by change in the ultraviolet spectrum of the sample.

Some further chemical transformations of I will be reported at a later date.

EXPERIMENTAL[4]

Benzocyclobutene-1-carboxylic acid (II). 1-Cyanobenzocyclobutene[1] (1.0 g.) was dissolved in saturated ethanolic potassium hydroxide (6 ml.). The solution was allowed to stand for twenty-four hours at room temperature, then diluted with water (2 ml.), refluxed for three hours, and poured into water (50 ml.). The resulting suspension was extracted with ether; then the aqueous layer was separated, acidified with 6*N* hydrochloric acid, and re-extracted with ether. The second (acid-containing) ether extract was dried over magnesium sulfate and evaporated to dryness. The residue was taken up in a minimum amount of warm petroleum ether (b.p. 30–60°), and the solution was decanted from an insoluble oily residue, seeded with a crystal of acid, and chilled to 10° to give acid II (0.835 g., 73%), m.p. 72–73°; reported[1] 76.5°.

1-Hydroxymethylbenzocyclobutene (III). A solution of acid II (1.505 g.) in ether (75 ml.) was added dropwise under nitrogen to a stirred solution of lithium aluminum hydride (0.830 g.) in ether. After being stirred overnight, the reaction mixture was treated with a saturated aqueous solution of sodium sulfate (*ca.* 4 ml., added dropwise). The resulting clear ethereal layer was drawn off, and the remaining aqueous sludge was washed with ether (25 ml.). The ether extracts were combined, dried over sodium sulfate, and evaporated to give alcohol III (1.250 g., 86%) as a colorless oil, b.p. 93–95° (4 mm.); n_D^{25} 1.5567, d^{25} 1.071. The analytical sample was obtained by molecular distillation in a semimicro apparatus.

Anal. Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.55; H, 7.82.

1-Hydroxymethylbenzocyclobutene tosylate (IV). Finely powdered *p*-toluenesulfonyl chloride (1.24 g.) was added to a solution of alcohol III (0.888 g.) in pyridine (6 ml.). The reaction mixture was allowed to stand at room temperature for twenty-four hours and was then poured into petroleum ether (100 ml.), b.p. 30–60°. The resulting suspension was washed with cold 2*N* sulfuric acid (100 ml.), then with sodium bicarbonate (50 ml., 5%), and finally with water (100 ml.). The organic layer was dried over magnesium sulfate, filtered, and allowed to evaporate slowly at room temperature through a loose cotton plug. After standing for six days, the solution had deposited tosylate IV (1.153 g., 60%) as clusters of pure white needles, m.p. 49–55°. A second crop, obtained by chilling the mother liquor to 5°, raised the total yield of crude product to 1.308 g. (73.6%). The sample, m.p. 73–74°, was recrystallized from *t*-butyl alcohol.

1-Methylbenzocyclobutene (V). A solution of tosylate IV (1.000 g.) in ether (75 ml.) was added dropwise to a solution of lithium aluminum hydride (1.0 g.) in ether (75 ml.). The resulting suspension was stirred for four hours at room temperature and was then treated with a saturated aqueous solution of sodium sulfate to decompose the excess hydride. The dried ether layer was concentrated to a small volume by carefully distilling off the ether through a fractionating column. The residual oil (1.2 g.) was passed through a gas chromatographic column (30% Apiezon M on fire-brick, helium at 105°) to give pure 1-methylbenzocyclobutene (0.157 g., 38%), n_D^{25} 1.5195, d^{25} 0.924.

Anal. Calcd. for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.14; H, 8.65.

The ultraviolet spectrum (ethanol) showed the following maxima: λ_{max} 260 (log ϵ 3.08), 265.5 (3.24), and 271 (3.19) mμ.

Methylenebenzocyclobutene (I). A solution of tosylate IV (2.000 g.) in warm *t*-butyl alcohol (10 ml.) was added to a solution of potassium *t*-butoxide (prepared from 0.300 g. of potassium and 6 ml. of *t*-butyl alcohol). The reaction mixture was stirred at 75–80° for 15 minutes and was then poured into cold water (15 ml.). The resulting suspension was extracted four times with 5-ml. portions of petroleum ether (b.p. 30–60°). The aqueous layer was filtered to give an amorphous sulfur-free polymer (0.413 g.). The organic extracts were combined, dried over magnesium sulfate, and concentrated to 2 ml. by fractional distillation. Chilling the pot residue to −20° gave unchanged tosylate (0.275 g.), obtained as pure white needles. The mother liquor was vacuum distilled in an all-glass, hermetically sealed apparatus, and the distillate was subjected to gas chromatography (30% Apiezon M on fire-brick, helium at 130°) to give olefin I (0.165 g., 41%) as a colorless liquid, n_D^{25} 1.5679.

Anal. Calcd. for C_9H_8: C, 93.06; H, 6.94. Found: C, 93.87; H, 6.18.

The infrared spectrum of methylenebenzocyclobutene showed absorption bands at 5.96, 6.01, and 11.6 μ, characteristic of the exo methylene group. The ultraviolet spectrum is reproduced in Fig. 1.

Hydrogenation of methylenebenzocyclobutene gave 1-methylbenzocyclobutene. Thus, 0.0162 g. of the olefin was dissolved in ethanol (5 ml.) and was hydrogenated at atmospheric pressure in the presence of palladium (0.001 g., 10%) on charcoal catalyst (reaction time, four minutes). The reaction mixture was filtered quantitatively through Celite, diluted to 10.0 ml. in a volumetric flask, and analyzed spectrophotometrically for 1-methylbenzocyclobutene.

Anal. Calcd. for 1-methylbenzocyclobutene: 0.0165 g. Found: 0.0141 g.

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(4) Melting points are corrected. The analyses were carried out by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Some Organofluorosilanes[1]

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Organoalkoxysilanes with the general structure RSi(OEt)$_2$R'Si(OEt)$_2$R[2,3] are converted readily to the corresponding fluorosilanes when they are treated with boron-trifluoride etherate.

The use of covalent halides in the preparation of halosilanes from alkoxysilanes is well known.[4]

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(1) This research was supported by the United States Air Force, Air Research and Development Command, under Contract AF 33(616)-6916 and monitored by Materials Central, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio.

(2) L. W. Breed, *J. Org. Chem.*, **25**, 1198 (1960).

(3) L. W. Breed, W. J. Haggerty, Jr., and F. Baiocchi, *J. Org. Chem.*, **25**, 1633 (1960).

(4) C. Eaborn, *Organosilicon Compounds*, Academic Press, New York, 1960, pp. 170–171, 304–307.

Boron trifluoride etherate is effective in converting siloxanes to fluorosilanes,[5–7] but only meager details are reported on the use of this convenient reagent with alkoxysilanes. In a patent, Sommer cites the preparation of difluoromethylphenylsilane, fluorotrimethylsilane, and silicon tetrafluoride from alkoxysilanes and boron trifluoride etherate without giving experimental details.[7]

Only impure difluoromethylphenylsilane could be isolated from a mixture obtained by treating diethoxymethylphenylsilane with a 10% molar excess of boron trifluoride etherate. Several higher boiling fluorosilanes, however, were prepared in good yields by this procedure when a 50 mole per cent excess of boron trifluoride etherate was used. The properties of five new fluorosilanes prepared by this method are described in Table I.

EXPERIMENTAL

p-Phenylenebis(difluoromethylsilane). A mixture of 43.1 g. (0.126 mole) of freshly distilled *p*-phenylenebis(diethoxymethylsilane) and 35.5 g. (0.25 mole) of boron trifluoride etherate was heated for 3 hr. at 58°. Fractional distillation gave 21.6 g. (82%) of the product boiling at 99° at 32 mm. The properties and analyses of this compound and other fluorosilanes that were similarly prepared from the corresponding alkoxysilanes are given in Table I.

Difluoromethylphenylsilane. After a mixture of 52.6 g. (0.25 mole) of diethoxymethylphenylsilane and 26.0 g. (0.18 mole) of boron trifluoride etherate was heated at 60–70° for 3 hr., fractional distillation of the product gave the following fractions boiling above 125°: A, 125–135°, 9.8 g.; B, 135–145°, 16.4 g.; C, 145–155°, 8.2 g.; and D, residue, 10.6 g. Fraction B represented a 41.7% yield of impure difluoromethylphenylsilane. The boiling point reported for this compound is 141–142°.[8]

Hydrolysis of difluoromethylphenylsilane. Over a 15-min. period, a solution of 16.0 g. (0.102 mole) of difluoromethylphenylsilane (Fraction B, above) was added to 9.7 g. (0.24 mole) of sodium hydroxide in 100 ml. water. During the addition the mixture was maintained at 0° by external cooling, and at the end of the addition the mixture was still alkaline. Insoluble salts were separated by filtration, and the filtrate was washed three times with 50 ml. portions of ether. Evaporation of the combined ether extracts gave 4.7 g. of crude product that was recrystallized from hexane to yield 1.9 g. (23%) of 1,3-dimethyl-1,3-diphenyldisiloxanediol melting 80–82°. Reported melting points are 112–113°[9] and 82–84°, 110–111°.[10]

Anal. Calcd. for $C_{14}H_{18}O_3Si_2$: C, 57.89; H, 6.25; Si, 19.34. Found: C, 58.70; H, 6.80; Si, 19.57.

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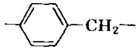
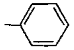
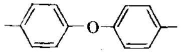
TABLE I

ORGANOFLUOROSILANES

$R'SiF_2RSiF_2R'$

R	R′	B.P.	Mm.	M.P.	Yield, %	Formula	Calcd., % C	Calcd., % H	Calcd., % F	Calcd., % Si	Found, % C	Found, % H	Found, % F	Found, % Si
	CH_3	99	32	—	82	$C_8H_{10}F_4Si_2$	40.31	4.41	—	23.50	40.14	4.11	—	23.17
	CH_3	118	29	—	78	$C_9H_{12}F_4Si_2$	42.83	4.79	30.11	22.26	42.56	4.84	30.03	22.11
		186–187	0.25	55–60	17	$C_{18}H_{14}F_4Si_2$	59.64	3.89	20.97	15.50	59.34	4.23	20.57	15.10
	CH_3	105–115	0.05	58–61	43	$C_{14}H_{14}F_4OSi_2$	50.89	4.16	22.99	17.00	50.91	4.16	22.63	16.66
$—(CH_2)_6—$	CH_3	100–102	29	—	77	$C_8H_{18}F_4Si_2$	38.99	7.36	30.84	22.80	38.92	7.35	30.56	22.53

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(7) L. H. Sommer, U. S. Patent **2,713,063** (1955).

(8) Robert O. Sauer, U. S. Patent **2,647,136** (1953); U. S. Patent **2,730,540** (1956).

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(10) W. H. Daudt and J. F. Hyde, *J. Am. Chem. Soc.*, **74**, 386 (1952).