TABLE I

4,4'-BIPIPERIDINES $R'\overset{+}{\underset{X\cdot}{-}N}\underset{CH_2CH_2}{\overset{R}{<}}\overset{CH_2CH_2}{\underset{CH_2CH_2}{>}}C\overset{H}{<}C\overset{CH_2CH_2}{\underset{CH_2CH_2}{>}}\overset{+}{\underset{\cdot X^-}{N}}\overset{R}{-}R'$

R	R'X	M.p., °C.[a]	Crystn. solvent[b]	Formula	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
H	HCl[c]	310	M	$C_{10}H_{22}N_2Cl_2$	49.8	49.9	9.2	9.0
CH₃	HCl[d]	320–322	A	$C_{12}H_{26}N_2Cl_2$	53.5	53.1	9.7	9.6
CH₃	HI[e]	304–305	M	$C_{12}H_{26}N_2I_2$	31.8	31.7	5.8	5.7
C₂H₅	HI[f]	312–314	M	$C_{14}H_{30}N_2I_2$	35.0	35.2	6.3	6.2
CH₃	CH₃I[g]	320	W.Ac	$C_{14}H_{30}N_2I_2$	35.0	34.9	6.3	6.1
CH₃	C₂H₅I[h]	293–295	A	$C_{16}H_{34}N_2I_2$	37.8	38.0	6.7	6.7
CH₃	n-C₃H₇I	218–219	M	$C_{18}H_{38}N_2I_2$	40.3	40.5	7.2	7.3

[a] Melting points are uncorrected; yields in general were greater than 90%. [b] A = ethanol; Ac = acetone; M = methanol; W = water. [c] The base, m.p. 167–168°, crystals from benzene. has been described earlier, see references 4, 5, 6. [d] From 4,4'-bipiperidine, formaldehyde and formic acid by the Eschweiler[7]–Clarke[8] method. [e] By catalytic hydrogenation of 4,4'-bipyridine dimethiodide. [f] By catalytic hydrogenation of 4,4'-bipyridine diethiodide. [g] Prepared in three ways as shown in Fig. 1. [h] Made by two routes as shown in Fig. 1.

37% aqueous formalin was heated on a steam-bath for three to four hours. Another 5 cc. of formic acid and 5 cc. of formalin was added and heating was continued for one more hour. Methanol, 100 cc., and concentrated hydrochloric acid, 15–20 cc., were added and the solution was evaporated to dryness. The residue was purified by recrystallization from methanol, and from ethanol, m.p. 320–322°.

After liberation of the free base, N,N'-dimethyl-4,4'-bipiperidine, with alkali several diquaternary salts were prepared from it by refluxing in methanol solution with the appropriate alkyl halide. Details for all the bipiperidines are summarized in Table I.

A few simple derivatives of N-methylpiperidine have been prepared for comparison of their melting points and solubilities with the almost isomeric bipiperidine derivatives. This was felt to be desirable because ordinary analytical results would not distinguish the two series of compounds. The melting points and solubilities of the mono- and bipiperidine derivatives were different in each case, and the monopiperidine compounds were much more easily soluble in alcohols than the bipiperidines.

N-Methylpiperidine[11] was made by the Eschweiler[7]–Clarke[8] methylation of piperidine and its hydrochloride melted at 211–212°, after recrystallization from ethanol–ether mixtures.

N-Methylpiperidine methiodide[12–14] melted above 340°, and was crystallized from methanol–ether mixtures.

N-Methylpiperidine ethiodide, m.p. 304–305°, from methanol–ether. Anal. Calcd. for C₈H₁₈NI: C, 37.7; H, 7.1. Found: C, 37.7; H, 6.9.

N-Methylpiperidine n-propiodide, m.p. 179–180°, from ethanol–ether. Anal. Calcd. for C₉H₂₀NI: C, 40.1; H, 7.5. Found: C, 40.4; H, 7.5.

Acknowledgment.—The authors are indebted to Mr. Samuel W. Blackman for the microanalyses included and to Dr. Kenneth Colville for the pharmacological results summarized here.

(11) H. W. Magnusson and E. R. Schierz, Univ. Wyoming Pub., 7, 1 (1940); C. A., 34, 6867² (1940).

(12) A. W. Hofmann, Ber., 14, 659 (1881).

(13) A. Ladenburg, Ann., 247, 1, 56 (1888).

(14) E. Wedekind and R. Oechslen, Ber., 35, 1075 (1902).

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## Disproportionation of Phenylsilanes with Aluminum Chloride as the Catalyst

BY JOHN L. SPEIER AND RUTH E. ZIMMERMAN[1]

Disproportionation of groups attached to silicon in certain silanes has been observed numerous times. A very early account describing disproportionation

is given by Friedel and Ladenburg[2a] who treated triethoxysilane with sodium to form silane according to the equation
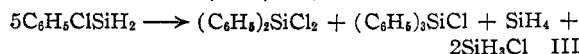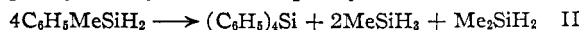
$$4(EtO)_3SiH \longrightarrow 3(EtO)_4Si + SiH_4$$
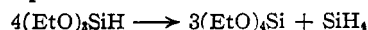
More recently Benkeser[2b] and co-workers have described disproportionation reactions of silanes of the type $(C_6H_5)_xSiCl_{4-x}$, $(C_6H_5)_xSiH_{4-x}$ and $(C_6H_5)_x\text{-}Me_ySiH_{4-x-y}$ in the presence of sodium or sodium–potassium alloy. Reactions very similar to these recently have been discovered in our laboratory to occur very smoothly and rapidly under the influence of aluminum chloride.

During the course of a series of experiments occasion arose to add a small amount of aluminum chloride to a dilute benzene solution of phenylsilane at room temperature. Immediately a gas was produced, the mixture began to bubble and a violent explosion shattered the flask. With suitable precautions the experiment was repeated in a flask under a stream of dry nitrogen. Again a gas was produced which ignited spontaneously and burned in air with a bright flame at the outlet of the system producing clouds of silica soot.

Investigation into the cause of this unexpected behavior showed that phenylsilane disproportionated quantitatively in the presence of aluminum chloride according to the equation

$$4C_6H_5SiH_3 \longrightarrow (C_6H_5)_4Si + 3SiH_4 \qquad \text{I}$$
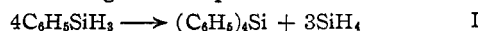
Further, this type of change also occurred with phenylmethylsilane and phenylchlorosilane.

$$4C_6H_5MeSiH_2 \longrightarrow (C_6H_5)_4Si + 2MeSiH_3 + Me_2SiH_2 \qquad \text{II}$$

$$5C_6H_5ClSiH_2 \longrightarrow (C_6H_5)_2SiCl_2 + (C_6H_5)_3SiCl + SiH_4 + 2SiH_3Cl \qquad \text{III}$$

The speed of the reaction in benzene solution at room temperature or slightly above and the quantitative description of the changes described by equations I and II are surprising, especially in the case II where a methyl group is involved.

Experimental

Phenylsilane (27 g., 0.25 mole) in 19.5 g. of benzene in a flask equipped with a condenser and a tube through which dry nitrogen was blown over the liquid was treated with one lump (0.5 g.) of aluminum chloride at 29°. Bubbles of

(2) (a) C. Friedel and A. Ladenburg, Ann., 143, 124 (1867); (b) R. A. Benkeser, H. Landesman and D. J. Foster, ibid., 74, 648 (1952); R. A. Benkeser and D. J. Foster, ibid., 74, 4200 (1952); 74, 5314 (1952).

gas formed on the surface of the aluminum chloride immediately. The flask was warmed to 50° at which temperature the aluminum chloride dissolved or dispersed in the liquid and a very vigorous evolution of gas took place. After a few hours at 50° no more gas was produced and suddenly the liquid crystallized to a solid mass. This was broken up in water to remove the aluminum chloride, filtered and dried. The dried product was essentially pure tetraphenylsilane (20.6 g., 0.061 mole, 97.6% yield based on equation I), m.p. 234-235°. It showed no depression of m.p. mixed with authentic tetraphenylsilane.[3] The explosion and spontaneous flammability of the gas agrees well with the properties of silane.[4]

In the presence of ether even on prolonged refluxing no such reaction occurs. This is probably due to the formation of the etherate of aluminum chloride which is ineffective as a catalyst for disproportionation making possible the successful synthesis of silanes by reduction of chlorosilanes with lithium aluminum hydride.[5]

Phenylmethylsilane and Aluminum Chloride.—Phenylmethylsilane (64 g., 0.524 mole) under the same conditions also yielded tetraphenylsilane m.p. 210-233°. Recrystallized once from alcohol the m.p. became 233-234°, yield 96% based on equation II.

In this case the gaseous products were swept on the stream of nitrogen through a small tower packed with glass helices and filled with absolute ethanol made alkaline with sodium ethoxide to convert the silanes to ethoxysilanes. Distillation of the solution from this tower yielded first a mixture of alcohol and a silicon compound boiling constantly at 77°. This was presumed to be alcohol and the alcohol–dimethyldiethoxysilane azeotrope reported to boil at 77°[6] containing 17% dimethyldiethoxysilane. This was followed by methyltriethoxysilane (48 g., 0.26 mole, 99% yield based on equation II), b.p. 143° at 743 mm.[7]

Phenylchlorosilane and Aluminum Chloride.—Phenylchlorosilane (71 g., 0.5 mole) was used under the same conditions and also gave evidence of disproportionation. Unfortunately the products caught fire while being made ready for distillation. Enough silane or chlorosilane may have remained in the liquid to cause its ignition. The fire was extinguished and the material remaining was distilled. Diphenyldichlorosilane (14 g., 0.051 mole, 51% yield) was obtained, b.p. 183-184° at 25 mm.[8]; neut. equiv. 125; calcd. neut. equiv. 126.5. An impure black crystalline residue of triphenylchlorosilane remained, m.p. 80-90°, 0.054 mole, 54% yield based on equation III; neut. equiv. 254, calcd. neut. equiv. 294, 16 g. The melting point became 90-92° after the product was recrystallized once from hexane,[9] neut. equiv. 285.

No other silicon compound was detected in the liquid products.

(3) F. S. Kipping and A. G. Murray, *J. Chem. Soc.*, **132**, 360 (1929), give the m.p. as 235-236°; J. S. Peake, W. H. Nebergall and Yun Ti Chen, THIS JOURNAL, **74**, 1526 (1952), reported m.p. 234-235°.

(4) A. Stock and C. Somieski, *Ber.*, **49**, 111 (1916).

(5) W. H. Nebergall, THIS JOURNAL, **72**, 4702 (1950).

(6) L. H. Horsley, "Azeotropic Data," American Chemical Society, 1155 16th St., N.W., Washington, D.C., 1952, p. 63.

(7) H. J. Fletcher and M. J. Hunter, THIS JOURNAL, **71**, 2922 (1949), reported b.p. 143° at 760 mm.

(8) A. C. Jenkins and G. A. Chambers, *Ind. Eng. Chem.*, **46**, 2367 (1954), give the Antoine equation constants for diphenyldichlorosilane: from this is calculated a b.p. of 181° at 25 mm.

(9) C. Curran, R. Witucki and P. A. McCusker, THIS JOURNAL, **72**, 4471 (1950), give m.p. 94-95°.

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Cyclopropanes. II. A Cyclopropylcarbinyl Rearrangement

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In connection with other investigations in this

(1) This paper is based on a portion of the thesis submitted by F. M. Hornyak in 1955 to the Florida State University in partial fulfillment of the requirements for the Ph.D. degree in chemistry.

Laboratory concerning cyclopropane derivatives[2] an attempt was made to synthesize 1-benzoyl-2,2-diphenylcyclopropane by the reaction of 2,2-diphenylcyclopropane carbonyl chloride with phenylmagnesium bromide following the procedure described by Lyle.[3] Acid hydrolysis of the Grignard adduct did not yield the desired ketone but gave, as the principal product, 1,1,4,4-tetraphenylbutadiene-1,3 (I).

It was reasoned that 2,2-diphenylcyclopropyldiphenylcarbinol (II) was produced, which on acid hydrolysis underwent a facile rearrangement, (III-IV), which is characteristic of cyclopropylcarbinyl intermediates.[4-9]
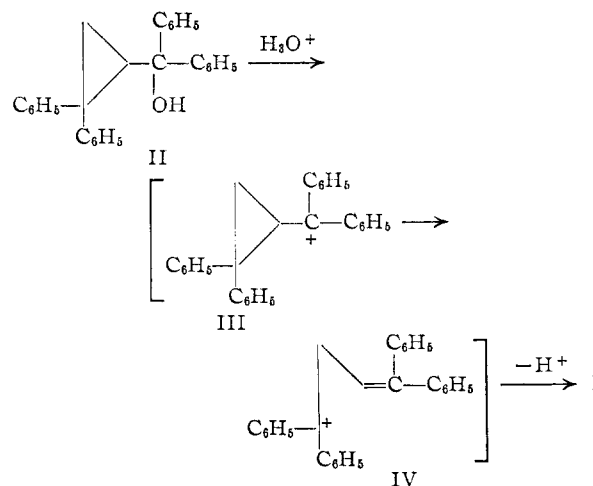
It was of interest to confirm this transformation. The alcohol II was prepared in 62% yield by the reaction of phenylmagnesium bromide with methyl 2,2-diphenylcyclopropanecarboxylate and decomposition of the intermediate with a saturated solution of ammonium chloride. Treatment of the alcohol II with sulfuric acid, boric anhydride, thionyl chloride, acetyl chloride, acetyl chloride–pyridine and phosphorus tribromide produced, in all cases, 1,1,4,4-tetraphenylbutadiene-1,3. (The structure was proved by comparison with an authentic sample.)

The ready formation of I is explained by reference to the intermediate forms III and IV. The relief of ring strain and the formation of the resonance-stabilized diphenylmethyl-type carbonium ion are strong influences aiding ring opening. The stable nature of the extensively conjugated tetraphenylbutadiene favors its formation, by proton ejection, rather than the reaction of IV with a nucleophilic reagent.

Experimental

Attempted Preparation of 1-Benzoyl-2,2-diphenylcyclopropane.—To a boiling ethereal solution of 0.021 mole of 2,2-diphenylcyclopropanecarbonyl chloride[2] was slowly

(2) H. M. Walborsky and F. M. Hornyak, THIS JOURNAL, **77**, 6026 (1955).

(3) R. E. Lyle and G. G. Lyle, *ibid.*, **74**, 4061 (1952).

(4) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2512 (1951).

(5) C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

(6) M. Doyarenka, *Ber.*, **60B**, 1536 (1927).

(7) T. A. Favorskaya and N. B. Shcherbinskaya, *Zhur. Obshchei Khim.*, **23**, 1667 (1953).

(8) P. Lipp, J. Buchkremer and H. Seeles, *Ann.*, **499**, 1 (1932).

(9) P. Bruylants and A. Dewael, *Bull. soc. chim. Belg.*, **14**, 140 (1928).