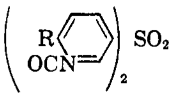
TABLE I

3,3′-SULFONYLBIS(PHENYL ISOCYANATES)



	R	Formula	Yield, %	M.P.^{a}	N Calcd.	N Found	S Calcd.	S Found
I	H	$C_{14}H_8N_2O_4S$	40–50	126–129	9.32	9.13	10.67	10.70
II	Cl	$C_{14}H_6Cl_2N_2O_4S$	68	149–150	7.58	7.30	8.65	8.54
III	CH_3	$C_{16}H_{12}N_2O_4S$	77	132–134	8.53	8.52	9.76	9.96
IV	$(CH_3)_3C$	$C_{22}H_{24}N_2O_4S$	73	120	6.79	6.69	7.77	7.79

^{a} Melting points are uncorrected.

ml. by distillation at atmospheric pressure. The concentrate was placed in a 250-ml. filter flask and the remaining solvent removed by heating in an oil bath under vacuum. The diisocyanates were taken up in a small volume of dry benzene and crystallized from that solvent. They were further purified by trituration with petroleum ether (b.p. 30–60°) and were obtained as white or faintly yellow solids.

The relatively low yield of I was accompanied by the formation of a considerable amount of high melting, insoluble polyurea which was removed by filtration of the hot chlorbenzene solution. The other three products were accompanied by only small amounts of such a polymer.

Compound IV was converted into the corresponding diethylurethane, 5,5′-sulfonylbis(2-*tert*-butyl)carbanilic acid, ethyl ester, by reaction with ethyl alcohol. This derivative after crystallization from carbon tetrachloride and trituration with petroleum ether (b.p. 30–60°) melted at 135°.

Anal. Calcd. for $C_{26}H_{36}N_2O_6S$: N, 5.55; S, 6.35. Found: N, 5.41; S, 6.18.

The relative reactivities of the four diisocyanates were studied by the procedure of Bailey and co-workers[3] using a Beckman IR-5 spectrophotometer with sodium chloride 0.102 mm. absorption cells. From the data obtained the times required for 50% completion and practical completion of the reaction with 2-ethylhexanol were determined for each diisocyanate.

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Communications TO THE EDITOR

Titanium-Catalyzed Reduction and Rearrangement in Grignard Coupling Reaction with Silicon Halides[1]

Sir:

Adding 0.1 wt. % titanium tetrachloride to triethylchlorosilane alters the course of its reaction with isopropylmagnesium bromide, producing reduction $[(C_2H_5)_3\,SiCl + (CH_3)_2CHMgBr \rightarrow (C_2H_5)_3\,SiH + C_3H_6]$ and rearrangement $[(C_2H_5)_3\,SiCl + (CH_3)_2CHMgBr \rightarrow (C_2H_5)_3Si(CH_2)_2CH_3]$. Titanium tetrachloride also catalyzed reduction and rearrangement in the reaction of diethyldichlorolane with isopropylmagnesium bromide $[(C_2H_5)_2SiCl_2 + (CH_3)_2CHMgBr \rightarrow (CH_3)_2CHSi(C_2H_5)_2H + CH_3(CH_2)_2Si(C_2H_5)_2H + C_3H_6)]$; details of our work on this reduction and rearrangement prior to our recognizing the titanium tetrachloride catalysis and the propylene formation should appear shortly.[2] Titanium tetrachloride also catalyzed participation of hexene-1 in the reaction of diethyldichlorosilane with isopropylmagnesium bromide to produce *n*-hexyldiethylsilane $[(C_2H_5)_2SiCl_2 + (CH_3)_2CHMgBr + CH_3(CH_2)_3CH = CH_2 \rightarrow n\text{-}C_6H_{13}Si(C_2H_5)_2H + (CH_3)_2CHSi(C_2H_5)_2H + CH_3(CH_2)_2Si(C_2H_5)_2H + C_3H_6]$.

Such catalyses have not been reported in over fifty years of widespread use of the Grignard reagent for synthesizing organosilicon compounds. However analogous reductions and rearrangements proceeding without known catalysis have been reported for organoboron[3,4] and organoaluminum compounds.[5]

The new reactions outlined above are described in greater detail below. They have since been shown by our associates to involve titanium-catalyzed isomerization of the Grignard reagent and titanium-catalyzed olefin exchange with the Grignard reagent.[6,7]

Refluxing 150 g. of triethylchlorosilane contain-

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(1) P. D. George and J. R. Ladd, Paper presented at the 140th National Meeting of the American Chemical Society, September 5, 1961.

(2) P. D. George and J. R. Ladd, *J. Org. Chem., in press.*

(3) G. F. Hennion, P. A. McCusker, E. C. Ashby, and A. J. Rutkowski, *J. Am. Chem. Soc.*, **79**, 5190 (1957).

(4) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6434 (1959).

(5) K. Ziegler *et al*, *Ann.*, **589**, 91 (1954) and **629**, 53 (1960).

(6) G. D. Cooper and H. L. Finkbeiner, Paper presented before the 140th National Meeting of the American Chemical Society, September 5, 1961.

(7) G. D. Cooper and H. L. Finkbeiner, *J. Org. Chem.*, **26**, 4779 (1961).

ing 0.14 g. titanium tetrachloride for 14.5 hr. with isopropylmagnesium bromide made conventionally from 131 g. isopropyl bromide, 26 g. magnesium turnings, and 375 ml. anhydrous ether gave 11,056 ml. STP, 49% yield of propylene, b.p. −48.5° (740 mm.), identified by its infrared spectrum. Other volatile products were distilled by heating the reaction mixture with a boiling water bath for 3 hr. at atmospheric pressure and 2 hr. more as the pressure was reduced gradually to 1 mm. Fractional distillation gave ether and 55.7 g. (48%) of triethylsilane, b.p. 109.5–110.5°, n_D^{20} 1.4117–1.4122, identified by its infrared spectrum. Hydrolysis and fractional distillation of 65.3 g. boiling below 170° gave (1) 11.4 g. (7%) of propyltriethylsilane, b.p. 56.5–65° (19 mm.), n_D^{20} 1.4310–1.4312, containing 84% of the *n*-propyl isomer and (2) 22 g. (18% recovery of triethylsilyl groups as hexaethyldisiloxane) b.p. 104.5–117.5° (19 mm.), n_D^{20} 1.4339–1.4341.

Carrying out the reaction without the added titanium tetrachloride gave no propylene, no triethylsilane, and no *n*-propyltriethylsilane. There was obtained a complex mixture of products shown by infrared analysis to consist of a 7% yield of isopropyltriethylsilane and about 80% recovery of triethylchlorosilane and triethylbromosilane from halogen interchange.

Refluxing 140 g. diethyldichlorosilane containing 0.1 wt. % titanium tetrachloride for 18 hr. with isopropylmagnesium bromide (made conventionally from 250 g. isopropyl bromide, 49 g. magnesium turnings, and 750 ml. anhydrous ether), distilling the ether by heating the reaction mixture on boiling water bath for 5 hr., heating the residue on a boiling water bath for 20 hr., distilling all volatile products by gradually reducing the pressure to 1 mm. in about 1 hr., and finally fractionally distilling all the volatile products from the reaction gave: (1) 0.79 mole propylene, b.p. −48° (740 mm.), identified by its infrared spectrum and (2) 69.7 g., b.p. 132.5°, n_D^{20} 1.4189–1.4190, 0.54 mole, 60% yield of a mixture of propyldiethylsilanes containing 54% of the *n*-propyl isomer and 50% of the isopropyl isomer, the total being more than 100% owing to experimental error.

Adding 151 g. of hexene-1 to 2 moles of isopropylmagnesium bromide just prior to adding 140 g. diethyldichlorosilane containing 0.1 wt. % titanium tetrachloride and then carrying out the reaction as before gave: (1) 97.6 g., 64% recovery, of hexene-1, b.p. 62.5–63.5°, n_D^{20} 1.3878 identified by its infrared spectrum; (2) 0.71 mole propylene, b.p. −48° (740 mm.), identified by its infrared spectrum; (3) 53 g., b.p. 128–132°, n_D^{20} 1.4183–1.4198, 46% yield of a mixture containing 42% *n*-propyldiethylsilane and 57% isopropyldiethylsilane; and (4) 14.9 g., b.p. 58–70° (7.5 mm.), n_D^{20} 1.4323–1.4329, 9.8% yield of *n*-hexyldiethylsilane (Calcd. for $C_{10}H_{24}Si$: C, 69.6; H, 14.0; Si−H, 1.00. Found: C, 70.0; H, 14.4; Si−H, 0.98.) identical with an authentic specimen by infrared comparison.

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Novel Ring Expansion and Nitrogen Insertion Reactions of Isatogens[1]

Sir:

We wish to report two types of novel ring expansion and nitrogen insertion reactions of isatogens. Action of tetracyanoethylene[2] on 2-phenylisatogen[3] (Ia) in equimolar proportions in refluxing xylene for 1.5–10 hours produced a black solution from which the known 3,4-dihydro-2-phenyl-4-quinazolinone[4] (IIa) was isolated in 30–39% yield; long white needles (from acetone), m.p. 242.5–243.5°; reported m.p. 235–236°[4]; the mixed melting point with a sample (m.p. 241–243°) prepared by heating anthranilic acid with thiobenzamide[4] was undepressed, 241–243°, and the infrared spectra in Nujol were identical; ν_{NH} 3170m, 3120m, 3060m (CH?, strongest), $\nu_{C=O}$ 1666s, $\nu_{C=N,\ C=C}$ 1605ms cm.$^{-1}$ in Nujol; λ_{max} (95% C_2H_5OH) mμ (log ϵ): 218 (4.38), 237 (4.45), 290 (4.18); 317 infl. (3.98). Our sample of IIa from Ia was also converted[4] by action of phosphorus pentachloride in refluxing phosphorus oxychloride to the known[4] derivative, 4-chloro-2-phenylquinazoline (III); white crystals (after sublimation at 100°/0.5 mm.), m.p. 127.5–128.5°; reported m.p. 124–124.5°[4]; λ_{max} (tetrahydrofuran) mμ (log ϵ): 260 infl. (4.60), 266 (4.64), 286 infl. (4.26), 324 infl. (3.63), 338 infl. (3.46). Hydrogenation at 2 atm. of IIa in methanol over Raney nickel catalyst gave a decahydro derivative in 64% yield; colorless platelets (from methanol–water), m.p. 202–202.5° (sublimes above 150°); ν_{NH} 3310w, 3140w, $\nu_{C=O}$ 1649s, $\nu_{C=C}$ 1607m cm.$^{-1}$ in Nujol; λ_{max} (95% C_2H_5OH) mμ (log ϵ): 230 (3.86), 235 infl. (3.83), 270 (3.82), 315 infl. (2.19).

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[2] R. A. Carboni, *Org. Syntheses*, **39**, 64 (1959).

[3] (a) F. Kröhnke and M. Meyer-Delius, *Chem. Ber.*, **84**, 932 (1951); (b) F. Kröhnke and I. Vogt, *Chem. Ber.*, **85**, 376 (1952).

[4] M. M. Endicott, E. Wick, M. L. Mercury, and M. L. Sherrill, *J. Am. Chem. Soc.*, **68**, 1299 (1946).