REACTION BETWEEN DIORGANODICHLOROSILANES AND CATECHOL

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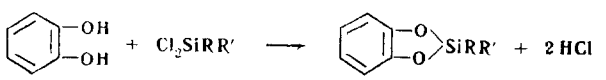
The reaction of diorganodicylorosilanes with catechol gives benzo-2, 2-diorgano-2-sila-1, 3-dioxacyclopentanes. It is shown that such heterocyclic compounds are always formed in the reaction, no matter what the sizes of the organic groups on the silicon atom.

The literature [1–3] describes benzo-2,2-dimethyl-2-sila-1,3-dioxacyclopentane. Studies have also been made of reactions, which give heterocyclic compounds, between 2,2'-diphenols and substituted bifunctional and trifunctional silanes [4, 5], as well as of aromatic p-dihydroxy compounds with diorganochloro(dialkoxy, diaroxy)silanes [6].

It was of interest to investigate the reaction between various dialkyl-, diaryl-, alkylalkenyl-, and diaryldichlorosilanes with catechol, and to trace the effects of different organic groups on the silicon atom on the course of the reaction. It might be expected that placing of voluminous groups on the silicon atom would promote formation of non-cyclic compounds.

Investigation of the reaction of diorganodichlorosilanes, containing various organic groups on the silicon atom, starting with low-volume methyl, and ending with spatially hindering phenyl and β-cyanoethyl, with catechol, showed that in all cases the equation for the reaction is:



$R = R' = CH_3$, C_2H_5, C_6H_5; $R = CH_3$; $R' = C_6H_5$, $CH_2=CH$, CH_2CH_2CN

Reaction product yield fluctuates between 40 and 80%. No non-cyclic compounds were isolated.

The I compounds prepared were all crystalline, except benzo-2,2-diethyl-2-sila-1,3-dioxacyclopentane, which was liquid at room temperature.

The table gives the physical properties and analytical data for the compounds synthesized.

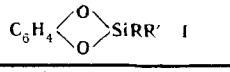
Consideration of the properties of I, particularly of the boiling points and molecular weights, reveals lack of correspondence between them. Judging by boiling points and analytical data, the I correspond to the formulas given in the table. But their molecular weights are doubled, and correspond to the dimer. Attempts to ascertain the cause of this lack of correspondence did not lead to positive results (the research is being continued). However, we do not exclude possible association of these compounds in solution, and possibly this is responsible for the increased molecular weights.

EXPERIMENTAL

Benzo-2, 2-dimethyl-2-sila-1, 3-dioxacyclopentane. A 3-necked flask was fitted with a stirrer, dropping funnel, and reflux condenser, and charged with 25.82 g (0.182 mole) dimethyldichlorosilane and 200 ml dry benzene, the mixture heated to 80°, stirred, and a solution of 10 g (0.091 mole) catechol dissolved in 150 ml dry benzene plus 25 ml dry ether, slowly dropped in. Reaction was allowed to proceed until HCl ceased to be evolved. Yield of I ($R = R' = CH_3$) 97–100° (5–7 mm) 50%.

The rest of the I's were prepared similarly.

Physical Constants and Analytical Data for Benzo-2,2-diorgano-1,3-dioxacyclopentanes



I

R	R'	Bp, °C (pressure, mm)	Mp, °C	M (cryoscopic in benzene) found	M (cryoscopic in benzene) calculated	Formula	Found, % C	Found, % H	Found, % Si	Calculated, % C	Calculated, % H	Calculated, % Si	Yield, %
CH_3	CH_3	97—100 (5—7)	71—72	317	166.25	$C_8H_{10}O_2Si$	57.67; 57.84	5.75; 6.06	16.07; 16.22	57.80	6.06	16.90	50
CH_3	$CH=CH_2$	113,5—115 (5—6)	74	362	178.26	$C_9H_{10}O_2Si$	60.66; 60.95	5.71; 5.74	15.38	60.63	5.65	15.76	73
CH_3	CH_2CH_2CN	196—197 (5—6)	90	435; 450	205.32	$C_{10}H_{11}NO_2Si$**	58.53; 58.90; 58.95	5.81; 5.58; 5.93	13.63; 13.66	58.49	5.60	13.68	80
CH_3	C_6H_5	123—125 (1—2)	109	415	228.32	$C_{13}H_{12}O_2Si$	68.01; 68.09	5.43; 5.16	12.09; 12.55	68.38	5.29	12.30	45.6
C_6H_5	C_6H_5	203—208 (1—2)	157—158	550; 587	290.38	$C_{18}H_{14}O_2Si$	74.86; 74.39	5.23; 5.38	9.24	74.4	4.84	9.67	40
C_2H_5	C_2H_5*	99—102 (5—6)	—	385	194.33	$C_{10}H_{14}O_2Si$	61.65; 61.65	7.21; 7.11	14.12; 14.24	61.80	7.26	14.45	52

* n_D^{20} 1.5286; d_4^{20} 1.1223; MR_D 52.91. Calculated MR_D 53.37.

**Found: N 7.17; 7.17%. Calculated: N 6.82%.

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PREPARATION OF 8-ALKYLAMINOQUINOLINES FROM 8-CHLOROQUINOLINES

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The chlorine of 8-chloroquinoline undergoes a metathetical reaction with methylamine or ethylamine in aqueous solution under pressure in the presence of cuprous chloride, to give 8-methylaminoquinoline and 8-ethylaminoquinoline. The preparation of 8-aminoquinoline from 8-chloroquinoline is confirmed.

Previously S. P. Mitsengendler and one of us developed a method of preparing 8-aminoquinoline (I) from 8-chloroquinoline (II) by the action of aqueous ammonia [1]. Continuing that work, we have prepared from II, by the action of methylamine and ethylamine, 8-methylaminoquinoline and 8-ethylaminoquinoline. Previously these 8-alkylaminoquinolines were obtained by alkylating I [2, 3] (only the picrates had been described).

In a monograph [4] R. Elderfield, referring to his own unpublished results, throws doubt on the results given in [1], since his "experiments on the ammonlysis of 8-halogenoquinolines were unsuccessful, even with an iodo derivative." So we repeated run 4 (optimum) of the paper referred to, and found that using the methods of isolation and purification given in it, I was obtained in yield close to that given.

We did not run a reaction with 8-iodoquinoline, and we cannot say whether it is possible to synthesize I from it. However, the chemist can easily prepare II from the more accessible I, using the results set out in [1].

EXPERIMENTAL

8-Methylaminoquinoline III. 1.34 g freshly-distilled II, 0.13 g CuCl, 10.4 ml 29% aqueous $MeNH_2$, were heated together in a sealed tube for 5 hr at 150°. The products were extracted with ether, the ether distilled off, and the residue vacuum-distilled, bp 90–93° (~1 mm). Yellow liquid, yield 0.78 g (60%).

8-Methylaminoquinoline hydrochloride. Prepared by passing dry HCl gas into an ether solution of III. Red needles ex EtOH, mp 175–184° (decomp.). Found: C 61.90, 61.60, H 5.57, 5.46; Cl 18.38, 18.19; N 14.20; 14.16%. Calculated for $C_{10}H_{10}N_2 \cdot HCl$. C 61.84; H 5.67; Cl 18.27; N 14.43%.

8-Methylaminoquinoline picrate. Prepared by mixing together hot ether solutions of III and picric acid. Orange-red crystals ex EtOH, mp 187–190.5° (decomp.). The literature gives mp 185–186 [2], 187–188° [3]. Found: C 50.13; 49.79; H 3.43; 3.34; N 18.28; 18.14%. Calculated for $C_{10}H_{10}N_2 \cdot C_6H_3N_3O_7$. C 49.63; H 3.38; N 18.08%.

The benzoyl derivative of 8-methylaminoquinoline was prepared by shaking an alkaline emulsion of III with benzoyl chloride. Colorless small tablets from EtOH, mp 139–140°. Found: N 10.45; 10.69%. Calculated for $C_{17}H_{14}N_2O$: N 10.69%.

Benzoyl derivative of 8-ethylaminoquinoline IV. 1.87 g freshly-distilled II, 0.19 g CuCl, 14 ml 33% aqueous $EtNH_2$ were heated together in a sealed tube for 5 hr at 200°. The products were extracted with ether, the extract evaporated, and the residual oil mixed with excess 10% NaOH solution, and benzoylated with benzoyl chloride by the Schotten-Baumann reaction. Yield of impure product 2.2 g (69.5%). After recrystallizing from EtOH, using decolorizing charcoal, it formed slightly yellowish small tablets, mp 135–136°. Found: C 78.89; 78.80; H 5.73; 5.68; N 10.07; 9.80%. Calculated for $C_{18}H_{16}N_2O$: C 78.20; H 5.84; N 10.12%. 8-Ethylaminoquinoline picrate. 0.36 g IV and 7 ml 50% H_2SO_4 were refluxed together for 7 hr 30 min, cooled, and the benzoic acid filtered off. The filtrate was treated with ether, then made alkaline, the amine which separated was extracted with ether, and the extract treated with an ether solution of picric acid. The precipitate weighed 0.33 g (63.5%), and after recrystallizing from EtOH formed orange-red needles mp 175–176° (decomp.). The literature gives mp 173° [2], 180° [3] (decomp.). Found: C 50.66; 50.87; H 3.89; 3.97; N 17.19; 17.23. Calculated for $C_{11}H_{12}N_2 \cdot C_6H_3N_3O_7$. C 50.90; H 3.77; N 17.46%.

8-Aminoquinoline I. 10.1 g freshly-distilled II, 78 ml 30% aqueous ammonia, and 1.01 g CuCl were heated together for 5 hr at 200° in a rotating autoclave. The crude I was filtered off from the ammonia solution. The solid was extracted with ether in a Soxhlet apparatus, and the ammoniacal solution was also extracted with ether. After distilling off the ether, two recrystallizations from petrol ether gave I, 4.72 g (53%). In [1] the content of compound I as found by analysis is given as 69.3%. Glistening pale-yellow crystals, 63.5–64.5°. Found: N 19.31; 19.28%. Calculated for $C_9H_8N_2$. N 19.43%.

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