acid, with 50 ml. of another solution containing 3.8 g. of ammonium thiocyanate in water, and allowing the mixture to stand for 30 minutes.

**Analysis of the Compound.**—Selenium was determined by weighing out a 0.3 to 0.5 g. sample, transferring to a 250-ml. beaker by means of a porcelain spatula (metal is attacked), and dissolving in 10 ml. of concd. nitric acid. The beaker was washed down with distilled water, placed on a steam-bath, and the solution evaporated nearly to dryness. It was then diluted, with 5 *N* hydrochloric acid, hydroxylamine hydrochloride was added, and selenium determined by the procedure described by Hillebrand and Lundell.[8]

Sulfur was determined in the filtrate from the selenium determination. The solution was diluted to 250 ml. and a 50-ml. aliquot was evaporated nearly to dryness on a steam-bath. The subsequent operations were carried out by the method described by Rieman, Neuss and Naiman.[9]

Carbon was determined by a micro method.[10]

For the determination of nitrogen, a 0.5-g. sample was weighed into a Kjeldahl flask, digested with a sulfuric acid–salicylic acid mixture and treated as described by Hillebrand and Lundell.[11]

The results of these determinations are: Calcd. for $Se(SCN)_2$: Se, 40.47; S, 32.86, C, 12.31; N, 14.35. Found: Se, 40.44; S, 32.72; C, 12.5; N, 14.3.

**Properties of Selenium Dithiocyanate.**—The crystal structure of selenium dithiocyanate has been determined by X-ray diffraction methods. The results will be presented in a separate communication.

Selenium dithiocyanate is fairly stable if kept in a cool, dark place, out of contact with water vapor. The dry compound can be kept for weeks in a tightly stoppered container, in a refrigerator (at 5°). If heated, it decomposes

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[1] From a thesis submitted by Stanley M. Ohlberg to the Graduate Faculty of Rutgers University in partial fulfillment of the requirements for the Ph.D. degree.

(2) H. A. Ljung, *Ind. Eng. Chem., Anal. Ed.*, **9**, 328 (1937).

(3) W. T. Hall, *ibid.*, **10**, 395 (1938).

(4) V. N. Ivanov, *J. Russ. Phys. Chem. Soc.*, **40**, 661 (1908).

(5) A. Baroni, *Reale Accademia del Lincia*, **23**, 139 (1936).

(6) Best grade, furnished by American Smelting and Refining Co.

(7) W. Gluud, K. Keller and W. Klempt, *Ber.*, **58B**, 1384 (1926).

(8) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 265.

(9) W. Rieman, J. D. Neuss and B. Naiman, "Quantitative Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 280.

(10) The carbon determinations were performed by Dr. Carl Tiedcke, Teaneck, N. J.

(11) W. F. Hillebrand and G. E. F. Lundell, ref. 8., p. 639.

suddenly at 83–85° yielding an orange smoke and a maroon-colored residue. Chemical analysis indicated that neither of these were pure substances.

The compound is practically insoluble in bromoform, symmetrical tetrachloroethane, hexane, heptane and carbon tetrachloride. It is slightly soluble in diethyl ether, benzene, carbon disulfide and liquid sulfur dioxide, and appreciably soluble in the following solvents: anhydrous dioxane, anhydrous acetone, acetophenone, vinyl trichloride and glacial acetic acid. If small amounts of water are added, decomposition takes place. However, the solutions are reasonably stable if kept in tightly stoppered containers and stored in a dark place. Attempts to obtain accurate solubility data have not been successful, but are being continued.

Selenium dithiocyanate is best recrystallized by carefully adding anhydrous ether to a saturated solution of selenium dithiocyanate in anhydrous dioxane until a faint turbidity persists and then keeping the mixture at 0° for eight hours.

The density of crystalline selenium dithiocyanate was determined by preparing a mixture of bromoform and symmetrical tetrachloroethane having the same density as the crystals. The density found in this manner was $2.265 \pm 0.005$.

The molecular weight of the compound was determined by cryoscopic method using acetophenone in one case, and dioxane in another, as the solvents. The molecular weight found in acetophenone was 206, and in dioxane 204. Although the experimentally determined values are all higher than the calculated value (195) based on the simple formula, the existence of selenium dithiocyanate in the monomeric form is definitely established.

Selenium dithiocyanate decomposes more or less rapidly at room temperature in the following liquids: water, dilute hydrochloric acid solution, dilute sodium hydroxide solution, methyl-, ethyl-, propyl-, *t*-butyl alcohol and pyridine. It also decomposes violently in liquid ammonia.

While it was not found possible accurately to represent the reaction between selenious acid and thiocyanic acid by a single equation, the following appears to be the main reaction

$$3H_2SeO_3 + 7HSCN = 3Se(SCN)_2 + 5H_2O + HCN + H_2SO_4$$

To ascertain whether this equation correctly represents the main reaction, the preparation of selenium dithiocyanate from selenious acid and thiocyanic acid, as described above, was carried out in a closed vessel attached to a suction flask through a tube provided with a sintered glass disc. The suction flask contained sodium hydroxide in excess of that required to neutralize all of the acid.

When the reaction was completed the liquid part of the contents of the reaction vessel were passed through the sintered disc into the sodium hydroxide solution, while the selenium dithiocyanate was retained on the disc. Air was aspirated through the apparatus to complete the transfer of hydrogen cyanide to the caustic soda solution, which contained, in addition to the hydrogen cyanide also the sulfuric acid formed in the reaction. The tube with the sintered disc was then disconnected from the reaction vessel and washed with small portions of nitric acid. Selenium and sulfur were determined in the nitric acid solution as described above.

The potassium hydroxide solution to which the liquid part of the reaction mixture had been added was analyzed for cyanide and sulfate. Cyanide was determined by the Liebig[12] method. An aliquot was acidified slightly with nitric acid, the thiocyanate precipitated with silver nitrate, and the filtrate was used for the sulfate determination. The results are given in Table I.

TABLE I

FORMATION OF SELENIUM DITHIOCYANATE, HYDROGEN CYANIDE AND SULFURIC ACID FROM SELENIOUS AND THIOCYANIC ACID.

| Millimoles formed | Millimoles HCN Theory | Millimoles HCN Found | Millimoles $H_2SO_4$ Theory | Millimoles $H_2SO_4$ Found |
|---|---|---|---|---|
| 6.83 | 2.28 | 1.61 | 2.28 | 2.12 |
| 15.37 | 5.12 | 3.84 | 5.12 | 4.93 |
| 16.41 | 5.47 | 3.93 | 5.47 | 5.15 |

It is apparent, that while the equation as written does not describe quantitatively the over-all reaction involved in the formation of selenium dithiocyanate, the results indicate that this equation is in agreement with the main reaction.

The fact that less than the theoretical amounts of hydrogen cyanide and sulfuric acid were found is in agreement with the work of other investigators[13] who studied the hydrolysis of thiocyanogen.

**Reaction of Selenium Dithiocyanate with Water.**—The decomposition of selenium dithiocyanate by water yields, as the major products, elemental selenium, selenious acid and thiocyanate ion. As a result of the interaction of selenious acid with thiocyanic acid there is also formed a considerable amount of sulfate ion. This result is in agreement with an observation of Hall.[3]

**Synthetic Applications.**—Selenium dithiocyanate can be used as a reagent for introducing the thiocyanate group into organic compounds. For example, the treatment of dimethylaniline with selenium dithiocyanate in glacial acetic acid yields *p*-thiocyanodimethylaniline, with a yield of 55%.

In the same manner, the reaction between 1-naphthol and selenium dithiocyanate in glacial acetic acid results in the formation of 4-thiocyano-1-naphthol, with a yield of 60%.

The compound will also react with an olefinic type of double bond. Attempts to thiocyanate cyclohexene yielded a crystalline addition product whose empirical formula corresponded to one molecule of selenium dithiocyanate and two molecules of cyclohexene.

Finally, the intermediate oxidation state of the selenium suggests that selenium dithiocyanate might find further application as either an oxidizing agent or a reducing agent for synthetic purposes.

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[12] W. W. Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 661.

[13] H. Lecher, M. Wittmer and W. Speer, *Ber.*, **56**, 1104 (1923).

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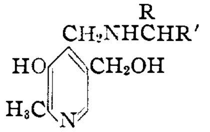
## The Microbiological Activity of Pyridoxylamines

BY JESSE C. RABINOWITZ[1] AND ESMOND E. SNELL[2]

RECEIVED OCTOBER 18, 1952

Several pyridoxylamines (I), recently described by Heyl, *et al.*,[3] were reported to possess vitamin $B_6$ activity for rats 50 to 100% that of pyridoxine, although the corresponding pyridoxylamino acids[4] (II) possessed relatively low activity. Because of this high activity, and because comparable structural modifications of other vitamins with similar maintenance of activity has not proved possible, they suggested that "compounds of this type may occur in living systems as members of the vitamin $B_6$ group or as intermediates in their function."



I, R = H, R' = H or organic radical
II, R = -COOH, R' as in I

In view of these suggestions, it appears worthwhile to present results of assays of these compounds with other organisms that require vitamin $B_6$ (Table I). For *Saccharomyces carlsbergensis*, *Streptococcus faecalis* and *Lactobacillus casei*, most of the compounds have negligible activity, pyri-

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[1] Division of Plant Biochemistry, University of California, Berkeley.

[2] Department of Chemistry, University of Texas, Austin.

[3] D. Heyl, E. Luz, S. A. Harris and K. Folkers, THIS JOURNAL, **74**, 414 (1952).

[4] D. Heyl, S. A. Harris and K. Folkers, *ibid.*, **70**, 3429 (1948).

TABLE I

MICROBIOLOGICAL ACTIVITY OF PYRIDOXYLAMINES

| | Activity[b] for | | | | |
|---|---|---|---|---|---|
| Product,[a] hydrochloride of pyridoxyl- | *Neurospora sitophila* 299 | | *Saccharomyces carlsbergensis*[e] | *Streptococcus faecalis*[e] | *Lactobacillus casei*[e] |
| | Autoclaved[c] | Filtered[d] | | | |
| Benzylamine | 0.65 | | 0.0008 | 0.003 | <0.0002 |
| Ethylamine | .91 | 0.80 | .018 | .0001 | .0002 |
| Methylamine | | .70 | | | |
| Ethanolamine | .44 | .001 | .0008 | .001 | .001 |
| Isopropanolamine | .030 | | .001 | .001 | .0006 |
| Histamine | .058 | | .0035 | .006 | .0008 |
| β-Phenylethylamine | .37 | | < .0005 | .002 | |
| 3-Phenylpropylamine | .24 | .062 | | | |
| 3,4-Dihydroxy-β-phenylethylamine | .005 | | | | |
| Arterenol | .050 | | | | |
| Tryptamine | .034 | | .0009 | < .0009 | < .0002 |
| Tyramine | .082 | | .0007 | .001 | |

[a] We are indebted to Dr. Karl Folkers for samples of these products. [b] The growth-promoting activity is compared on a molar basis with that of pyridoxal hydrochloride, assigned an activity of 1.0. [c] Ten minutes at 15 lb. pressure. [d] Sterilized by filtration and added aseptically to the sterile medium. [e] Compounds dissolved in sterile water and added aseptically to the sterile medium.

doxylethylamine being the only one to show activity greater than 1.8% that of an equimolar amount of pyridoxal. The pyridoxylamino acids were similarly inactive for these organisms.[5] For *Neurospora sitophila*, many of these compounds are of low activity, but others show activity approaching that of pyridoxal. In some cases, but not all, this activity appears due to breakdown during autoclaving with the medium.[5] The pyridoxylamino acids also showed higher activity for *Neurospora* than for other vitamin $B_6$-requiring organisms.[5]

The ease with which decomposition (*via* dehydrogenation and hydrolysis) of such compounds to pyridoxal or pyridoxamine can occur has been discussed,[5] and the high activity of certain of them for *Neurospora* (and rats[3]) suggests that this decomposition may occur enzymatically, and thus explain their activity in replacing vitamin $B_6$. The most active compounds are of the general type oxidized by monoamine oxidase, which occurs widely distributed in mammalian tissues[6] and probably in molds.[7] The view that the pyridoxylamines act *via* pyridoxal (or pyridoxamine) is also consistent with the fact that pyridoxylethylamine was less than $^1/_{20}$ as active as pyridoxamine, and less than $^1/_{500}$ as active as pyridoxal or pyridoxine in counteracting the inhibitory effects of 4-desoxypyridoxine for *Neurospora sitophila* (Table II). The inactivity of the pyridoxylamines for most of the organisms tested indicates that they have no general utility as sources of vitamin $B_6$ in living systems, and there is no evidence as yet to indicate their natural occurrence.

TABLE II

INHIBITION OF GROWTH OF *Neurospora sitophila* 299 BY 4-DESOXYPYRIDOXINE AND ITS COUNTERACTION BY VARIOUS COMPOUNDS WITH VITAMIN $B_6$ ACTIVITY

| | Level of reversing agent | | |
|---|---|---|---|
| | $1\gamma$ | $5\gamma$ | $10\gamma$ |
| Reversing agent | Inhibition index[a] | | |
| Pyridoxine·HCl | 630 | | 1000 |
| Pyridoxal·HCl | 500 | | 1000 |
| Pyridoxamine·2HCl | 17 | 19 | 23 |
| Pyridoxylethylamine·HCl | 0.73 | 0.73 | 1.1 |

[a] The inhibition index is the molar ratio of 4-desoxypyridoxine to reversing agent at which growth of the organism is 50% of that obtained in the absence of the inhibitor.

### Experimental

Test organisms, procedures and basal media employed were those described[5] in a similar study of the pyridoxylamino acids.

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[5] E. E. Snell and J. C. Rabinowitz, THIS JOURNAL, **70**, 3432 (1948).

[6] H. A. Lardy, "Respiratory Enzymes," Burgess Publ. Co., 1949, p. 237.

[7] J. W. Foster, "Chemical Activities of Fungi," Academic Press, Inc., New York, N. Y., 1949, p. 516.

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## Concerning the Absorption Spectrum of Bacteriochlorophyll

BY JOHN W. WEIGL

RECEIVED SEPTEMBER 4, 1952

In the course of a survey of the vibrational spectra of chlorophyll and related compounds,[1] the author had occasion several times to measure the electronic spectra of bacteriochlorophyll and bacteriopheophytin. This work has revealed that the main near-ultraviolet peak of both compounds has a prominent violet shoulder, that the "orange" peak of bacteriochlorophyll is strongly shifted by polar solvents, and that the spectrum of the pheophytin is surprisingly independent of *p*H.

Bacteriochlorophyll was prepared from *Rhodospirillum rubrum* by the method of French,[2] slightly modified. Because of the reported photo-lability of this compound, it was not purified chromatographically. Bacteriopheophytin was produced by treating the chlorophyll with an excess of $4 \times 10^{-2}$ $N$ sulfuric acid in ether for about one hour. The solution was neutralized with an equivalent amount of ammonia, or with excess basic magnesium carbonate, then extracted with water. Solvent transfers were carried out by evaporating the solution to near dryness under a stream of inert gas, and then rediluting with the desired solvent. The pigments were kept cold and in dim light during extraction and all subsequent experiments. All spectra were run within 24–48 hours of initial extraction in a Beckman quartz spectrophotometer which had been calibrated against Hg, H, Na, K and Cs emission lines. Pigment concentrations were adjusted to about $10^{-5}$ $M$, to permit the use of 10-mm. silica cells.

In one set of experiments, a measured volume of bacteriochlorophyll solution was converted to the pheophytin, and the latter was dissolved in a known volume of chloroform. The optical density of this solution was compared to the absolute extinction coefficients determined by French[2] for a sample of bacteriopheophytin prepared by van Niel. This permitted calculation of absolute extinction coefficients for both pigments in several

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[1] R. Livingston and J. W. Weigl, to be published.

[2] C. S. French, *J. Gen. Physiol.*, **23**, 483 (1940).

TABLE I

ABSORPTION PEAKS

| Solvent | Peak 1 |  | Peak 2 |  | Peak 3 |  | Peak 4 |  | Violet shoulder |  | Violet peak |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | λ, mμ | $\alpha_{rel.}$ | λ, mμ | $\alpha_{rel.}$ | λ, mμ | $\alpha_{rel.}$ | λ, mμ | $\alpha_{rel.}$ | λ, mμ | $\alpha_{rel.}$ | λ, mμ | $\alpha_{rel.}$ |
|  |  |  |  |  | Bacteriochlorophyll |  |  |  |  |  |  |  |
| *In vivo*[b] | 881 ± 1 | 1.00 | 805 ± 2 | 0.13[d] | 762 ± 5 | 0.06 | 588 ± 2 | 0.18 | (Obscured by carotenoids?) |  | 378 ± 1 | 0.81 |
| Ether | 772 ± 0.5 | 1.00[a] | 697 ± 2 | .12[d] | 575 ± 2 | .23 | 526 ± 2 | .13[c] | 391 ± 2 | 0.55 | 358 ± 0.5 | .89 |
| Benzene | 782 ± 0.5 | 1.00 | 705 ± 5 | .12[d] | 581 ± 1 | .25 | 543 ± 2 | .17[c] | 396 ± 0.5 | 0.55 | 362.5 ± 1 | .85 |
| Acetone | 771 ± 2 | 1.00 | 698 ± 5 | .14[d] | 580 ± 2 | .31 | 528 ± 5 | .15[c] | Not resolved |  | 358 ± 1 | 1.19 |
| Methanol | 771 ± 1 | 1.00 | 695 ± 5 | .27[d] | 609 ± 1 | .32 | 530 ± 3 | .16[c] | Not resolved |  | 364 ± 1 | 1.26 |
|  |  |  |  |  | Bacteriopheophytin |  |  |  |  |  |  |  |
| Ether[f] | 750 ± 0.5 | 1.00[a] | 680 ± 2 | 0.15 | 620 ± 5 | 0.05 | 525 ± 1 | 0.43[e] | 384.5 ± 1 | 0.97 | 357 ± 0.5 | 1.72 |
| Chloroform[g] | 758 ± 1 | 1.00[a] | 686 ± 3 | .20 | 625 ± 5 | 0.07 | 531.5 ± 1 | .43[e] | 389 ± 1 | 0.89 | 362 ± .5 | 1.66 |
| Neutral MeOH | 752 ± 2 | 1.00 | 680 ± 5 | .28 | *c* 625 | *c* 0.12 | 528 ± 1 | .56[e] | Not resolved |  | 358 ± .5 | 2.26 |
| Basic MeOH | 757 ± 2 | 1.00 | 683 ± 5 | .22 | *c* 625 | *c* 0.11 | 526 ± 1 | .46[e] | Not resolved |  | 358 ± .5 | 2.11 |

[a] Absolute extinction coefficients (log 10, in liters/mole cm.); bacteriochlorophyll in ether 9.6 × $10^4$; bacteriopheophytin in ether 6.3 × $10^4$, in chloroform 5.8 × $10^4$. [b] Suspension of *R. rubrum* in 90% glycerol; approximately corrected for residual scattering. [c] May be due largely to carotenoid impurities. [d] Shoulder, resolved approximately by subtraction. [e] Probably includes a little absorption due to carotenoids. [f] Acidic, neutral or basic ether. [g] Chloroform containing 0.5% ethanol as preservative.

solutions which had been prepared by quantitative volumetric transfers.

Table I summarizes the absorption bands of bacteriochlorophyll and bacteriopheophytin between 330 and 1000 mμ, in several solvents. The infrared peak positions of the chlorophyll *in vivo* and in solution are in agreement with those reported by Katz and Wassink[3] while the spectrum of bacteriopheophytin in chloroform matches that of French[2] very closely. The spectrum found for bacteriochlorophyll in methanol differs from that reported by Manten[4] in revealing an unresolved but definite shoulder to the main near-ultraviolet peak at about 390 mμ, and two minor bands at about 525 and 500 mμ. While the former is certainly significant, the latter may be due to traces of carotenoids.

The near-ultraviolet double band of these pigments resembles that of chlorophyll and pheophytin *a*, with the difference that the relative intensities of the peaks are reversed.[5] The two peaks are clearly resolved in solvents of low dielectric constant, such as ether, benzene and chloroform.

In all solvents tried, as well as *in vivo*, the spacings (on an energy scale) of bands 1, 2 and 4 of both pigments were found so nearly constant that the corresponding energy levels appear to be closely related. (Band 2 very probably represents a vibrational excited state of level 1.) All three of these peaks shift slightly with changes in the polarizability of the solvent, in the manner shown by Katz and Wassink[3] for peak 1. In bacteriochlorophyll, band 3 (the "orange" band) is, however, drastically shifted toward the red by polar solvents, such as ethanol and methanol; for this reason it appears to pertain to a different electronic transition.

By contrast, the spectrum of bacteriopheophytin is quite constant in a variety of solvents and over a wide *p*H range (4 × $10^{-2}$ $N$ $H_2SO_4$ to 0.3 $N$ $NH_3$ in ether; neutral to 1.5 $N$ $NH_3$ in methanol[6]). In this respect it differs sharply from pheophytin-*a*, which is a *p*H indicator, having reversible acid, neutral and basic forms.[7,8]

The band pattern of bacteriochlorophyll and bacteriopheophytin closely resembles that of chlorophyll and pheophytin-*a*. Our evidence does not support Rabinowitch's suggestion[9] that reduction of dihydroporphin to tetrahydroporphin derivatives produces a new, low-energy electronic transition; rather, there appears to be a general spreading of energy levels.

The observations are more nearly in agreement with the theoretical predictions of Platt and coworkers,[10,11] according to which bands 1 and 3 and the two violet peaks correspond to four electronic levels, differing in angular momentum and polarization, and bands 2 and 4 are vibrational satellites of bands 1 and 3. However, the theory so far developed predicts an intensity ratio of the two violet peaks which is the reverse of that observed; it also does not account for the relatively great intensity of band 4 in bacteriopheophytin or for the selective effect of polar solvents on the position of the "orange" band of bacteriochlorophyll.

**Acknowledgments.**—This investigation was made possible by generous contributions of *R. rubrum* from Mr. James Johnston and Dr. A. W. Frenkel of the Department of Botany, University of Minnesota, and from Dr. Martin Kamen of Washington University. The author is indebted to Dr. E. E. Jacobs of the University of Illinois for permission to examine some of his unpublished data, and to Professor Robert Livingston of this department for his interest and advice.

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(3) E. Katz and E. C. Wassink, *Enzymologia*, **7**, 97 (1939).

(4) A. Manten, Thesis, University of Utrecht, 1948.

(5) A similar reversal of the corresponding peaks of bacteriomethyl-pheophorbide was noted by A. Stern and F. Pruckner, *Z. physik. Chem.*, **A185**, 140 (1939).

(6) The pheophytin was found to decompose in 0.4 $N$ acidic acetone and methanol.

(7) R. Pariser, Ph.D. Thesis, University of Minnesota, 1950.

(8) Compare E. I. Rabinowitch, "Photosynthesis," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1951, p. 624.

(9) Reference 8, pp. 619-624, 630-633; *Rev. Mod. Phys.*, **16**, 226 (1944).

(10) H. C. Longuet-Higgins, C. W. Rector and J. H. Platt, *J. Chem. Phys.*, **18**, 1174 (1950).

(11) J. H. Platt in "Radiation Biology, Vol. III. Biological Effects of Visible Radiation," McGraw-Hill Book Co., Inc., New York, N. Y., in press.

## The Solubility of Oxygen in, and the Oxides of, Tantalum

By R. J. Wasilewski

Received October 15, 1952

The purpose of the work described below was to determine the solid solubility of oxygen in tantalum and the existence of any intermediate structures in the range 0–18.11 weight per cent. of oxygen, particularly at the composition corresponding to the formula $Ta_2O_4$ (15.03% oxygen), since the existence of this oxide had not been definitely established.

**Previous Work.**—The structure of tantalum metal is body-centered cubic, and the lattice parameter values varying from 3.337 to 3.272 Å. have been reported. The value $a_0 = 3.3026 \pm 0.0003$ Å., as given by Neuburger,[1] has been accepted as the most accurate.

There are very little data on the tantalum–oxygen compounds, apart from that on the pentoxide. The X-ray diffraction pattern of the latter is given in the A.S.T.M. Index,[2] but although it is stated to be orthorhombic, the structure has not been determined. Recently, Lagergren and Magneli[3] have reported the existence of a high temperature form of the pentoxide, the transition taking place at 1310°. The reported existence of $Ta_2O_4$, said to be formed by the reduction of the pentoxide by carbon or magnesium at high temperatures, or by electrolysis of tantalum salts, has been questioned.[4]

Since tantalum is closely related to columbium, some similarities can be expected between the oxides of the two metals. Grube, *et al.*,[5] investigated the reduction of $Cb_2O_5$ by hydrogen. They reported the existence of different structures corresponding to the compositions $Cb_2O_5$, $Cb_2O_4$, CbO and $Cb_2O$, while the sesquioxide was found to be a mixture of the mono- and dioxide. A later investigation by Brauer[6] confirmed most of the above data. He was unable, however, to observe the suboxide structure, and concluded that the pattern reported for it must have been caused by impurities. The pentoxide he found to exist in three temperature dependent modifications, the transition temperatures being approximately 950° and 1100°.

### Experimental Procedure

**Materials.**—1, MUREX, Grade A tantalum powder, prepared by sodium reduction of $K_2TaF_7$. This powder contained less than 0.1% each of oxygen and columbium, and traces of $SiO_2$ and CaO. 2, Secondary tantalum powder, containing approximately 0.7% oxygen, 0.1% each of Cb and Fe. 3, MUREX tantalum pentoxide, analyzing 99.85+% $Ta_2O_5$.

For the determination of the lattice parameter of the pure metal, filings from a melted end of an oversintered bar were used. This material was spectroscopically pure, and gave the theoretical gain in weight on ignition (22.11%).

**Preparation of the Specimens.**—A small quantity of the metal powder was heated at 1000–1050° in a molybdenum boat, in an atmosphere of electrolytic hydrogen containing traces of oxygen and water vapor. There was no detectable pick-up of molybdenum from the boat. The oxidation of tantalum was slow and fairly uniform, so that by varying the heating time the extent of oxidation could be easily controlled. The powder could be oxidized to pentoxide within 24 hours.

When oxidized, the sample was cooled in hydrogen, then ground in an agate mortar, and annealed for 72 hours at 1050° at a pressure below $5 \times 10^{-4}$ mm. This annealing period was sufficient to remove the hydrogen absorbed during the previous heating, and to ensure the homogeneity of the powder. The oxygen content was determined on 1-g. samples by gain in weight on ignition. Powder diffraction patterns were taken using CuK radiation and a standard 9-cm. diameter camera, although in a few cases CrK radiation and a 19 cm. diameter camera were used.

### Experimental Data

The parameter values corresponding to varying oxygen content are shown in Table I. The value found for the gas-free metal agrees well with that reported by Neuburger, and corresponds to an X-ray density of 16.671 g. cm.$^{-3}$, taking as unit atomic weight $1.6603 \times 10^{-24}$.[7]

Table I

Tantalum Lattice Parameter with Increasing Oxygen Content

| Material | Oxygen wt. % | X-Ray method | Lattice parameter, Å. |
|---|---|---|---|
| Annealed wire | Nil | Powder | 3.3026 ± 0.0002 |
| Melted bar tip | Nil | Back reflection | 3.3026 ± .0002 |
| Filings | Nil | Powder | 3.3026 ± .0003 |
| Electrolytic powder | 0.22 | Powder | 3.3055 ± .0003 |
| Murex, oxidized | 0.65 | Powder | 3.3124 ± .0003 |
| Murex, oxidized | 0.84 | Powder | 3.3157 ± .0003 |
| Murex oxidized | 0.93 | Powder | 3.3163 ± .0002 |
| Murex, oxidized | 1.96 | Powder | 3.3163 ± .0003 |

The solubility limit of oxygen in tantalum at 1050° is thus found to be 0.9% by weight. The parameter increase is linear with the oxygen content, within the accuracy of the oxygen determination. As will be mentioned later, however, there are indications that the solubility is considerably higher at higher temperatures.

The metal lattice persists up to approximately 3.9 weight % oxygen content, the first lines of a new structure, however, were obtained at 1.8% oxygen. This structure appeared homogeneous at 4.2% oxygen. The homogeneity range of this structure appears to be very narrow, since no difference in the spacing of the planes giving rise to the highest angle reflection could be detected within the range 3.0–8.0% oxygen.

A third structure appeared at just below 8%, and was found to be homogeneous above 17% oxygen content. This structure was found to be that of the pentoxide, as confirmed by comparing its pattern with that of the commercial $Ta_2O_5$. The diffraction pattern of this structure is very complex, and the high angle reflections are very diffuse.

Since no pattern was found corresponding to the composition $Ta_2O_4$, attempts were made to reduce the pentoxide by heating with carbon at 1770°. The pentoxide became black after heating for 90 minutes, and the total loss in weight corresponded very closely to that expected, had the reduction to $Ta_2O_4$ taken place. A new diffraction pattern was obtained from this sample, but the maximum intensity line of the suboxide was also observed. In a second experiment, $Ta_2O_5$ was heated at 1770° with tantalum. Again the new pattern, together with that of the suboxide, were found.

Neither of the diffraction patterns observed so far corresponded with that given for $Ta_2O_5$ in the A.S.T.M. Index.[2] An investigation was therefore made concerning the existence of other forms of the oxide. It was found that the precipitated oxide, containing some 40% moisture, is amorphous, as stated by Huttig and Konig.[8] However, a crys-

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[1] M. C. Neuburger, *Z. Krist.*, **93**, 312 (1936).

[2] A.S.T.M. Index of X-ray diffraction patterns.

[3] S. Lagergren and A. Magneli, *Acta Chem. Scand.*, **6**, 444 (1952).

[4] B. S. Hopkins, "Chemistry of the Less Familiar Elements," Stipes, Chicago, 1939, Chapt. 15, p. 16.

[5] G. Grube, O. Kubaschewski and K. Zwiauer, *Z. Elektrochem.*, **45**, 885 (1939).

[6] G. Brauer, *Z. anorg. allgem. Chem.*, **248**, 1 (1941).

[7] C. S. Smithells, "Metals Reference Book," Butterworths, London, 1949, p. 48.

[8] G. F. Huttig and A. Konig, *Z. anorg. allgem. Chem.*, **193**, 100 (1930).

talline pattern, although indicating poor structure, was found for a hydrated oxide approximating to the composition $Ta_2O_5 \cdot 4.28H_2O$. The structure observed for the oxide heated between 650° and 1300° is identical with that obtained for the commercial oxide, and was found to be isomorphous with the low temperature modification of $Cb_2O_5$ reported by Brauer.[6] When heated to higher temperatures, the pentoxide was found to transform, and the pattern obtained was that observed previously for the "reduced" oxide. The low temperature structure persisted up to 1300°, the high temperature structure having been obtained after heating to 1350°, in agreement with the findings of Lagergren and Magneli.[3]

The transition of the pentoxide appeared to involve considerable structural changes, judging from the diffraction patterns. The high temperature structure remained unchanged after heating at 1300° for 48 hours. Neither of the diffraction patterns obtained corresponded to that given in the A.S.T.M. Index,[2] and the attempts at growing single crystals of the oxide, suitable for rotation photographs, were unsuccessful.

### Discussion of Results

The discrepancies in the values reported for the tantalum lattice parameter previously are thought to have been due to oxygen present in the metal used. Andrews[9] and Myers[10] have observed the increase of the metal lattice parameter on addition of oxygen. While it has been stated,[11] that hydrogen also causes a lattice expansion, a slight expansion only was found by Burgers and Basart[12] in the metal prepared under conditions facilitating the solution of hydrogen. During the author's experiments the expansion was found to be small, a far more marked effect of the absorption having been the widening of the diffraction lines, consistent with high stresses being set up in the metal lattice.

The solubility of oxygen in the metal appears to be higher at temperatures of the order of 2000°, as found during an investigation of a sintered metal bar, showing considerable surface oxidation. Both the suboxide and the body-centered cubic metal patterns were obtained from this specimen, the parameter of the latter, however, was found to be 3.340 Å.; *i.e.*, considerably higher than that found for the maximum oxygen content at 1050°. This solubility must, however, decrease with further temperature increase, since the oxygen or the oxide is expelled by heating above about 2200° *in vacuo*.[9,10,13]

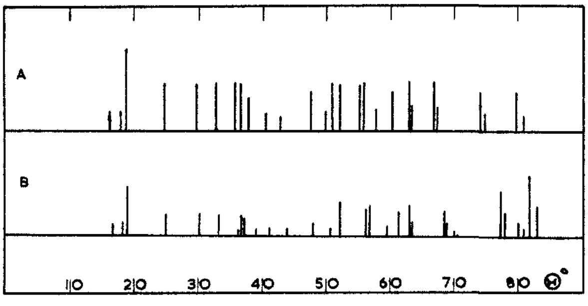

Fig. 1.—Debyograms of $Cb_2O$ (A), from Kubaschewski[5,14] and tantalum suboxide (B). The relative intensities were estimated visually (A), and by means of a microphotometer (B).

The photogram of the pattern obtained with tantalum containing 4.2% oxygen was compared with that given by Kubaschewski for $Cb_2O$.[14] Figure 1 shows the similarity of the patterns, and consequently the structure is thought to correspond to the composition $Ta_2O$. An attempt was made to determine the symmetry of the unit cell, following the method of Jacob and Warren.[15] It was found that an orthorhombic cell of $a = 5.29$, $b = 4.92$ and $c = 3.05$ Å. would account for all the lines present. The experimental density being 15.52 g. cm.$^{-3}$, the cell contains two formula units of $Ta_2O$, the corresponding X-ray density being 15.8 g. cm.$^{-3}$.

It is evident that no confirmation of the existence of the dioxide has been found, and it is doubtful whether, in fact, any structure intermediate between $Ta_2O$ and $Ta_2O_5$ exists, since the first new pattern obtained on the reduction of the pentoxide is that of the suboxide. Thus the "dioxide" appears to be a mixture $Ta_2O \cdot 3Ta_2O_5$, obtained by partial reduction of the pentoxide.

The reaction of the pentoxide with tantalum metal appears to be very rapid in the temperature range 1700–2200°. This indicates that the diffusion of oxygen through the metal must be rapid, which would account for the difficulty in obtaining oxygen-free metal, if it is cooled slowly through this critical range after sintering.

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(9) M. R. Andrews, THIS JOURNAL, **54**, 1845 (1932).

(10) R. H. Myers, *Metallurgia*, **41**, 301 (1950).

(11) E. Pietsch and H. Lehl, *Kolloid Z.*, **68**, 226 (1934).

(12) W. G. Burgers and J. C. M. Basart, *Z. anorg. allgem. Chem.*, **216**, 223 (1934).

(13) "Tantalum, The Metal," Fansteel Metal Corporation, 1939.

(14) O. Kubaschewski, *Z. Elektrochem.*, **46**, 284 (1940).

(15) C. W. Jacob and B. E. Warren, THIS JOURNAL, **59**, 2588 (1937).

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## The Partial Hydrolysis of Chlorosilanes

BY ROBERT WEST

RECEIVED OCTOBER 23, 1952

Schumb and Stevens have shown that hexachlorodisiloxane can be prepared in fair yield by the partial hydrolysis at −78° of silicon tetrachloride dissolved in ether.[1] We have extended this work by studying the partial hydrolysis of trichlorosilane,[2] dichlorosilane and methyltrichlorosilane, under similar conditions. With trichlorosilane, 5 to 10% yields of 1,1,3,3-tetrachlorodisiloxane (a new compound) are obtained, but with dichlorosilane and methyltrichlorosilane only traces of partially-hydrolyzed products could be isolated. The reason for the diminished yields is not known; however, recent unpublished work in this Laboratory indicates that among these chlorosilanes the tendency toward the formation of addition compounds with amines[3] falls off in the same order.

In the titration of 1,1,3,3-tetrachlorodisiloxane (in acetone solution) with standard alcoholic sodium

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(1) W. C. Schumb and A. J. Stevens, THIS JOURNAL, **69**, 726 (1947); **72**, 3178 (1950).

(2) The complete hydrolysis of trichlorosilane has been studied recently; see G. H. Wagner and A. N. Pines, *Ind. Eng. Chem.*, **44**, 321 (1952).

(3) W. R. Trost, *Can. J. Chem.*, **29**, 877, 1075 (1951).

hydroxide, an indicator with a color change above *p*H 7 cannot be used, because of the lability of the silane hydrogen in the presence of excess base. Satisfactory titrations were obtained using brom thymol blue (*p*H 6.0–7.6). However, equally good results were obtained without an added indicator; the first appearance of bubbles of hydrogen in the solution gave an accurate end-point.

### Experimental

**1,1,3,3-Tetrachlorodisiloxane.**—To 70 ml. of anhydrous ethyl ether was added 47 g. (0.35 mole) of trichlorosilane (Anderson Laboratories). This solution was cooled to −78° in a Dry Ice–acetone-bath and stirred vigorously while 3.4 g. (0.19 mole) of water was added from a buret over a period of 30 minutes. The mixture was then stirred for several hours while it warmed to room temperature. Fractional distillation of the solution was carried out using a 50-cm. column packed with stainless steel helices. The product distilled at 99–100° (763 mm.); a trace of chlorine-containing material boiling at 145° was also found (probably hexachlorotrisiloxane). The yield was 3.2 g., or 8.5%. Yields from similar runs varied from 5 to 10%. The product was a colorless mobile liquid with $n^{25}\text{D}$ 1.4075 and $d^{25}{}_4$ 1.347. The molecular weight by the vapor-density method was 222 (calcd. 216).

*Anal.* Calcd. for $H_2Si_2OCl_4$: Cl, 65.67. Found: Cl, 65.6, 65.7.

The infrared absorption spectrum of tetrachlorodisiloxane vapor was obtained using a cell of 3-cm. path length with KBr windows. The spectrum in the sodium chloride region was measured with a Baird automatic recording infrared spectrophotometer (Fig. 1); the region from 450 to 650 cm.$^{-1}$ was studied with a Perkin–Elmer spectrophotometer using a KBr prism. Strong absorption bands in this region were found centered at 533 and 604 cm.$^{-1}$. For most of the absorption bands, analogies are found in the spectrum of $HSiCl_3$.[4,5] However, the bands at 871, 912 and 1128 cm.$^{-1}$ have no counterparts in the $HSiCl_3$ spectrum.

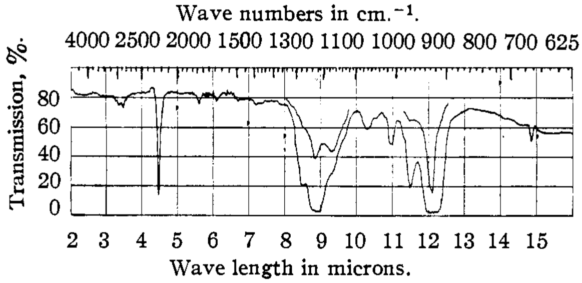

Fig. 1.—Infrared absorption spectrum of 1,1,3,3-tetrachlorodisiloxane. The lower line is at 40 mm., while the upper line is at 4 mm.

**Partial Hydrolysis of Dichlorosilane.**—The hydrolysis was carried out in the same way as that of trichlorosilane, except that *n*-propyl ether was used in place of ethyl ether. From 35 g. of dichlorosilane,[6] about 1 g. (4%) of product was obtained boiling over the range 70–81%. This material probably contained some *n*-propyl ether. Analysis gave 42.9% Cl; dichlorodisiloxane requires 48.2%.

In the course of this and other experiments with dichlorosilane, it was found that when a large quantity of the gas is vented in air, it inflames spontaneously and explosively. This is contrary to the findings of Stock,[7] who was working only with very small quantities. The liquid could be handled with relative safety if kept at −78°.

**Partial Hydrolysis of Methyltrichlorosilanes.**—The hydrolysis was performed in the same way as that of trichlorosilane. Only a trace of chlorine-containing material, boiling near 110°, was found.

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(4) T. C. Gibian and D. S. McKinney, THIS JOURNAL, **73**, 1431 (1951).

(5) C. A. Bradley, *Phys. Rev.*, **40**, 908 (1932).

(6) The dichlorosilane was a gift from the Linde Air Products Co., of Tonawanda, N. Y.

(7) A. Stock and C. Somieski, *Ber.*, **52**, 718 (1919).

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# COMMUNICATIONS TO THE EDITOR

## THERMODYNAMIC AND KINETIC CONSTANTS FOR THE DIBORANE-BORINE EQUILIBRIUM

*Sir:*

We have succeeded in making a reliable estimate of the equilibrium constant for the dissociation of diborane into borine groups. The method is an indirect one. It is now clear why physical experiments designed to detect directly borine in diborane[1] have failed; at 155° and one atmosphere, the degree of dissociation of diborane as computed from the equilibrium constant given below is $1.63 \times 10^{-5}$, and at that temperature its general pyrolysis is fairly rapid.

The enthalpy change for the association reaction $2BH_3 = B_2H_6$ was deduced as follows. We measured the heats of reaction of trimethylamine with diborane and tetramethyldiborane, to produce the solid and liquid association products, respectively, using a precision vacuum ice calorimeter. These were corrected to the gas phase reactions and combined with the value given by Brown[2] for the heat of reaction of trimethylamine with boron trimethyl. Thus the three values (−17.3, −11.0, −17.6 kcal./mole of amine) demonstrate the effect of methyl substitution on the acidity of the boron unit, as well as on the strength of the $(BH_2B)$ bridge. By making suitable corrections for inductive, steric and mesomeric contributions from the methyl groups as deduced from other data, we arrived at $\Delta H^\circ_{273} = -32\,^{+1}_{-2}$ kcal. per mole of diborane, for the above reaction.

The entropy change for the association of two borines was computed. Based on the structure of diborane as reported by Hedberg and Schomaker,[3] its translational plus rotational entropy is 53.70 ±

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(1) A. Stock and E. Kuss, *Ber.*, **56B**, 789 (1923); G. C. Pimentel and K. S. Pitzer, *J. Chem. Phys.*, **17**, 882 (1949).

(2) H. C. Brown, H. Bartholomay and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944).

(3) K. Hedberg and V. Schomaker, *ibid.*, **73**, 1482 (1951).