968. *Aromatic Reactivity: Part XVIII.*[1] *Acid Cleavage of Trimethylsilyl Derivatives of Diphenyl Ether, Diphenyl Sulphide, Furan, Thiophen, Benzothiophen, Dibenzofuran, Dibenzothiophen, and 9-Ethylcarbazole.*

By C. Eaborn and J. A. Sperry.

We have prepared the 2- and 4-trimethylsilyl derivatives of diphenyl ether and diphenyl sulphide, the 2-derivatives of furan and thiophen, the 2- and 3-derivatives of benzothiophen, the 1-, 2-, 3-, and 4-derivatives of dibenzofuran and dibenzothiophen, and the 3-derivative of 9-ethylcarbazole, and have measured their rates of cleavage at 50° by a mixture of methanol (5 vol.) and aqueous perchloric acid (2 vol.). The results are analysed and, where possible, compared with those for common electrophilic substitutions in the parent aromatic compounds.

We have prepared some mono-trimethylsilyl derivatives of diphenyl ether, diphenyl sulphide, furan, thiophen, benzothiophen, dibenzofuran, dibenzothiophen, and 9-ethylcarbazole, and have measured spectrophotometrically their rates of cleavage at 50° by mixtures of methanol (5 vol.) and aqueous perchloric acid (2 vol.). The results are shown in the Table as observed first-order rate constants, k, at the (added-)acid concentrations listed, along with rates, k_{rel}, relative to that of phenyltrimethylsilane. The wavelengths, λ, used to study the cleavage are also listed. Not all the compounds were examined at the same acid concentration, and some values of k_{rel} are derived by the "overlap" procedure used before.[2,3]

The value of k_{rel} for the compound x-$Me_3Si{\cdot}Ar$ is referred to below, loosely but conveniently, as the reactivity of the x-position of the aromatic compound ArH in protodesilylation; this facilitates comparison of the results with those for simple electrophilic substitutions, such as halogenation, nitration, and detritiation. In the diagrams below, the reactivities are shown at the appropriate positions of the aromatic systems.

The features of the results are as follows:

(i) The 2- and the 4-position of diphenyl ether are distinctly less reactive in protodesilylation than the corresponding positions of anisole (for which k_{rel} is 1510 for the 4- and 355 for the 2-position [2]). The difference is relatively greater for the 2- than for the 4-position.

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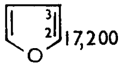
[1] Part XVII, Eaborn and Pande, *J.*, 1961, 3715.
[2] Eaborn, *J.*, 1956, 4858.
[3] Deans and Eaborn, *J.*, 1959, 2299.

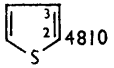
The 2- and the 4-position of diphenyl sulphide are much less reactive than the corresponding positions of diphenyl ether, as would be expected from the smaller $+T$ effect of a sulphur atom than of an oxygen atom.

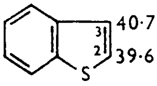
(ii) The 2-position of furan is several times more reactive than the 2-position of thiophen. It seems to be accepted that this is generally the case in electrophilic substitution, but, as far as we are aware, the present results represent the first measurement of the relative reactivities. The lower reactivity of thiophen is another consequence of the smaller $+T$ effect of a sulphur than of an oxygen atom.

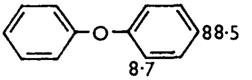
(iii) Fusion of a benzene ring with a thiophen ring, to give benzothiophen, results in a large decrease in reactivity at the 2-position of the thiophen ring and a comparatively small decrease at the 3-position. The large change at the 2-position can be associated with the fact that the $+T$ effect of the sulphur atom can only reach this position in benzothiophen by disturbing the conjugation within the benzene ring, as shown in structure (I) for the Wheland intermediate.[4,5] This is not so for the 3-position [see structure (II)], and the small lowering of reactivity at this position can be attributed to a drawing-off of part of the $+M$ effect of the sulphur atom from the thiophen ring into the benzene ring [cf. process (III)].

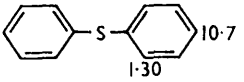
It is noteworthy that the reactivities of the 2- and the 3-position of benzothiophen are nearly equal in protodesilylation. In detritiation, the 3-position is clearly the more reactive, but it is less than 1·5 times as reactive as the 2-position.[6] On nitration only the 3-nitro-product has been isolated,[7] but a recent preliminary communication indicates, more acceptably, that at least 10—15% of 2-substitution also occurs.[8] Friedel–Crafts acylation gives up to 33% of 2- along with predominant 3-substitution,[9] but molecular bromination,[10] chloromethylation,[11] and mercuration [12] seem to result in 3-substitution only.

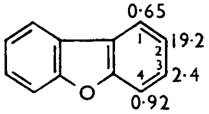


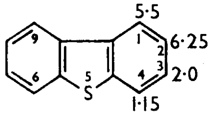


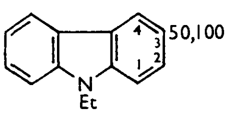












(iv) Closure of the five-membered ring on going from diphenyl ether or diphenyl sulphide to dibenzofuran or dibenzothiophen is associated with a lowering of reactivity at positions *ortho* and *para* to the heteroatom, as has been noted for the oxygen compounds in nitration.[13] In part this may be because the 4- and the 2-position of the dibenzo-compounds, while *ortho* and *para*, respectively, to the heteroatoms, are also *meta* to a substituted phenyl

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[4] Hartough and Meisel, " Heterocyclic Compounds. Compounds with Condensed Thiophene Rings," Interscience Publ. Inc., New York, 1954, p. 5.

[5] Katritzky and Lagowsky, " Heterocyclic Chemistry," Methuen and Co., Ltd., London, 1960, p. 162.

[6] Eaborn and Baker, unpublished results.

[7] Fries and Hemmecke, *Annalen*, 1929, **470**, 1; ref. 4, p. 48.

[8] van Zyl, van Dyke, Heasley, de Jongh, Bredeweg, and Neckers, 4th Report on Research under Sponsorship of Petroleum Research Fund, Amer. Chemical Soc., Washington, 1960, p. 39.

[9] Farrar and Levine, *J. Amer. Chem. Soc.*, 1950, **72**, 4433.

[10] Komppa, *J. prakt. Chem.*, 1929, **122**, 319; Crook and Davies, *J.*, 1937, 1697; Szmuszkovicz and Modest, *J. Amer. Chem. Soc.*, 1950, **72**, 571.

[11] Blicke and Sheets, *J. Amer. Chem. Soc.*, 1948, **70**, 3768.

[12] Challenger and Miller, *J.*, 1939, 1005.

[13] Dewar and Urch, *J.*, 1957, 345; 1958, 3079.

Cleavage of $ArSiMe_3$ compounds at 25°.

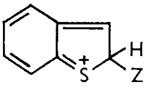
Parent compd. ArH	Posn. of Me_3Si	λ (mμ)	$[HClO_4]$ [a] (M)	10^3k (min.$^{-1}$)	k_{rel}
Benzene	1	270	9·45	1·92	1
	1	270	12·07	7·86	1
Toluene	4	273	9·45	38·3	20·0
	4	273	7·66	14·7	—
Ph_2O	2	285	12·07	68·7	8·73
	4	250	6·05	27·5	—
	4 [b]	250	7·66	65·0	88·5
	4 [b]	250	7·66	65·0	88·5
Ph_2S	2	304	12·07	10·2	1·30
	4	303	9·45	20·5	10·7
Furan	2	231	0·56	42·2	17,200
Thiophen	2	255	0·56	11·8	(4810) [c]
Benzothiophen	2	306	9·45	76·1	39·6
	2	306	6·05	12·5	—
	3	306	9·45	78·1	40·7
Dibenzofuran	1	254	12·07	5·12	0·65
	2	224	9·45	36·9	19·2
	3	255	9·45	4·58	2·39
	3	255	12·07	18·9	2·41
	4	236	12·07	7·26	0·92
Dibenzothiophen	1	291	12·07	43·6	5·53
	2	286	9·45	12·0	6·25
	3	290	12·07	15·7	2·00
	4	291	12·07	9·03	1·15
2,4,6-$C_6H_3Me_3$	1	277	0·20	40·3	53,000 [d]
9-Ethylcarbazole	2	270	0·20	38·1	50,100

[a] Concn. of aqueous acid, 2 ml. of which were added to 5 ml. of a methanolic solution of the organosilane. [b] One sample was made by the Wurtz–Fittig reaction and the other by use of a Grignard reagent. [c] Unpublished result by Miss P. M. Greasley. [d] Value from ref. 2.

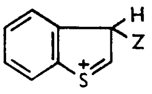
group, which, like the phenyl group itself,[14] probably deactivates *meta*-positions. Mainly, however, it can be attributed to the fact that in the closed-ring compounds the lone-pairs of electrons of oxygen and sulphur are largely engaged in the resonance which gives aromatic character to the five-membered ring, and the $+T$ effects of these atoms can reach the exposed positions of the benzene rings only at the expense of this aromatic character.

It is not clear why the reduction in reactivity should be greater for the oxygen than for the sulphur compounds. The relatively large reduction of reactivity *ortho* to the hetero-atom in the case of the oxygen compounds, and the very small corresponding reduction in the case of the sulphur compounds, result in the 4-position of dibenzofuran's being less reactive than that of dibenzothiophen, although the 2-position of diphenyl ether is several times more reactive than that of diphenyl sulphide. The 2-position of dibenzofuran, however, is several times more reactive than that of dibenzothiophen.

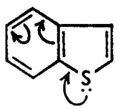
Almost certainly the 3-positions of diphenyl ether and diphenyl sulphide are deactivated in protodesilylation (compare the deactivation by a *m*-OMe group [3]), but the corresponding positions, the 3-positions, in the dibenzo-compounds are clearly activated. This activation can be associated with the phenyl group *para* to the 3-position, electron-release from this group being facilitated by the coplanarity of the two benzene rings (cf. ref. 15).



(I)



(II)



(III)

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[14] Eaborn and Taylor, *J.*, 1961, 1012.

[15] de la Mare and Ridd, "Aromatic Substitution. Nitration and Halogenation," Butterworths Scientific Publ., London, 1959, p. 158.

Halogenation [16,17] and sulphonation [18,19] of dibenzo-furan and -thiophen seem to take place exclusively at the 2-position,* and, since these are reactions of higher selectivity, this is consistent with the protodesilylation results (the reactivity of the 1-position of dibenzothiophen in this reaction being neglected for reasons given below). Nitration of dibenzothiophen, while complicated by oxidation at the sulphur atom, seems to occur wholly or mainly at the 2-position,[16,20] but nitration of dibenzofuran is reported to give, in acetic acid, predominant 3-substitution (up to 80%,[22] we ourselves obtaining 75% of the 3-nitro-compound), or, in acetic anhydride, equal amounts of 2- and 3- along with considerable 1-substitution.[13] It has been suggested that the 3-orientation in dibenzofuran arises from prior protonation of the oxygen atom, which would cause preferential deactivation of 2- and 4-positions,[23] but this would result in overall deactivation of all positions, whereas the partial rate factor for both the 2- and the 3-position in nitration in acetic anhydride is 94. The nitration result is at present inexplicable,† as is the exclusive 4-substitution reported in mercuration.[25]

(v) There is a fairly large difference between the measured reactivity of the 1-position in dibenzofuran and in dibenzothiophen, the former being somewhat deactivated and the latter activated several-fold. At first sight the reactivity of the 1-position of dibenzothiophen might appear much too high, since 1-substitution is not reported in the common electrophilic substitutions. However, protodesilylation is known to be liable to steric acceleration by *ortho*-substituents,[26,27] and the high reactivity of the 2-position of biphenyl in this reaction ($k_{rel} = 6{\cdot}0$) compared with that of the 4-position ($k_{rel} = 2{\cdot}8$) ‡ has been attributed to interference between the 2′-H atom and the 2-Me_3Si group.[27] The relative reactivities of the 1- and the 3-position of dibenzothiophen are in good agreement with the results in biphenyl if it assumed that similar interference occurs between the 1-Me_3Si group and the 9-H atom, and that the sulphur atom affects the 1- and the 3-position which are both *meta* to it, to about the same extent.

It thus seems that it is the low reactivity of the 1-position of dibenzofuran which is anomalous; similar steric acceleration would be expected, and it is difficult to believe that a six-fold deactivation by polar effects exists to compensate for it.

(vi) In the study of 9-ethyl-3-trimethylsilylcarbazole, it was first shown spectrophotometrically that 9-ethylcarbazole was not protonated to a detectable extent even in media much stronger in acid than that used for cleavage, and it can be safety assumed that the trimethylsilyl derivative was also present wholly as free base.

The reactivity of the 3-position (the most reactive position) of 9-ethylcarbazole in protodesilylation is very much greater than that of the corresponding 2-position in dibenzofuran or -thiophen, and accords with the much greater reactivity of the compound

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* The facts are that only the 2-substituted compound was isolated pure in each case. The possibility of formation of other isomers is not excluded by the experimental results. Acetylation of dibenzothiophen almost certainly gives other isomers, but only the 2-acetyl derivative has been isolated in appreciable quantity, along with small amounts of the 4-isomer.[20, 21]

† In a recent theoretical paper, however, the nitration results are considered to be typical and all the other anomalous.[24]

‡ These rate factors refer to measurements in sulphuric acid–acetic acid mixtures,[27] and slightly larger values would be expected in aqueous-methanolic perchloric acid.[3]

[16] Cullinane, Davies, and Davies, *J.*, 1936, 1435.
[17] Mayer and Krieger, *Ber.*, 1922, **55**, 1659.
[18] Gilman, Smith, and Oatfield, *J. Amer. Chem. Soc.*, 1934, **56**, 1412.
[19] Courtot, *Compt. rend.*, 1934, **198**, 2260.
[20] Gilman and Nobis, *J. Amer. Chem. Soc.*, 1949, **71**, 274.
[21] Burger, Wartman, and Lutz, *J. Amer. Chem. Soc.*, 1938, **60**, 2628.
[22] Cullinane, *J.*, 1930, 2267; Gilman, Bywater, and Parker, *J. Amer. Chem. Soc.*, 1935, **57**, 885.
[23] Ref. 4, p. 12.
[24] Brown and Coller, *Austral. J. Chem.*, 1959, **12**, 152.
[25] Gilman and Young, *J. Amer. Chem. Soc.*, 1934, **56**, 1415.
[26] Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1954, **76**, 6353; Benkeser, Hickner, Hoke, and Thomas, *ibid.*, 1958, **80**, 5289; Eaborn and Moore, *J.*, 1959, 3640; Eaborn, Lasocki, and Webster, *J.*, 1959, 3034.
[27] Deans, Eaborn, and Webster, *J.*, 1959, 3031.

p-$Me_2N{\cdot}C_6H_4{\cdot}SiMe_3$ ($k_{rel} = 3 \times 10^7$) than of the compound *p*-$MeO{\cdot}C_6H_4{\cdot}SiMe_3$ ($k_{rel} = 1510$). Since the spread of rates is normally much greater in nitration than in protodesilylation it is surprising that the partial rate factor for the 3-position of carbazole in nitration, *viz.*, 79,000, is not much greater than the value of k_{rel} in protodesilylation (*viz.*, 50,100), the 9-ethyl group being unlikely to have a large effect. If the nitration results are correct, they seem to indicate that polarizability effects are less important relative to polarization effects in the carbazole system than in dibenzo-furan and -thiophen.

EXPERIMENTAL

General.—Ethylene dibromide was used in the entrainment method of making Grignard reagents,[28] and was added during at least 12 hr. to the refluxing mixture of aryl halide, magnesium, and ether.

Coupling of the Grignard reagent with chlorotrimethylsilane was normally followed by treatment of the reaction mixture with saturated ammonium chloride solution, though sometimes a little dilute sulphuric acid had to be added to produce two clear layers. Washing and drying (Na_2SO_4) of the ethereal layer was followed by removal of the solvent through a short fractionating column and fractional distillation of the residue, usually at reduced pressure, through a more efficient column, and by recrystallization where appropriate.

The excess of lithium was removed by filtration from ethereal solutions of organolithium reagents before coupling. Cross-metallation or metallation was carried out with a slight excess of n-butyl-lithium in ether unless otherwise stated. Coupling with chlorotrimethylsilane was followed by addition of 5% aqueous sulphuric acid, and the organic layer was worked up as described above.

Wurtz–Fittig couplings were followed by filtration through kieselguhr and fractionation of the toluene solution.

In all preparations our aim was to obtain pure samples rather than high yields.

x-*Trimethylsilyldiphenyl Ethers.*—2-Lithiodiphenyl ether, prepared [29] from diphenyl ether (70 g., 0·41 mole) in ether (500 ml.), was coupled during 6 hr. under reflux with chlorotrimethylsilane (50 g., 0·46 mole), to give 2-*trimethylsilyldiphenyl ether* (62 g., 62%), b. p. 137—139°/6 mm. n_D^{20} 1·5525 (Found: C, 74·6; H, 7·7. $C_{15}H_{18}OSi$ requires C, 74·4; H, 7·5%).

Boiling 4-chlorodiphenyl ether (56 g., 0·27 mole), chlorotrimethylsilane (32 g., 0·30 mole) and sodium (14 g., 0·6 g.-atom) in toluene (200 ml.) for 2 hr. gave 4-*trimethylsilyldiphenyl ether* (39 g., 59%), b. p. 147—148°/6 mm., n_D^{20} 1·5505 (Found: C, 74·7; H, 7·4%).

An identical product was obtained in 42% yield from coupling of chlorotrimethylsilane with the Grignard reagent prepared from 4-bromodiphenyl ether by the entrainment method.

x-*Trimethylsilyldiphenyl Sulphides.*—Diphenyl sulphide (100 g., 0·54 mole) was metallated in ether (500 ml.). Coupling during 6 hr. under reflux with chlorotrimethylsilane (62 g., 0·58 mole) gave 2-*trimethylsilyldiphenyl sulphide* (32 g., 23%), b. p. 132—136°/2 mm., n_D^{20} 1·5908 (Found: C, 69·9; H, 7·3. $C_{15}H_{18}SSi$ requires C, 69·7; H, 7·0%).

The Grignard reagent prepared by the entrainment method from 4-bromodiphenyl sulphide (38 g., 0·14 mole) in ether (250 ml.) was coupled during 6 hr. under reflux with chlorotrimethylsilane (19·5 g., 0·18 mole), to give 4-*trimethylsilyl sulphide* (22 g., 60%), b. p. 167—168°/3 mm., n_D^{20} 1·5903 (Found: C, 69·9; H, 7·1%). Attempts to make this compound from 4-chlorodiphenyl sulphide, either by Wurtz–Fittig coupling or through the Grignard reagent, led to recovery of unchanged aryl halide.

2-*Trimethylsilylfuran.*—This ether, b. p. 124—125°, n_D^{20} 1·4467, was prepared by Benkeser and Currie's method.[30].

2-*Trimethylsilylthiophen.*—This compound, prepared from 2-thienyl-lithium and chlorotrimethylsilane in ether, had b. p. 165·5°, n_D^{20} 1·4960 (previously misreported [31] as n_D^{20} 1·4996).

x-*Trimethylsilylbenzothiophens.*—A slight excess of n-butyl-lithium in ether was added to a solution of benzothiophen (50 g., 0·37 mole) in tetrahydrofuran (500 ml.) the mixture being kept at −10°. The volume of ether was made up to that of the tetrahydrofuran, and the

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[28] Pearson, Cowan, and Beckler, *J. Org. Chem.*, 1959, **24**, 504.

[29] Gilman and Bebb, *J. Amer. Chem. Soc.*, 1939, **61**, 109.

[30] Benkeser and Currie, *J. Amer. Chem. Soc.*, 1948, **70**, 1780.

[31] Deans and Eaborn, *J.*, 1959, 2303.

mixture was stirred for 2 hr. at room temperature.[32] Coupling during 20 hr. at room temperature with chlorotrimethylsilane (42 g., 0·39 mole) gave 2-*trimethylsilylbenzothiophen* (20 g., 25%), b. p. 123°/7 mm., n_D^{20} 1·5759 (Found: C, 64·3; H, 7·0. $C_{11}H_{14}SSi$ requires C, 64·0; H, 6·8%).

The Grignard reagent prepared by the entrainment method from 3-bromobenzothiophen (81 g., 0·38 mole) in ether (200 ml.) was coupled during 4 hr. under reflux with chlorotrimethylsilane (45 g., 0·41 mole), to give 3-*trimethylsilylbenzothiophen* (39 g., 48%), b. p. 120—122°/7 mm., n_D^{20} 1·5800 (Found: C, 64·1; H, 6·7%).

A similar experiment involving 3-chlorobenzothiophen gave only unchanged aryl chloride.

x-*Trimethylsilyldibenzofurans*.—1-Bromo- was prepared from 4-amino-dibenzofuran by Gilman and Van Ess's method.[33] Cross-metallation (10 min. at 0°) of the bromide (23 g., 0·093 mole) in ether (200 ml.), followed by coupling during 18 hr. at room temperature with chlorotrimethylsilane (12 g., 0·11 mole), gave 1-*trimethylsilyldibenzofuran* (8 g., 36%), b. p. 163—164°/7 mm., n_D^{20} 1·6040 (Found: C, 75·4; H, 6·9. $C_{15}H_{16}OSi$ requires C, 75·0; H, 6·7%).

Contrary to an earlier report,[34] when bromine (160 g., 1 mole) was added to a solution of dibenzofuran (84 g., 0·5 mole) in glacial acetic acid (250 ml.) at 0° no reaction was apparent, but hydrogen bromide was evolved when the mixture was warmed. The temperature was maintained at 50° for 4 hr., and the mixture then added to water. Benzene extraction, followed by removal of the benzene and distillation of the residue, gave 2-bromodibenzofuran (100 g., 80%), m. p. 107—108°. This (50 g., 0·21 mole) was cross-metallated (20 min. under reflux) in ether (200 ml.), and coupling (1 hr. under reflux) with chlorotrimethylsilane (27 g., 0·25 mole) then gave material (24 g., 48%) of m. p. 39—41°. Recrystallization from methanol gave 2-*trimethylsilyldibenzofuran*, m. p. 44° (Found: C, 75·2; H, 6·8%).

A product obtained by Wurtz–Fittig coupling from the 2-bromo-compound could not be satisfactorily purified.

3-Nitro- was converted into 3-amino-dibenzofuran,[35] and from this the 3-bromo-compound, m. p. 120—122°, was prepared by the Sandmeyer reaction. The bromide (45 g., 0·16 mole), chlorotrimethylsilane (19·5 g., 0·18 mole) and sodium (8·5 g., 0·37 g.-atom) in boiling toluene (200 ml.) (2 hr.) gave an oil, b. p. 140—148°/3—4 mm., and recrystallization from methanol gave 3-*trimethylsilyldibenzofuran* (12 g., 27%), m. p. 49° (Found: C, 74·8; H, 6·6%).

Dibenzofuran (35 g., 0·21 mole) was metallated (24 hr. under reflux) in ether (200 ml.). Coupling (4 hr. at room temperature, then 2 hr. under reflux) with chlorotrimethylsilane (26 g., 0·24 mole) gave an oil, b. p. 143—147°/3 mm., which recrystallized from methanol, to give dibenzofuran (10·5 g., 0·063 mole) and 4-*trimethylsilyldibenzofuran* (12 g., 54% based on unrecovered dibenzofuran), m. p. 41° (Found: C, 74·9; H, 6·9%).

x-*Trimethylsilyldibenzothiophens*.—1-Bromo- was prepared from 2-acetamidodibenzothiophen.[36] The bromide (13 g., 0·049 mole) was cross-metallated (15 min. at 0°) in ether (100 ml.); coupling during 2 hr. under reflux with chlorotrimethylsilane (6·5 g., 0·06 mole) gave 1-*trimethylsilyldibenzothiophen* (7 g., 51%), b. p. 160—161°/2—3 mm., n_D^{20} 1·6408 (Found: C, 70·4; H, 6·4. $C_{15}H_{16}SSi$ requires C, 70·3; H, 6·3%) (cf. ref. 37).

The 2-isomer, m. p. 49°, was made in 71% yield by Illuminati, Nobis, and Gilman's method,[38] 10 min. being allowed for cross-metallation.

The 3-isomer, m. p. 104—105°, was made in 64% yield by Illuminati, Nobis, and Gilman's method.[38]

The 4-isomer, b. p. 153°/1 mm., n_D^{20} 1·6342, was made in 45% yield by Gilman and Nobis's method,[39] 19 hr. being allowed for metallation.

9-*Ethyl*-3-*trimethylsilylcarbazole*.—3-Bromo-9-ethylcarbazole (40 g., 0·145 mole) in benzene (300 ml.) was stirred for 3 hr. at room temperature with n-butyl-lithium (0·15 mole) in ether (200 ml.). Coupling during 20 hr. at room temperature with chlorotrimethylsilane (21·5 g., 0·2 mole) gave an oil, b. p. 160—170°/1 mm., which crystallised from methanol to give 9-*ethyl*-3-*trimethylsilylcarbazole* (31 g., 77%) (Found: C, 76·1; H, 8·0. $C_{17}H_{21}NSi$ requires C, 76·35; H, 7·9%).

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Rate Measurements.—Reaction mixtures consisted of 2 ml. of aqueous perchloric acid (of strength shown in the Table) and 5 ml. of a solution of organosilane in methanol (usually 2—10 mg./50 ml.). Rates at 50·00° ± 0·03° were measured as previously described, some " infinite time " values of the optical density being measured on samples kept in sealed tubes.[2,3,27] Rate-constants could be duplicated to within ±1%.

This research was made possible by the support and sponsorship of the U.S. Department of the Army through its European Office. We thank the Royal Society for the loan of apparatus purchased through the Government Grant-in-Aid.

The University, Leicester. [*Received, May* 18*th*, 1961.]