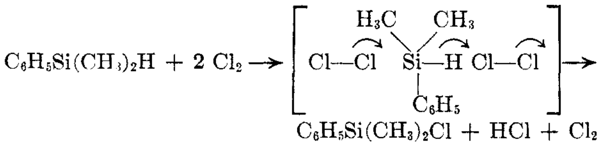
electrophilic attack on hydrogen and nucleophilic attack on silicon.[7]



$$C_6H_5Si(CH_3)_2H + 2\ Cl_2 \rightarrow \left[Cl{-}Cl \quad \overset{H_3C\quad CH_3}{\underset{C_6H_5}{Si}}{-}H \quad Cl{-}Cl \right] \rightarrow C_6H_5Si(CH_3)_2Cl + HCl + Cl_2$$

In both the photochemical and dark reactions of chlorine with phenyldimethylsilane it was observed that only substitution occurred; one mole of hydrogen chloride and one mole of alkyl and silyl chlorides were formed for each mole of chlorine added. This demonstrates that addition of chlorine to the aromatic ring did not occur and that cleavage of the silicon-phenyl bond by chlorine,[8] or by hydrogen chloride,[9] or the cleavage of the silicon-hydrogen bond by hydrogen chloride,[10] did not compete with the cleavage of a silicon-hydrogen bond by chlorine. If any of these reactions had occurred less than one mole of hydrogen chloride would have been formed per mole of alkyl and silyl chlorides.

The fact that the chlorination product formed in the absence of illumination could be quantitatively and easily hydrolyzed indicates that the reaction product was phenyldimethylchlorosilane and that aromatic substitution did not occur. The small amount of unhydrolyzable chloride formed in the photochemical chlorination has thus been attributed to free radical attack on the methyl groups of phenyldimethylsilane.

EXPERIMENTAL

Preparation of phenyldimethylsilane. Phenyldimethylchlorosilane was prepared by Dr. J. R. Ladd by the reaction of methylmagnesium chloride and phenyltrichlorosilane. Material boiling at 85.5° at 21 mm. was reduced by lithium aluminum hydride. To 10 g. of lithium aluminum hydride in 200 ml. of ethyl ether 128 g. of phenyldimethylchlorosilane was added over a three-hour period. The solution was refluxed for three hours before the excess lithium aluminum hydride was destroyed by ethyl acetate. The reaction mixture was poured over ice, the ether layer separated from the aqueous layer, and the aqueous layer extracted twice with 200 ml. of ether. The etheral solution was dried over sodium sulfate and distilled until a pot temperature of 85° was reached. The residue did not give a qualitative test for chlorine. The residue upon distillation through a small packed column (*ca.* 5 plates) under nitrogen gave 99 g. (97%) of phenyldimethylsilane, b.p. 57° at 20 mm., n_D^{20} 1.4988, d_4^{20} 0.876; lit.[11] n_D^{20} 1.4995, d_D^{20} 0.889.

Anal. Calc'd for $C_8H_{12}Si$: C, 70.5; H, 8.8; Si, 20.6. Found: C, 70.5; H, 9.1; Si, 20.6.

The molar refraction, 45.62, was in excellent agreement with the value of 45.73 calculated from the data of Warrick.[12]

Chlorination procedure. The chlorination procedure was similar to that used in the chlorination of cumene.[2] Phenyldimethylsilane was placed in a 200-ml. three-necked flask containing a True-Bore stirrer, a gas inlet capillary tube, and a Dry Ice condenser. The amount of chlorine used was estimated from measurement of the volume of liquid chlorine at −34°. The chlorine from a calibrated tube was allowed to vaporize into a stream of dry nitrogen and after passing through a 500-ml. gas mixing bulb was introduced in the phenyldimethylsilane through the capillary tube. The flask was maintained at 80 ± 1° by a water-bath and was illuminated by a 300-watt bulb approximately 2 inches from the flask. A large excess of nitrogen was used and after passing through the Dry Ice condenser, hydrogen chloride was removed from the nitrogen by a sodium hydroxide trap. Chlorine could not be detected in the exit gases from the chlorination flask. After the desired amount of chlorine had been introduced over a one-hour period, the solution was degassed for several hours with dry nitrogen to remove the last trace of hydrogen chloride. The sodium hydroxide trap was analyzed for chlorine content as was the chlorination product.

The chlorination product was hydrolyzed by shaking with water and the aqueous layer analyzed for chloride ion. Unreacted phenyldimethylsilane had to be completely removed from the aqueous layer since it reduced silver ion. The same amount of chloride ion was found when the hydrolysis was conducted for $^1/_2$, 2, or 24 hours.

Chlorination results. Photochlorination of 0.24 mole of phenyldimethylsilane at 80° with 0.060 ± .006 mole of chlorine yielded 0.0538 mole of hydrogen chloride. The chlorination product contained 0.0539 mole of alkyl and silyl chlorides from which 0.0523 mole of chlorine ion was immediately liberated upon hydrolysis. The remaining 0.0016 mole of chlorine was not ionized by prolonged contact with water. The hydrolyzable chloride is undoubtedly phenyldimethylchlorosilane while the unhydrolyzable chloride is most likely phenyl(chloromethyl)methylsilane.

When the above experiment was repeated in the absence of illumination the amounts of hydrogen chloride, total alkyl and silyl chlorides and hydrolyzable chloride were identical within experimental error. This result indicates that the 0.0016 mole of unhydrolyzable chloride formed in the photochemical reaction is not a product of ionic aromatic substitution, but most likely results from the attack of a chlorine atom on a methyl group of phenyldimethylsilane.

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[7] D. R. Deans and C. Eaborn, *Research*, **5**, 592 (1952); *J. Chem. Soc.*, 3169 (1954).

[8] B. O. Pray, L. H. Sommer, G. M. Goldberg, K. T. Kerr, P. A. Di Giorgio and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 433 (1948).

[9] H. Gilman and F. J. Marshall, *J. Am. Chem. Soc.*, **71**, 2066 (1949).

[10] H. E. Opitz, J. S. Peake, and W. H. Nebergall, *J. Am. Chem. Soc.*, **78**, 292 (1956).

[11] R. A. Benkeser and D. J. Foster, *J. Am. Chem. Soc.*, **74**, 5314 (1952).

[12] E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

Polynitrogen Systems from the Hydrazinocarbonic Acids. Part VII. Some Reactions of 1-Phenyl-5-methylmercaptotetrazole

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In connection with other work, it became of interest to examine some properties of 1-phenyl-5-

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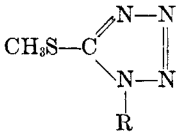
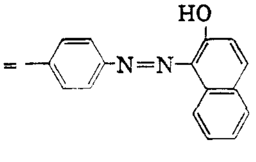
methylmercaptotetrazole (IB). The alkylmercapto group of IB, as with the parent compound IA,[2] was resistant to displacement by ammonia or amines under a variety of conditions.[3,4] Compound IB underwent nitration in a mixture of concentrated nitric and sulfuric acids to give the *p*-nitro derivative (IC). The position of the nitro group was proven by cleavage of IC with hot concentrated hydrochloric acid to yield *p*-nitroaniline. The influence of the tetrazole group[5] in directing substitution to the *para* position of the phenyl ring has been reported earlier, again under strongly acidic conditions, by Garbrecht and Herbst.[6] The nitro group of IC was reduced with aluminum amalgam, and the resulting amino group underwent diazotization in the normal manner. The diazonium compound was allowed to couple with β-naphthol, dimethylaniline, and phenol.

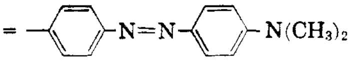


IA, R = H
IB, R = C_6H_5
IC, R = p-NO_2—C_6H_4
ID, R = p-$NH_2C_6H_4$

IE, R=



IF, R=



The reaction of IB with bromine in acetic acid resulted in cleavage of the tetrazole ring. The products isolated were 2,4,6-tribromoaniline and its acetyl derivative.

EXPERIMENTAL[7]

1-Phenyl-5-methylmercaptotetrazole (IB) was prepared by the method of Stolle and Strittmatter[8,9] and was obtained as cream-colored plates of m.p. 80–82° (reported[8] m.p. 80°).

Anal. Calc'd for $C_8H_8N_4S$: N, 29.2; S, 16.6. Found: N, 29.2; S, 16.5.

Attempted displacement of the alkylmercapto group. Only faint traces of desulfurized material were encountered when IB was refluxed with 1 to 3 equivalents of aniline in ethanolic solution for from 3 to 8 hours. A similar stability was displayed towards ammonia, diethylamine, and various arylamines, IB being recovered from such abortive aminolyses in *ca.* 90% yields. Refluxing with diethylamine for 40 hours was analogously unsuccessful, while treatment of IB with this amine in a sealed tube at 110° for a similar time resulted in extensive decomposition, the only product being a black tarry mass.[3]

Nitration of IB. To 10 ml. of concentrated sulfuric acid containing 5.0 g. of 1-phenyl-5-methylmercaptotetrazole was added 6 ml. of concentrated nitric acid, the temperature being maintained at 0° throughout. To the light yellow mixture was added a further 20 ml. of concentrated sulfuric acid, and the resulting liquor then was allowed to stand at room temperature overnight. It was heated on a steam-bath *ca.* 4 hours until nitrous fumes ceased to evolve, and then was poured cautiously onto an excess of crushed ice. It was then either neutralized with sodium hydroxide (which gave greater yields) or extracted with ether (which afforded purer products). The former technique, in the present instance, yielded 5.7 g. (93% yield) of a grey-brown substance, of m.p. 138–144°. After 3 recrystallizations from ethanol, compound IC was obtained as small light-grey needles of m.p. 147–148°.

Anal. Calc'd for $C_8H_7N_5SO_2$: C, 40.5; H, 2.95; N, 29.5; S, 13.5. Found: C, 40.7; H, 3.1; N, 29.4; S, 13.4.

IC could be obtained in the following forms: amorphous, plates, needles or granules, depending on the volume of solvent used in the crystallization and the temperature range, and velocity of cooling utilized.

Orientation of the mononitroderivative (IC). To 50 ml. of concentrated hydrochloric acid were added 2.0 g. of IC. The mixture was refluxed for 3 hours with the addition of a further 20 ml. of acid after 90 minutes. A yellow color developed during the reaction and a strong odor of methyl mercaptan was noted. The solution was cooled to 0°, poured onto ice, and neutralized with 10% sodium hydroxide solution. A yellow amorphous solid separated out (m.p. 140–147°, weight 0.72 g., 62% yield) which after 4 recrystallizations from aqueous ethanol was obtained as yellow needles

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(2) F. L. Scott, D. G. O'Donovan, and J. Reilly, *J. Appl. Chem.*, **2**, 368 (1952).

(3) It is felt that controlled pyrolysis, or acidolysis at elevated temperatures, may offer the best techniques for such dethiolations. Such experiments are under way.

(4) Compare the unreactivity of the 5-methyl group as commented on by C. R. Jacobson, and E. D. Amstutz, *J. Org. Chem.*, **18**, 1183 (1953).

(5) Under the nitration conditions used both in the present work and those of ref. 6, the tetrazole ring is undoubtedly protonated [*cf. e.g.*, A. Hantzsch, *Ber.*, **63**, 1782 (1930)], and the orientation encountered is that of the protonated species. In each case, the nitrated compound is largely the *p*-derivative. Therefore, in both instances, it would seem that protonation occurs at a position in the substituted tetrazole ring other than the 1-position. In our reaction, the 4-position appears a likely alternative [compare P. A. S. Smith, *J. Am. Chem. Soc.*, **76**, 436 (1954)] and in Garbrecht and Herbst's work, positions 5 and/or 4 appear possible as protonation sites. An analogous effect is encountered in the nitration of many other phenyl-substituted polynitrogen heterocyclic compounds and the general effect in many instances appears the same, *viz.* protonation at a site other than that next to the phenyl ring with subsequent *o,p*-nitration in the latter. Compare K. Schofield, *Quart. Revs.*, **4**, 382 (1950).

(6) W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.*, **18**, 1014 (1953).

(7) All melting points are uncorrected. All microanalyses are by Drs. Wieler and Strauss, Oxford, England.

(8) R. Stolle and A. Strittmatter, *J. prakt. Chem.*, **133**, 60 (1932); *vide* R. Stolle and F. Henke-Stark, *J. prakt. Chem.*, **124**, 261 (1930).

(9) The infrared spectra of this, and related substances with their concomitant (sic) anomalies (*e.g.* the apparent absence of azide absorption at 2160–2120 cm.$^{-1}$ in the thiocarbamyl azides we have examined), etc. will be reported on later.

(10) I. Heilbron and H. M. Bunbury, *Dictionary of Organic Compounds*, 4th Edition, Eyre and Spottiswoode, London, 1953; (a) Vol. 3, p. 629; (b) Vol. 4, p. 544.

of m.p. 148°. A mixture m.p. determination with pure *p*-nitroaniline (reported[10a] m.p. 148°), indicated no depression; a mixture m.p. with IC showed the mixture to melt at 103–113°. Thus IC was 5-methylmercapto-1-*p*-nitrophenyltetrazole.

Reduction of IC. To 1.0 g. of IC dissolved in 75 ml. of 90% ethanol was added 1 g. of aluminum foil (which had been amalgamated by immersion for 10 minutes in an aqueous, 6%, solution of mercuric chloride). The mixture was allowed to stand at room temperature for three hours, during which time a slow evolution of gas was detectable. The resulting sludge then was filtered off and on cooling to 0° for 24 hours, the filtrate yielded 0.69 g. (81% yield) of light-brown colored needles of m.p. 156–159°. After 4 recrystallizations from absolute ethanol, the 5-methylmercapto-1-*p*-aminophenyltetrazole (ID) was obtained as cream needles of m.p. 160–161°.

Anal. Calc'd for $C_8H_9N_5S$: C, 46.4; H, 4.3; N, 33.8; S, 15.5. Found: C, 46.9; H, 4.2; N, 33.2; S, 15.3.

Diazotization and coupling of ID. To a suspension of 0.5 g. of ID in 30 ml. of water was added 0.45 ml. of hydrochloric acid. To the well stirred mixture, whose temperature was maintained below 10° throughout, was added, dropwise, a solution of 0.5 g. of sodium nitrite in 5 ml. of water. After a further 10 minutes, during which most of the suspended ID went into solution, *ca.* 1 g. of urea was added to remove excess nitrite. The mixture was stirred, its temperature being still kept below 10°, for a final 15 minutes, then it was filtered and the filtrate was added dropwise to a solution of 0.7 g. of β-naphthol in 30 ml. of *ca.* 0.1 *N* sodium hydroxide solution. Immediate deposition of IE as a deep red solid began. After 2 hours, it was filtered and washed with warm water, dried, and obtained as 0.77 g., 87.5% yield, of material of m.p. 230–232°. This, after recrystallization from chloroform, separated as fine orange-red needles of m.p. 233.5–234.0°.

Anal. Calc'd for $C_{13}H_{14}N_6OS$: C, 59.7; H, 3.9; N, 23.2; S, 8.8. Found: C, 59.9; H, 4.0; N, 22.8; S, 8.8.

The coupling product with N,N-dimethylaniline was formed analogously, except that the amine substrate was dissolved in ethanolic hydrochloric acid solution prior to coupling. The product (IF) was formed in 88% yield and was crystallized as fine red needles, of m.p. 190–191°, from chloroform.

Anal. Calc'd for $C_{16}H_{17}N_7S$: C, 56.6; H, 5.0; N, 28.9; S, 9.4. Found: C, 56.4; H, 4.8; N, 28.8; S, 9.5.

With phenol, an analogous compound was formed in similar yield, m.p. 208–209°.

Anal. Calc'd for $C_{14}H_{12}N_6OS$: C, 53.8; H, 3.8; N, 26.9; S, 10.3. Found: C, 53.2; H, 3.7; N, 27.0; S, 10.3.

Reaction of the above 5-methylmercapto-1-*p*-diazoniumphenyltetrazole salt with benzal guanyl- or phenylhydrazones, or with benzal diaminoguanidine or anisal guanyl hydrazone resulted in failure to isolate a coupling product under a variety of conditions.

Bromination of IB. To a solution of 3 g. of IB in 25 ml. of glacial acetic acid was added 2 ml. of bromine, dissolved in 25 ml. of the same solvent. The addition was effected dropwise and the mixture was continuously agitated. After 60 minutes stirring at room temperature, the mixture was heated, at 100°, for 30 minutes, during which time the odor of methyl mercaptan was noted. On cooling and concentrating in a stream of air, 0.43 g. (9% yield) of an amorphous solid of m.p. 118–120°, was obtained. This on recrystallization from aqueous ethanol was obtained as tiny platelets, m.p. 120–122°, which did not depress the m.p. of authentic 2,4,6-tribromoaniline (reported[10(b)] m.p. 122°).

Anal. Calc'd for $C_6H_4Br_3N$: C, 21.8; H, 1.2; N, 4.2; Br, 72.7. Found: C, 22.6; H, 1.2; N, 4.4: Br, 72.5.

On working up the filtrate a further portion (0.22 g., 4% yield) of this material was obtained, together with 0.51 g., (9% yield) of 2,4,6-tribromoacetanilide which was obtained as white needles m.p. 232° (reported[10(b)] m.p. 232°) which did not depress the m.p. of an authentic sample.

Anal. Calc'd for $C_8H_6Br_3NO$: C, 25.8; H, 1.6; N, 3.8; Br, 64.5. Found: C, 26.3; H, 1.3; N, 4.0; Br, 64.7.

Comparable results were obtained when the bromination was effected in refluxing anhydrous chloroform solution with, or without, magnesium oxide as base.

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The Ultraviolet Absorption Spectra of the Pyridine Analogs of Chalcone

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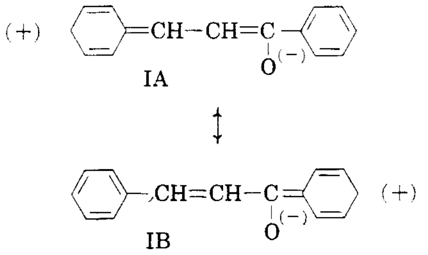
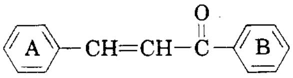
In connection with work on the synthesis of new monomers for free radical polymerization studies, a series of nine pyridine analogs of chalcone were prepared by the base-catalyzed condensation of the appropriate aldehyde and acetophenone or acetylpyridine.[2] The ultraviolet spectra of these *trans*-α,β-unsaturated ketones are of interest since they provide an opportunity for comparison with chalcone and its 2-furyl and 2-thienyl analogs. Szmant and co-workers[3] correlated the absorption spectra of substituted chalcones with the electronic nature of the substituents by considering the whole molecule of the chalcone as one conjugated system. The principal absorption band is assumed to originate from electronic oscillations represented by I.



I

Szmant found from experimental data that in α,β-unsaturated ketones represented by II, electron-attracting groups on ring A cause large hypsochromic shifts, but when present on ring B they tend to give bathochromic effects.



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[1] Present address: Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] Marvel, Coleman, and Scott, *J. Org. Chem.*, **20,** 1785 (1955).

[3] Szmant and Basso, *J. Am. Chem. Soc.*, **74,** 4397 (1952).