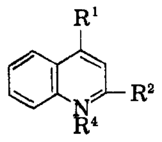
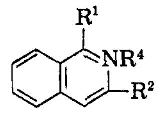


I



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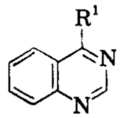
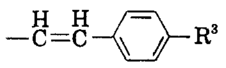


III



Y

	R¹	R²	R³	R⁴
Ia	Y	H	$(CH_3)_2N$—	none
Ib	Y	H	$(CH_3)_2N$—	CH_3I
Ic	H	Y	$(CH_3)_2N$—	none
Id	H	Y	$(CH_3)_2N$—	CH_3I
IIa	Y	H	$(CH_3)_2N$—	none
IIb	Y	H	$(CH_3)_2N$—	CH_3I
IIc	H	Y	$(CH_3)_2N$—	none
IId	H	Y	$(CH_3)_2N$—	CH_3I
IIe	Y	H	$(CH_3CH_2)_2N$—	none
IIf	Y	H	$O(CH_2CH_2)_2N$—	none
III	Y	H	$(CH_3)_2N$—	none

published in detail elsewhere, indicated that the IIa, IIc, IIe and III were all less active than Ia against Lymphoma 8. The methiodides were less active than the corresponding free bases. The presence of the morpholino group, in IIf, in place of the dialkylamino group, reduced toxicity and activity against Lymphoma 8.

EXPERIMENTAL

3-(*p*-Dimethylaminostyryl)isoquinoline (IIc) was obtained readily from its methiodide (IId) by the method of Erlenmeyer, Baumann, and Sorkin[9] although 1-(*p*-dimethylaminostyryl)isoquinoline (IIa) was not so readily obtained from its methiodide (IIb), and 4-(*p*-diethylaminostyryl)-quinoline methiodide (Ib) decomposed to yield an unidentified liquid resembling lepidine in odor.

1-(p-Dimethylaminostyryl)isoquinoline (IIa). A mixture containing 15 g. (0.105 mole) of 1-methylisoquinoline purchased from Sapon Laboratories, 135 g. (0.90 mole) of *p*-dimethylaminobenzaldehyde and 5.3 g. (0.039 mole) of zinc chloride was heated 6 hr. at 200°, cooled somewhat and dissolved in 250 ml. of chloroform. The solution was washed with 150 ml. of 8*N* sodium hydroxide, then with water, and dried over sodium sulfate, and the solvent was removed by evaporation. Excess aldehyde was removed by distillation at an oil bath temperature of 220° and a pressure of 0.5 mm. The residue was dissolved in benzene and some impurities were thrown out by addition of isopropyl ether. The solvent was removed by distillation and the canary yellow product was crystallized four times from ethyl acetate; yield 3.0 g., 10%, m.p. 118°.[10]

Anal. Calcd. for $C_{19}H_{18}N_2$: C, 83.17; H, 6.61. Found: C, 83.06, 82.95; H, 6.60, 6.77.[11]

1-(p-Diethylaminostyryl)isoquinoline (IIe). A mixture containing 10 g. (0.07 mole) of 1-methylisoquinoline, 23 g. (0.13 mole) of *p*-diethylaminobenzaldehyde, and 9.5 g. (0.07 mole) of anhydrous zinc chloride was heated 24 hr. at 115–120°. The mixture was extracted with chloroform. The chloroform solution was washed with 8*N* sodium hydroxide, then with water, and dried over sodium sulfate. Solvent and unreacted benzaldehyde were removed by vacuum distillation and the residue was dissolved in absolute ethanol. Addition of water and chilling several days produced yellow crystals which, after repeated recrystallization from ethanol and from isohexane, melted at 93°; yield 5 g., 24%.

Anal. Calcd. for $C_{21}H_{22}N_2$: C, 83.40; H, 7.33. Found: C, 83.39, 83.25; H, 7.11, 7.31.

1-(p-N-Morpholinostyryl)isoquinoline (IIf). A mixture of 1-methylisoquinoline 18.69 g. (0.131 mole) and 25 g. (0.131 mole) *p*-*N*-morpholinobenzaldehyde[12] was heated 2.5 hours at 270–275°, permitting water vapor to escape.[13] Repeated recrystallizations from ethyl acetate, from isopropyl ether, from isohexane, and from methanol yielded 5.86 g., 14%, 1-(*p*-*N*-morpholinostyryl)isoquinoline, dark yellow crystals, m.p. 149°.

Anal. Calcd. for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.37. Found: C, 79.78, 79.52; H, 6.35, 6.43.

4-(p-Dimethylaminostyryl)quinoline (III). A mixture of 4.3 g. (0.030 mole) of 4-methylquinazoline,[14] 8.6 g. (0.058 mole) of *p*-dimethylaminobenzaldehyde and 2.2 g. (0.016 mole) of zinc chloride was heated 24 hr. at 120° in a glass stoppered bottle. Unreacted aldehyde was removed by extraction with boiling chloroform and the residue was treated with excess concentrated ammonium hydroxide to liberate the free base and dissolve zinc salts. The tarry material and ammonium hydroxide were kept in contact, with occasional stirring, over a period of four days. The residue was washed with water, allowed to dry at room temperature, then ground. The product was extracted with boiling methylpentanes in a Soxhlet extractor and recrystallized twice from methanol to give bright red crystals, m.p. 138°. Yield 12%.

Anal. Calcd. for $C_{18}H_{17}N_3$: C, 78.51; H, 6.22. Found: C, 78.35, 78.58; H, 6.32, 6.20.

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(9) H. Erlenmeyer, H. Baumann, and E. Sorkin, *Helv. Chim. Acta*, **31**, 1978 (1948).

(10) All temperatures recorded are corrected.

(11) Analyses were carried out by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(12) E. I. du Pont de Nemours & Company, British Patent 607,920, Sept. 7, 1948.

(13) R. S. Tipson, *J. Am. Chem. Soc.*, **67**, 507 (1945).

(14) M. T. Bogert and F. P. Nabenhauer, *J. Am. Chem. Soc.*, **46**, 1932 (1924).

Some Tetrasubstituted Silanes Prepared by Free Radical Addition to Alkenes

R. H. MEEN AND HENRY GILMAN

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A recent communication from this laboratory[1] has described the benzoyl peroxide-catalyzed addition of triphenylsilane to long-chain terminal-unsaturated alkenes. We have extended this synthesis to the addition of triphenylsilane to the ethylenic linkages of allyltriphenylsilane and diallyldiphenylsilane. In both cases low yields of completely saturated crystalline compounds were isolated. Unsaturation tests with bromine and with aqueous

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(1) H. Merten and H. Gilman, *J. Am. Chem. Soc.*, **76**, 5798 (1954). This paper gives references to related free radical additions.

permanganate were negative. Although the structures of these products have not been proven we suggest structures based on addition of the triphenylsilyl radical to the terminal carbon atoms.

$$(C_6H_5)_3SiCH_2CH{=}CH_2 + (C_6H_5)_3SiH \xrightarrow{\text{peroxide}} (C_6H_5)_3SiCH_2CH_2Si(C_6H_5)_3$$

This reaction was attempted with triallylphenylsilane and with tetraallylsilane but as yet crystalline products have not been isolated.

It is noteworthy that a much cleaner reaction was obtained with triphenylgermane which added to allyltriphenylsilane in 76% yield.[2]

The compounds diallyldiphenylsilane and triallylphenylsilane were prepared by treatment of the appropriate chlorosilane with allylmagnesium bromide.[3] These reactions proceeded rapidly in refluxing ether solution which is in marked contrast to the sluggish reactions exhibited by most Grignard reagents in comparable reactions.[4]

EXPERIMENTAL[5]

Diallyldiphenylsilane. A solution of 0.448 mole of allylmagnesium bromide[6] in 350 ml. of ethyl ether was added to a solution of 47.2 g. (0.186 mole) of diphenyldichlorosilane in ethyl ether at such a rate that gentle refluxing occurred. A heavy precipitate formed during the addition. When 1.72 equivalents of the Grignard reagent had been added Color Test I[7] was negative, indicating a rapid reaction. The mixture was stirred under reflux for 12 hr. and then hydrolyzed with cold dilute hydrochloric acid. The ether layer was washed with water, dried over sodium sulfate and distilled, finally, at 1.2 mm., giving a main fraction of 25.1 g. (51%), b.p. 128–130°, $n_{\rm D}^{20}$ 1.5753, $d_{\rm D}^{20}$ 0.995.

Anal.[8,9] Calcd. for $C_{26}H_{20}Si$: Si, 10.6; M_D, 87.6. Found: Si, 10.8, 10.8; M_D 87.9.

Triallylphenylsilane. The preceding procedure was used with 0.696 mole of allylmagnesium bromide and 40.9 g. (0.194 mole) of phenyltrichlorosilane giving a main fraction of 33.6 g. (76%), b.p. 90–92° (0.8 mm.) $n_{\rm D}^{20}$, 1.5339, d_4^{20} 0.924.

Anal. Calcd. for $C_{15}H_{10}Si$: Si, 12.3; M_D 76.6. Found: Si, 12.4, 12.4; M_D, 76.9.

1,3-bis(Triphenylsilyl)propane. A mixture of 4.81 g. (0.016 mole) of allyltriphenylsilane,[10] 26.0 g. (0.10 mole) of triphenylsilane, 0.32 g. (0.0013 mole) of benzoyl peroxide, and 25 ml. of hexane was stirred in a 75° bath for 24 hr. Distillation gave a volatile fraction b.p. 110–135° (0.05 mm.) consisting of unchanged triphenylsilane and 0.50 g. (10%) of unchanged allyltriphenylsilane. The residue from the distillation was a viscous liquid. Dilution with a few milliliters of benzene and 50 ml. of absolute ethanol gave 1.1 g. of a solid melting at 123–132°, after several days at 0°. Repeated recrystallizations from benzene–absolute ethanol, *n*-propyl alcohol, and acetone gave 0.09 g. (1%) of crystals melting at 150–152°.

Anal.[11] Calcd. for $C_{39}H_{36}Si_2$: Si, 10.0. Found: Si, 10.2, 10.3.

When this procedure was repeated in a quartz flask at 45° with ultraviolet irradiation in place of the peroxide none of the product could be isolated.

Diphenyl-bis(3-triphenylsilylpropyl)silane. When 2.20 g. (0.0083 mole) of diallyldiphenylsilane was treated with 26.0 g. of triphenylsilane using peroxide catalyst as in the preceding experiment, there was obtained 0.61 g. (9%) of a solid melting at 108–111° after crystallization from *n*-propyl alcohol. Recrystallization from petroleum ether (b.p. 100–120°) gave 0.30 g. (5%) of crystals m.p. 115–117°.

Anal. Calcd. for $C_{54}H_{52}Si_3$: Si, 10.7. Found: Si, 10.7, 10.7.

1-Triphenylsilyl-3-triphenylgermanylpropane. A mixture of 2.40 g. (0.008 mole) of allyltriphenylsilane, 15.3 g. (0.05 mole) of triphenylgermane, 0.16 g. (0.00066 mole) of benzoyl peroxide, and 25 ml. of hexane was stirred at 75° for 24 hr. After distillation of unchanged triphenylgermane at 125–135° (0.05 mm.) there was obtained 5.3 g. of a viscous residue. Dilution with 12 ml. of petroleum ether (b.p. 60–70°) gave 4.52 g. (93%) of crystals that melted at 128–131°. Three recrystallizations from absolute ethanol–benzene gave 3.66 g. (76%) of crystals, m.p. 134–135°.

Anal. Calcd. for $C_{39}H_{36}GeSi$: $GeO_2 + SiO_2$, 27.2. Found: $GeO_2 + SiO_2$, 27.4, 27.4.

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(2) Dr. R. Fuchs has already demonstrated in this laboratory that triphenylgermane adds to octene-1 to give triphenyl-*n*-octylgermane.

(3) A. D. Petrov and V. F. Mironov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 635 (1952) [*Chem. Abstr.*, **47**, 10471 (1953)] have described the preparation of triallylphenylsilane by the simultaneous addition of phenyltrichlorosilane and allyl bromide to magnesium.

(4) See H. Gilman, J. Eisch, and T. Soddy, *J. Am. Chem. Soc.*, **79**, 1245 (1957) for the high reactivity of allylmagnesium types to the azomethine linkage.

(5) All melting and boiling points are uncorrected. All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen.

(6) H. Gilman and J. H. McGlumphy, *Bull. soc. chim. France* [4], **43**, 1322 (1928).

(7) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(8) Molar refractions were calculated from the values of A. D. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

(9) Silicon analyses were performed by the procedure of H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

(10) Prepared from triphenylchlorosilane and allylmagnesium bromide in accordance with directions provided by L. F. Cason and H. G. Brooks, in unpublished studies.

(11) Microdetermination of silicon, H. Gilman and L. S. Miller, *J. Am. Chem. Soc.*, **73**, 968 (1951).

Preparation of Alkylnaphthalenes

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Incidental to the preparation of some organosilicon compounds, 1-*n*-butylnaphthalene was isolated in 40 to 60% yields when 1-naphthyllithium was prepared by halogen-metal interconversion between 1-bromonaphthalene and *n*-butyllithium. This result was not surprising since this type of coupling reaction has been observed frequently.

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