diminished pressure at room temperature, affording a colorless crystalline mass which was dissolved in 25 ml. of distilled water. The solution was passed through a column (50 ml.) of Amberlite IR-100(H$^+$), washed in with 25 ml. of water, and the material eluted with five successive 50-ml. portions of water [the final aqueous wash had α − 0.04° (l, 2 dm.)]. The effluents were then passed, in the same order, through a column (50 ml.) of Amberlite IRA-400(OH$^-$) and six 50-ml. portions of effluent were collected [the final aqueous wash had α − 0.04 to 0.00° (l, 2 dm.)]. The effluents were combined, evaporated to dryness under diminished pressure at 30°, and dried by adding absolute ethanol and reevaporating. The resulting colorless, crystalline mass was dried at 0.1 mm.; wt., 3.6 g. This was dissolved in 117 ml. of boiling absolute ethanol under reflux, and the solution was cooled, affording colorless crystals (*A*); wt., 2.4 g.; m.p. 195–197°; $[\alpha]_{\mathrm{D}}^{21}$ − 23.4° (*c*, 1.006 in water) with no observable mutarotation—when diluted 1:10 with water, this solution gave no peaks in the ultraviolet and no change was observed after 42 hr. at room temperature. Periodate oxidation at *p*H 7.2 indicated that compound *A* had a pyranoid structure.[11] Its infrared absorption spectrum was recorded (Fig. 1, 6).

Anal. Calcd. for $C_7H_{13}NO_5$: C, 43.98; H, 6.85: N, 7.33; *N*-acetyl, 22.51. Found: C, 44.55; H, 6,85; N, 7.51; *N*-acetyl, 22.25.

"Unimolar" acetylation of D-*ribosylamine.* Glacial acetic acid (19 ml.) and 19 ml. of distilled water were placed in a 500-ml., round bottomed flask and cooled in ice to 4°. D-Ribosylamine (7.5 g., 0.05 mole) was added and the suspension was swirled and cooled; the temperature rose to 13° and then rapidly fell to 9°. Acetic anhydride (7 ml., 0.075 mole) was now added in one portion and the mixture was swirled; no rise in temperature occurred. The cooling bath was removed and, after the mixture had been swirled for 20 min., the D-ribosylamine had all dissolved; evaporation under diminished pressure (bath temp., 30°) was immediately started and, after 35 min., a yellow sirup resulted which was immediately dried at 0.1 mm., giving (after 30 min.) a colorless, crystalline mass which was processed within 3 hr. (if not used immediately, it was refrigerated). This material was dissolved in 100 ml. of distilled water, passed through a column of 300 ml. of mixed anion- and cation-exchange resin (Amberlite MB-3, which had previously been cautiously back-washed with just enough water to remove air bubbles), and eluted with water. The first 100 ml. of effluent was evaporated to dryness and dried at 0.1 mm., giving a colorless crystalline mass (*M*), wt., 2.0 g. The next five 100-ml. effluents were combined, evaporated, and dried at 0.1 mm., giving a clorless, crystalline mass (*N*), wt., 5.4 g. The next eight 100-ml. effluents were combined, evaporated, and dried at 0.1 mm., giving a colorless mixture of sirup and crystals (*P*), wt., 1.7 g. Crystals *M* were suspended in 20 ml. of absolute ethanol and boiled under reflux; the suspension was cooled, refrigerated, and filtered, giving colorless crystals *B*, wt., 1.2 g., m.p. 172–174°, $[\alpha]_{\mathrm{D}}^{23}$ +5.1° (*c*, 1.170 in water). Its infrared spectrum was recorded (Fig. 1, 7).

Anal. Calcd. for $C_7H_{13}NO_5$: C, 43.98; H, 6.85; N, 7.33; *N*-acetyl, 22.51. Found: C, 43.83; H, 6.79; N, 7.47; *N*-acetyl, 22.28.

Crystals *N* were treated with 54 ml. of absolute ethanol as for crystals *M*, giving colorless crystals *B*, wt., 3.2 g., m.p. 172–174°, $[\alpha]_{\mathrm{D}}^{23}$ + 5.6° (*c*, 1.072 in water). Its infrared absorption spectrum was identical with that of the first crop of *B*.

Anal. Found: C, 43.92; H, 6.96; N, 7.29.

Crystals *P*, treated with 10 volumes of absolute ethanol, as above, gave colorless crystals *C*, wt., 0.3 g., m.p. 198–200° (dec., softening and browning at 195°); $[\alpha]_{\mathrm{D}}^{23}$ +17.8° (*c*, 1.013 in water). Its infrared spectrum was recorded (Fig. 1, 5). Periodate oxidation at *p*H 7.2 indicated that materials *B* and *C* had a pyranoid structure.[11]

Anal. Found: C, 43.23; H, 6.73, N, 7.04; *N*-acetyl, 20.34.

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(11) The author thanks Dr. Calvin L. Stevens for this determination.

[CONTRIBUTION FROM THE MIDWEST RESEARCH INSTITUTE]

Interaction of Alkoxysilanes and Acetoxysilanes[1]

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In the presence of Lewis acid catalysts, mixtures of ethoxysilanes and acetoxysilanes give good yields of ethyl acetate. Thermal decomposition of the acetoxysilane with the intermediate formation of acetic anhydride does not have a role in the formation of the ethyl acetate. Ferric chloride was a satisfactory catalyst at temperatures as low as 130° while low yields of ethyl acetate were obtained from other catalysts, aluminum isopropylate, *p*-toluenesulfonic acid, and sodium methoxide. Although extensive redistribution of silicon-attached functional groups and cleavage of silicon-phenyl bonds occurred at elevated temperatures in the presence of acid catalysis, a transesterification reaction also took place under these conditions.

Transesterification reactions, which have been very successful in the preparation of metallosiloxanes,[2–7] offer a potentially valuable tool for the preparation of siloxanes, provided side reactions

$$R_3SiOAc + R_3'SiOEt \longrightarrow R_3SiOSiR_3' + EtOAc$$

can be avoided. Although O'Brien[8] failed to obtain such a condensation, Henglein[9] and Andrianov[10]

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(2) K. A. Andrianov and L. M. Volkova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 303 (1957); *Chem. Abstr.*, **51**, 14544.

(3) D. C. Bradley and I. M. Thomas, *Chem. & Ind.*, 1231 (1958).

(4) E. F. Gibbs, H. Tucker, G. Shkapenko, and J. C. Park, WADC TR 55-453, Part II (1957), AD 131036.

(5) F. A. Henglein, R. Lang, and K. Scheinost, *Makromol. Chem.*, **15**, 177 (1955).

(6) F. A. Henglein, R. Lang, and K. Scheinost, *Makromol. Chem.*, **18–19**, 102; *Chem. Abstr.*, **51**, 2576 (1956).

(7) F. A. Henglein, R. Lang, and L. Schmack, *Makromol. Chem.*, **22**, 103 (1957).

TABLE I

TRANSESTERIFICATION REACTION

Run No.	1	2	3	4	5	6	7	8	9	10
p-Phenylenebis(dimethylethoxysilane) (mole)			0.05							0.088
p-Phenylenebis(diethoxymethylsilane) (mole)	0.029	0.029		0.015	0.015	0.015	0.15	0.15	0.15	
Acetoxytrimethylsilane (mole)			0.10							0.18
Methyltriacetoxysilane (mole)	0.039	0.039		0.020	0.020	0.020	0.20	0.20	0.20	
Catalyst (g.)	0.3		1.0	0.15	0.15	0.15	0.15	0.15	0.15	0.75
	Al-(O*iso*Pr)$_3$		H_2SO_4	Al-(O*iso*Pr)$_3$	Al-(O*iso*Pr)$_3$	Al-(O*iso*Pr)$_3$	$FeCl_3$	*p*-Toluenesulfonic acid	$NaOCH_3$	$FeCl_3$
Temperature	160°	160°	25°	100°	120°	140°	130°	145°	145°	140°
Time, hr.	26	24	15	20	20	20	20	20	20	20
Volatiles recovered (g.)	6.0	1.7	1.7	0.10	0.50	0.80	4.6	0.6	1.0	19.0
Gas chromatography Analysis of volatiles										
				(% Peak Area)						
Ethanol	6.7	17.2	2.1		3.6	2.6	10.1	12.7	2.4	Trace
Ethyl acetate	88.1	80.0	12.8		10.0	64.0	86.9	82.2	90.5	19.4
Isopropyl acetate	5.1				Trace	Trace				
Acetic acid		1.0	3.8					5.1		Trace
Acetoxytrimethylsilane			10.3							4.3
Hexamethyldisiloxane			20.1[a]							12.2[a]
Ethoxytrimethylsilane			50.3							64.1
Ethyl ether			0.5				3.0		3.9	
Cyclohexane					86.4[b]	33.4[b]				
Unknown									3.2	

[a] Analysis of the trimethylacetoxysilane indicated it contained an equivalent amount of hexamethyldisiloxane. [b] Aluminum isopropylate was introduced in cyclohexane solution.

have reported successful condensations when Lewis acids were used as catalysts. The use of such catalysts can be expected to initiate important competing reactions, since it is well known that they catalyze redistribution of functional groups in silicon-functional compounds,[11] redistribution of siloxane linkages,[12] and at higher temperatures cause significant silicon-phenyl cleavage.[13]

DISCUSSION

A study of the effects of temperature and catalyst in the transesterification reaction is shown in Table I.

Under the conditions described by Henglein[9] (Run No. 3), the chief product was ethoxytrimethylsilane when *p*-phenylenebis(dimethylethoxysilane) and acetoxytrimethylsilane reacted in the presence of sulfuric acid. Only a small amount of ethyl acetate was formed in the reaction. When low boiling silanes could distill from the mixtures, redistribution predominated and very little ethyl acetate was recovered. Under conditions that allow the ester to be fractionally distilled from the mixture without removing any of the possible silicon-containing products, the transesterification reaction gave good yields of ethyl acetate, but the resulting silanes were derived from the complex redistribution products rather than the starting materials.

In attempts to prepare *p*-phenylenebis(1,1,3,3-tetramethyl - 3 - phenyldisiloxane) (I), methyltris(dimethylphenylsiloxy)silane (II), and phenyltris(dimethylphenylsiloxy)silane (III), only pure I was obtained in any significant yield, and this experiment represented the simple case of the reaction of a difunctional and a monofunctional silane. Substitution of phenyl for methyl did not give a less complex product in the preparation of III over II. Neither did the more thermally stable monoacetoxysilane with a triethoxysilane permit less redistribution than the triacetoxysilane and monoethoxysilane in the preparation of III.

The similarity between the ethyl acetate elimination reaction and the well known ethyl chloride elimination between a silicon chloride and a silicon ethoxide[14-16] is shown in the experimental section.

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(8) J. F. O'Brien, WADC TR 57-507 (Oct. 1957). AD 142,100.

(9) F. A. Henglein and R. Schmulder, *Makromol. Chem.*, **13**, 53 (1954).

(10) K. A. Andrianov, N. N. Sokolov, and E. N. Khrustaleva, *J. Gen. Chem., U.S.S.R.*, 26, 1249 (1956).

(11) C. Eaborn, *Organosilicon Compounds*, Academic Press Inc., New York, 1960, pp. 187, 317.

(12) C. Eaborn, *Organosilicon Compounds*, Academic Press Inc., New York, 1960, p. 260.

(13) C. Eaborn, *Organosilicon Compounds*, Academic Press Inc., New York, 1960, p. 155.

(14) G. H. Wagner and C. E. Erickson, U. S. Patent 2,731,485 (Jan. 17, 1956); *Chem. Abstr.*, 50, 8247 (1956).

TABLE II

ALKYL AND ARYLACETOXYSILANES

Compound	B.P., Mm.	M.P.	Yield, %	n_D^{25}	d_4^{25}
Acetoxytrimethylsilane[17]	101–105	—	72	1.3899	0.879
Diacetoxydimethylsilane[18]	54–56 (7)	—	52	1.4020	1.050
Methyltriacetoxysilane[18]	107–109 (16)	26	61	1.4068	1.174
Tetraacetoxysilane[18]	—	108	21	—	—
Acetoxydimethylphenylsilane[19]	127–130 (44)	—	66	1.4868	1.005
Phenyltriacetoxysilane[20]	118 (0.10)	34	59	1.4738[a]	1.184[a]

[a] Super-cooled liquid.

Nearly identical yields of I and 1,3-diphenyltetramethyldisiloxane are obtained from the reaction of acetoxydimethylphenylsilane and *p*-phenylenebis(dimethylethoxysilane) and from chlorodimethylphenylsilane and *p*-phenylenebis(dimethylethoxysilane). The same result was observed in the two possible methods of preparing III.

In none of the experiments was acetic anhydride found as a volatile component of the product as might be expected from the mechanism proposed by Andrianov. He suggested that polymerization occurs through the thermal decomposition of the silicon acetates with the formation of siloxanes and acetic anhydride which, in turn, reacts with the alkoxysilane to give an ester and additional acetoxysilanes. In the presence of ferric chloride, we found that acetoxydimethylphenylsilane gave some acetic acid and acetic anhydride at 160°, but considerably less than the amount necessary to account for the ethyl acetate formed in the presence of alkoxysilanes.

The transesterification reaction is complicated by the cleavage of silicon-phenyl bonds, with the liberation of up to 8% of the available phenyl groups. A comparable amount of benzene was obtained by the action of ferric chloride on acetoxydimethylphenylsilane.

EXPERIMENTAL

In the experiments, reaction temperatures were determined by a thermometer inserted in the well of the flask. The volatiles were allowed to distill through a short Vigreux column and were collected in a Dry Ice trap.

The composition of the volatiles wes estimated with a Perkin-Elmer Model 154B Vapor Fractometer using column "A" (diisodecyl phthalate) at 75°. All yields calculations from vapor phase chromatographic analyses were based on percentage of peak area.

Acetoxydimethylphenylsilane. To a stirred mixture of 37.0 (0.46 mole) of pyridine, 72.0 g. (0.42 mole) of chlorodimethylphenylsilane, and 250 ml. anhydrous ether was added dropwise a solution of 25.0 g. (0.42 mole) glacial acetic acid in 75 ml. of ether. When the addition was complete (4.5 hr.), the reaction mixture was stirred for an additional hour, the pyridine hydrochloride salts were removed by filtration, and the residue was washed with a little anhydrous ether. After the combined filtrate and ether washings were concentrated by downward distillation, fractional distillation of the product through a 10-in. column packed with Berl saddles gave 53.1 g. acetoxydimethylphenylsilane.

Anal. Calcd. for $C_{10}H_{14}O_2Si$: Si, 14.46, MR$_D$ 55.49. Found: Si, 14.40, 14.33; MR$_D$ 55.63.

The procedure, which follows one described by Étienne[17] for acetoxytrimethylsilane was particularly convenient. Yields and physical constants of the acetoxysilanes prepared by this method are shown in Table II.

p-Phenylenebis(1,1,3,3-tetramethyl-3-phenyldisiloxane). A. From acetoxydimethylphenylsilane and *p*-phenylenebis(dimethylethoxysilane): When a mixture containing 19.4 g. (0.10 mole) acetoxydimethylphenylsilane, 14.2 g. (0.05 mole) *p*-phenylenebis(dimethylethoxysilane),[21] and 0.1 g. of ferric chloride was heated at 140° for 20 hr., 8.5 g. of volatile material was obtained. The volatile components were (percentage of total peak area given): ethyl ether (0.6), ethanol (3.6), ethyl acetate (86.0), and benzene (9.6). The benzene was equivalent to the cleavage of 4.2% of the phenyl group present as acetoxydimethylphenylsilane. About 83% of the expected ethyl acetate was collected.

The nonvolatile portion of the reaction product similarly prepared from 0.90 mole acetoxydimethylphenylsilane and 0.45 mole *p*-phenylenebis(dimethylethoxysilane) was filtered to remove the ferric chloride, diluted with 50 ml. ether, washed three times with water, once with 5% sodium bicarbonate, and once again with water, and stripped to remove the ether. Distillation of the residue gave 54.5 g. (42%) of the redistribution product, 1,3-diphenyltetramethyldisiloxane, boiling 157–157.5° at 13 mm., n_D^{25} 1.5148, d_4^{25} 0.984 (reported[22] b.p. 165° at 17 mm., n_D^{25} 1.5149, d_4^{25} 0.971) and 52.4 g. (22%) *p*-phenylenebis(1,1,3,3-tetramethyl-3-phenyldisiloxane) boiling 179–189° at 0.04–0.05 mm., n_D^{25} 1.5109, d_4^{25} 0.987.

Anal. Calcd. for $C_{26}H_{38}O_2Si_4$: C, 63.05; H, 7.74; Si, 22.70; MR$_D$ 150.60. Found: C, 63.11; H, 7.86; Si, 22.48; MR$_D$ 150.15.

B. From chlorodimethylphenylsilane and *p*-phenylenebis(dimethylethoxysilane): A mixture of 17.1 g. (0.010 mole) of chlorodimethylphenylsilane, 14.1 g. (0.05 mole) of *p*-phenylenebis(dimethylethoxysilane), and 0.1 g. of anhydrous ferric chloride was heated at 100° for 24 hr. A total of 5.0 g. or 93% of the calculated weight was lost. The product, neutralized and washed, was distilled at reduced pressure through a 2-in. column. The following fractions were collected: A, 133–134° (4.5 mm.), 6.6 g., n_D^{27} 1.5129; B, 130–70° (0.05 mm.), 3.3 g. n_D^{27} 1.5162; C, 167–82° (0.05–0.07 mm.), 1.7 g., n_D^{27}

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(15) A. Gancberg, U. S. Patent **2,768,152** (Oct. 23, 1956); *Chem. Abstr.*, **51**, 10121 (1957).

(16) E. Itsugi and M. Hisazumi, Japanese Patent **3694** (May 19, 1956); *Chem. Abstr.*, **51**, 10951 (1957).

(17) Y. Étienne, *Compt. rend.*, **235**, 966 (1952).

(18) H. A. Schuyten, J. W. Weaver, and J. D. Reid, *J. Am. Chem. Soc.*, **69**, 2110 (1947).

(19) K. A. Andrianov and N. V. Delazari, *Doklady Akad. Nauk S.S.S.R.*, **122**, 393 (1958); *Chem. Abstr.*, **53**, 2133 (1959).

(20) H. H. Anderson and T. C. Hager, *J. Am. Chem. Soc.*, **81**, 1584 (1959).

(21) L. Breed, W. J. Haggery, Jr., and F. Baiocchi, *J. Org. Chem.*, **25**, 1804 (1960).

(22) W. E. Daudt and J. F. Hyde, *J. Am. Chem. Soc.*, **74**, 386 (1952); *Chem. Abstr.*, **47**, 8671 (1953).

1.5156; D, residue 10.5 g. Fraction A corresponded to a 46.1% conversion to 1,3-diphenyltetramethyldisiloxane; fraction C was a 20% yield of crude *p*-phenylenebis(1,1,3,3-tetramethyl-3-phenyldisiloxane).

Phenyltris(dimethylphenylsiloxy)silane. A. From phenyltriacetoxyphenylsilane and dimethylethoxyphenylsilane: A mixture of 30.4 g. (0.169 mole) dimethylethoxyphenylsilane, 15.8 g. (0.056 mole) phenyltriacetoxysilane, and 0.1 g. of ferric chloride was heated for 24 hr. at 145–50°, then an additional 24 hr. at 150–158°. A total of 10.7 g. of distillate, which contained 67% of the expected ethyl acetate along with a small amount of ethyl alcohol and a trace of benzene, was obtained. The residue was dissolved in ether, filtered, neutralized with aqueous sodium bicarbonate, and devolatilized to give 29.4 g. of crude product. Fractional distillation gave 4.3 g. (17.7%) 1,3-diphenyltetramethyldisiloxane boiling 93–100° at 0.03–0.08 mm., n_D^{25} 1.5140, d_4^{25} 0.977, and 4.5 g. impure phenyltris(dimethylphenylsiloxy)-silane boiling 190–240° at 0.02 mm., n_D^{25} 1.529, d_4^{25} 1.076 (reported[23] b.p. 217–225° at 1.0 mm., n_D^{25} 1.528, d_4^{25} 1.060). MR$_D$ Calcd.: 165.48. Found: 160.3.

Many small intermediate fractions indicated that the product was a complex mixture of high molecular weight compounds.

B. From acetoxydimethylphenylsilane and phenyltriethoxysilane: After 29.2 g. (0.15 mole) of acetoxydimethylphenylsilane, 12.0 g. (0.05 mole) of phenyltriethoxysilane, and 0.10 g. of ferric chloride were heated at 160° for 48 hr. and the volatiles collected in a Dry Ice trap, the residue was devolatilized at 0.02 mm. for 2 hr. at room temperature. The final weight loss of the mixture was 10.7 g. or 81% of the theoretical amount. The residue was filtered, diluted with ether, washed and dried in the manner described earlier. Fractional distillation through a 2-in. column gave the following fractions: A, 143–144° (6.2 mm.) 10.5 g., n_D^{27} 1.5124; B, 80–84° (0.02 mm.) 1.2 g., n_D^{27} 1.5131; C, 87–140° (0.02 mm.) 1.0 g.; D, 143–170° (0.03 mm.), 0.8 g. n_D^{27} 1.5176; E, residue, 12.6 g. Fraction A represented a 55% yield of 1,3-diphenyltetramethyldisiloxane, but none of the desired tri(siloxy)silane was isolated.

C. From chlorodimethylphenylsilane and phenyltriethoxysilane: When a mixture of 18.5 g. (0.108 mole) of chlorodimethylphenylsilane, 8.7 g. (0.036 mole) of phenyltriethoxysilane, and 0.1 g. of ferric chloride was heated at 100°, ethyl chloride evolution ceased after 4 hr. The crude product, 20.0 g., represented a loss of 104% of the expected weight. Benzene was identified qualitatively by gas chromatography. The neutralized residue was distilled through a 2-in. column at reduced pressure. The following fractions were collected: A, 134–135° (5.0 mm.) 2.5 g., n_D^{27} 1.5096; B, 130–160° (0.05 mm.), 1.9 g., n_D^{27} 1.5156; C, 170–80° (0.05–0.06 mm.), 1.9 g., n_D^{27} 1.5260, d_4^{27} 1.048; D, residue, 9.0 g. Fraction A corresponds to a 46% conversion to 1,3-diphenyltetramethyldisiloxane and Fraction C to a 9% yield of the tri(siloxy)silane MR$_D$ Calcd.: 165.48. Found: 163.7.

Methyltris(dimethylphenylsiloxy)silane. From methyltriacetoxysilane and dimethylethoxyphenylsilane: When 14.1 g. (0.064 mole) of methyltriacetoxysilane, 34.0 g. (0.192 mole) of dimethylethoxyphenylsilane, and 0.1 g. of ferric chloride were heated for 20 hr. at 160°, a total of 15.5 g. of distillate was collected. The volatiles contained 83.4% of the theoretical ethyl acetate and benzene representing cleavage of 8.0% of the available phenyl groups. After the product was filtered and washed, distillation in a Hickman still gave 9.6 g. (35.2%) of 1,3-diphenyltetramethyldisiloxane, 90–95°, 0.002 mm., n_D^{25} 1.5118, d_4^{25} 0.978, a second fraction boiling 137–42° at 0.0001 mm. (2.3 g.), and 2.9 g. (7%) impure methyltris(dimethylphenylsiloxy)silane boiling 182–200° at 0.0001 mm., n_D^{25} 1.4903, d_4^{25} 1.001.

Anal. Calcd. for $C_{26}H_{36}O_3Si_4$: C, 60.42; H, 7.30; Si, 22.61, MR$_D$ 145.66. Found: C, 58.44; H, 7.45; Si, 25.79; MR$_D$ 143.65.

Thermal decomposition of acetoxydimethylphenylsilane. After 16.6 g. of acetoxydimethylphenylsilane was heated at 160° for 48 hr., the residue was devolatilized for 2 hr. at 0.5 mm. The volatile materials, collected in a Dry Ice trap, weighed 0.1 g. The heating of the residue at 160° was continued for 16 hr. after 0.1 g. of anhydrous ferric chloride was added, and the product was similarly devolatilized. An additional 1.0 g. of distillate was collected and the corresponding weight loss was found in the residue. Analysis indicated that benzene and acetic acid with traces of acetic anhydride and three unidentified components were present. The amount of benzene was equivalent to 7% of the available phenyl groups and the acetic acid to 7% of the available acetoxy groups.

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[23] J. F. Hyde, O. K. Johannson, W. H. Daudt, R. F. Fleming, H. B. Laudenslager, and M. P. Roche, *J. Am. Chem. Soc.*, **75**, 5615 (1953).

[CONTRIBUTION FROM HUGHES RESEARCH LABORATORIES, HUGHES AIRCRAFT CO.]

Syntheses and Reactions of Isopropoxy and Trimethylsiloxy Titanium Dichelates[1]

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Syntheses and reactions of diisopropoxy and bis(trimethylsiloxy) titanium dichelates are described. The chelating groups are those derived from 1,3-diphenyl-1,3-propanedione, 2,4-pentanedione, and 8-quinolinol. These compounds readily replace the isopropoxy and trimethylsiloxy groups attached to a titanium atom. In cases where both groups are present, the isopropoxy groups are preferentially replaced. Hydrolyses of the dichelated titanium derivatives are also described.

Organotitanium compounds have attracted attention in recent years as intermediates for the possible synthesis of semi-inorganic polymers capable of withstanding high temperatures. The excellent thermal stability of the metal chelates is well known, and because of the interest in thermally stable polymers, particularly in organometalloxanes, we have investigated the preparations and reactions of several dichelated titanium titanium derivatives.

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