TABLE I

Compound	pK_a	λ_{max} ($m\mu$) ($\log \epsilon$)[e]
II	9.1 ± 0.2[a]	410–425 (3.88)[d]
III	11.1 ± 0.2[b]; 10.8 ± 0.2[c]	510 (3.89)
IV	11.5 ± 0.2[a]; $11.6 + 0.1$[b]; 11.3 ± 0.1[c]	533 (3.90)

[a] By titration in acetonitrile with dioxane–perchloric acid, according to the method of H. K. Hall, *J. Phys. Chem.*, **60**, 63 (1956). [b] Spectrophotometric, in dioxane, using piperidine–piperidine perchlorate as internal buffer, according to the method of L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932). [c] Spectrophotometric, as in footnote *b*, in acetonitrile. [d] Shoulder. [e] In isoöctane.

Compound II gives a colorless solution (λ_{max} 342, no shoulder at 410–425 $m\mu$) in ethanolic perchloric acid, signifying conversion to the conjugate acid; the change is quantitatively reversed by alkali, even after storage of the acidic solution. The unstable crystalline perchlorate of II is obtained as needles (from ethyl acetate–ethanol) which decompose above about 80°. *Anal.* Calcd. for $C_{11}H_{12}O_4NCl$: C, 51.26; H, 4.69. Found: C, 51.50; H, 5.20. This substance shows no $\equiv^{+}$N-H absorption in the infrared (KBr disc). Presumably, protonation occurs in the five-membered ring.

Further properties and reactions of II and related substances are being investigated.

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A NEW SYNTHESIS OF ARYLPHOSPHONOUS DICHLORIDES[1]

Sir:

A few years ago,[2] Doak and Freedman announced an aromatic phosphonic acid synthesis destined to become the most widely useful of the several methods known.[3] Readily prepared aryldiazonium fluoroborates are the starting materials; these are treated with phosphorus trichloride or tribromide in a dry solvent in the presence of a cuprous halide as catalyst. The mixture is then hydrolyzed and the phosphonic acid obtained generally in 30–50% yield. The intermediate of this reaction has not been subjected to study but has been suggested by Crofts[4] to be $ArPX_3{}^+BF_4{}^-$.

We reasoned that the intermediate, if hydrolyzable to a phosphonic acid, may well bear chemical similarity to an aryl tetrahalophosphorane, and hence might be reducible to an arylphosphonous dichloride, $ArPCl_2$.[5] We have indeed found that magnesium shavings added to the diazonium fluoroborate–phosphorus trichloride reaction product in ethyl acetate solvent effect this reduction. The reaction is exothermic but easily controlled. These known phosphonous dichlorides thus have been prepared: *p*-chlorophenyl-, b.p. 132–133° at 20 mm. (reported,[6] 133° at 20 mm.), 37% crude yield; *p*-tolyl-, b.p. 109–110° at 11 mm. (reported,[7] 107–110° at 10 mm.), 11% yield. Both compounds were analyzed and gave the correct values. Additional proof of their identity was obtained by hydrolysis to the corresponding phosphonous acids, each of which had melting points in agreement with literature values.

To demonstrate the versatility of the new method, two new and otherwise difficultly obtainable phosphonous dichlorides were prepared: *m*-chlorophenyl-, b.p. 124–125° at 18 mm., 33% yield (*Anal.* Calcd. for $C_6H_4Cl_3P$: C, 33.76; H, 1.89; P, 14.51. Found: C, 34.04; H, 2.06; P, 14.65). *p*-Cyanophenyl-, b.p. 127–128° at 4.5 mm., 25% yield (*Anal.* Calcd. for $C_7H_4Cl_2NP$: C, 41.21; H, 1.98; P, 15.19. Found: C, 41.42; H, 2.03; P, 15.17). Each was hydrolyzed to the phosphonous acid: *m*-chlorophenyl-, recrystallized from carbon tetrachloride, m.p. 90.5–91.5° (*Anal.* Calcd. for $C_6H_6ClO_2P$: C, 40.80; H, 3.43; P, 17.54. Found: C, 41.17; H, 3.65; P, 17.11). *p*-Cyanophenyl-, recrystallized from ethanol–carbon tetrachloride, m.p. 166–167° (*Anal.* Calcd. for $C_7H_6NO_2P$: C, 50.31; H, 3.62; P, 18.54. Found: C, 50.61; H, 3.87; P, 18.20).

The following experimental procedure is typical. All operations were conducted in a nitrogen atmosphere. To 200 ml. of dry ethyl acetate, 0.20 mole of *p*-cyanobenzenediazonium fluoroborate and 1.7 g. of cuprous bromide, was added 0.23 mole of phosphorus trichloride. After stirring for 30 min., the mixture was warmed to 40°, a vigorous reaction commencing. When complete, 0.20 mole of magnesium was added slowly with cooling to hold the temperature at 40–50°. The reaction mixture was freed of solvent and the residual semi-solid mass extracted with three 100-ml. portions of benzene–heptane mixture, 1:1 v./v., The extract was flash-distilled to remove solvent and the residual liquid then vacuum-distilled. There was obtained first a 2-g. fraction, b.p. 44–61° at 6 mm., solidifying at room temperature. This product is independent of the structure of the starting diazonium fluoroborate and variable in quantity; it is a fuming, phosphorus-free substance, and is believed to be the boron trifluoride–ethyl acetate complex (b.p. 123° at 772 mm., m.p. 37.5°[8]). The phosphonous dichloride (10 g.) was collected at 130–137° at 6 mm. It was redistilled through a 6 in. packed column, and after a small forerun the main cut was collected at 127–128° at 4.5 mm.; it provided the analytical data listed above. An alternative isolation procedure is to distill the solvent-free reaction product directly, eliminating the extraction. The large solid residue, however, makes this distillation somewhat difficult.

It appears that we have here a new method of synthesis of arylphosphonous dichlorides, and

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(1) Supported by a grant from the Duke University Research Council.

(2) G. O. Doak and L. D. Freedman, THIS JOURNAL, **73**, 5658 (1951).

(3) L. D. Freedman and G. O. Doak, *Chem. Rev.*, **57**, 479 (1957).

(4) P. C. Crofts, *Quart. Reviews*, **12**, 341 (1958).

(5) L. D. Quin and C. H. Rolston, *J. Org. Chem.*, **23**, 1693 (1958), and references cited therein. E. P. Komkov, K. U. Karavanov and S. Z. Even, *Zhur. obshchei Khim.*, **28**, 2963 (1958), have reported a somewhat similar preparation of alkylphosphonous dichlorides by reducing with metals the complex salts $RPCl_3{}^+ AlCl_4{}^-$ (J. P. Clay, *J. Org. Chem.*, **16**, 892 (1951)).

(6) D. R. Nijk, *Rec. trav. chim.*, **41**, 461 (1922).

(7) B. Buchner and L. B. Lockhart, Jr., THIS JOURNAL, **73**, 755 (1951).

(8) G. T. Morgan and R. Taylor, *J. Soc. Chem. Ind.*, **50**, 869 (1931).

hence of arylphosphonous acids, of potentially as wide versatility as the Doak–Freedman phosphonic acid synthesis. Work is continuing to define the scope of the synthesis and establish optimum reaction conditions.

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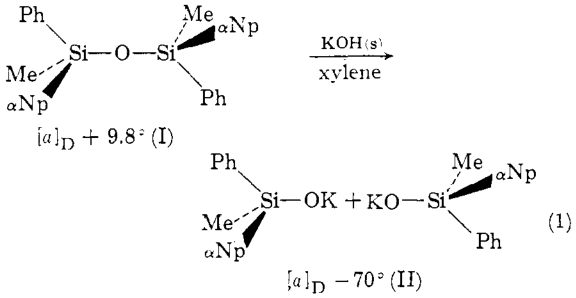
RECEIVED MAY 20, 1960

STEREOCHEMISTRY OF SUBSTITUTION AT SILICON. REACTIONS OF THE SILICON–OXYGEN BOND WITH INVERSION AND RETENTION OF CONFIGURATION

Sir:

For the first stereochemical studies of the silicon–oxygen bond we have used the optically active compounds R_3Si^*—O—, all of which contain the α-naphthylphenylmethylsilyl group (α-NpPhMe-Si-). Reaction (1) below is an unusual case in stereochemistry. Formation of optically pure potassium silanolate (II) rigorously proves *retention* of configuration as the stereochemical path.



$[\alpha]_D$ + 9.8° (I)

(1)

$[\alpha]_D$ − 70° (II)

The *optically active disiloxane* (I) was synthesized from II and (+)R_3Si^*Cl, and II was obtained from reaction of (+)R_3Si^*OH with either potassium hydroxide or potassium.

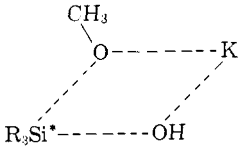
$$\underset{[\alpha]_D\ -16^\circ\ (III)}{R_3Si^*{-}OCH_3} \xrightarrow[\text{xylene}]{\text{KOH (s)}} \underset{[\alpha]_D\ +68^\circ\ (IV)}{R_3Si^*{-}OK} \qquad (2)$$

Retention of configuration in (2) is rigorously demonstrated by formation of III from IV and dimethyl sulfate, a reaction which does not involve the asymmetric center.

$$\underset{[\alpha]_D\ +18^\circ\ (V)}{R_3Si^*{-}O{-}COCH_3} \xrightarrow[\text{xylene}]{\text{KOH (s)}} \underset{[\alpha]_D\ +60^\circ\ (VI)}{R_3Si^*{-}OK} \qquad (3)$$

$$\underset{[\alpha]_D\ +16^\circ\ (V)}{R_3Si^*{-}O{-}COCH_3} \xrightarrow[\substack{\text{pentane;}\\ \text{amine}}]{CH_3OH} \underset{[\alpha]_D\ -12^\circ\ (VII)}{R_3Si^*{-}OCH_3} \qquad (4)$$

Predominant *inversion* in reactions (3) and (4) is demonstrated rigorously by formation of (−) $R_3Si^*{-}OCOCH_3$ from VI and acetyl chloride, a reaction which does not involve the asymmetric center. Sensitivity of stereochemistry to variations in leaving group and solvent is apparent. For more basic leaving groups (methoxy and siloxy relative to acetoxy) poor ionizing solvents favor retention probably by favoring SNi reaction of relatively undissociated complexes.



SNi retention in xylene

The change to a good ionizing solvent results in inversion reactions even for the methoxysilane (III). Thus, III is rapidly racemized in methanol solvents by small concentrations of methoxide ion. Furthermore, III is hydrolyzed by base in aqueous acetone to (+)R_3Si^*OH, $[\alpha]_D$ +2°, with predominant inversion in a reaction competitive with silanol racemization.

For the less basic leaving groups, inversion seems to be favored in both types of solvents for the α-naphthylphenylmethylsilyl compounds.

R_3Si^*OH,[1] $[\alpha]_D$ +26°, in xylene, shaken with powdered potassium hydroxide (KOH, 85%; H_2O, 13–14%) gave II. (Hydrolysis of II under controlled conditions yields the original silanol.) Reaction II with (+)R_3Si^*Cl[2] gave I (m.p. 88–89°; found: Si, 11.1; characteristic Si–O–Si infrared maximum at 9.55 microns). Reactants were heated (steam-bath) for one hour in reactions (1) and (2). Reaction of IV with dimethyl sulfate gave rapid formation of III,[1] $[\alpha]_D$ −16°, m.p. 64°. Reaction of II with excess acetyl chloride gave V (found: Si, 9.2; sapn. equiv., 306). Reaction (3) is rapid at 25° and gave VI in a reaction at least 85% stereospecific. Reaction (4) gave VII in 27% yield in a reaction at least 90% stereospecific.

We thank Dow Corning Corporation for generous support.

[1] L. H. Sommer and C. L. Frye, THIS JOURNAL, in press.

[2] L. H. Sommer and C. L. Frye, *ibid.*, **81**, 1013 (1959).

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RECEIVED MAY 28, 1960

THE MECHANISM OF THE VON RICHTER REACTION

Sir:

The transformation of aromatic nitro compounds to carboxylic acids through the agency of alcoholic potassium cyanide was first described in 1871 by von Richter.[1] Since the reaction was invariably attended by loss of the nitro function, von Richter initially assumed that cyanide ion, from which the carboxyl group derived, displaced the nitro group directly from its position on the aromatic nucleus.

The concurrent structural investigations of Meyer, Wurster, Solkowsky and especially of Griess and Korner[2] ultimately compelled von Richter to revise the structures assigned to his acidic products and, in 1875, in the last of his papers on the subject, he concluded that the carboxyl function must take up a position on the aromatic ring *ortho* to that vacated by the nitro group. This formulation of the reaction has since been amply

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[1] V. von Richter, *Ber.*, **4**, 21 (1871), and succeeding papers, *ibid.*, **4**, 459, 553 (1871); **7**, 1145 (1874); **8**, 1418 (1875).

[2] P. Griess, *ibid.*, **5**, 192 (1872); W. Korner, *Gazz. Chim. Ital.*, 306 (1874).