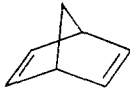


TABLE I
 REACTIONS OF N-CHLORODIALKYLAMINES WITH OLEFINS^a

Entry	Chloroamine ^b	Olefin ^c	Solvent ^d	Products ^e	Yield, %
1	(<i>n</i> -C ₄ H ₉) ₂ NCl	CH ₂ =CHCH=CH ₂	A	R ₂ NCH ₂ CH=CHCH ₂ Cl ^f R ₂ NH	60 9
2			70% aq. H ₂ SO ₄	R ₂ NCH ₂ CH=CHCH ₂ Cl	52
3			B	R ₂ NCH ₂ CH=CHCH ₂ Cl R ₂ NH	30 27
4			4 M H ₂ SO ₄ in nitro- methane	R ₂ NCH ₂ CH=CHCH ₂ Cl R ₂ NH	5 34
5			CCl ₄ / <i>hν</i> , ^g 2 hr.	no reaction	..
6	(<i>n</i> -C ₈ H ₁₇) ₂ NCl		A	R ₂ NCH ₂ CH=CHCH ₂ Cl ^h R ₂ NH	42 22
7	C ₆ H ₅ (CH ₂) ₄ N(Cl)CH ₂		A	R ₂ NCH ₂ CH=CHCH ₃ ⁱ R ₂ NH	53 13
8	(C ₂ H ₅) ₂ NCl		B	R ₂ NCH ₂ CH=CHCH ₂ OAc ^j	24
9	(<i>n</i> -C ₄ H ₉) ₂ NCl	(C ₆ H ₅) ₂ C=CH ₂ ^k	A	(C ₆ H ₅) ₂ C=CHCl R ₂ NH	66 84
10	(C ₂ H ₅) ₂ NCl		A	(VI + VII) ^k (VIII + IX) ^l	31 30

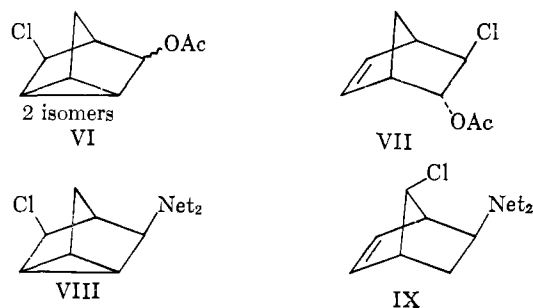
^a Every reaction (under nitrogen) proceeded spontaneously and rapidly (less than 30 min.) in the dark between -5 and +15°. ^b The chloroamines were used as obtained from the reaction between the amine and N-chlorosuccinimide in ether (ref. 3). ^c Added slowly to the chloroamine; all reactions were exothermic and complete on addition of one equivalent of the olefin. ^d Solvent A, 4 M H₂SO₄ and 1.5 M H₂O in acetic acid; solvent B, Eastman White Label trifluoroacetic acid. ^e Up to 10% of the further (ionic) condensation products (R₂NCH₂CH=)₂ were also obtained. ^f B.p. 99° (1.5 mm.), *n*_D²⁰ 1.4600, picrate m.p. 87.5-89.5°, hydrochloride m.p. 95.5-97.5°. ^g In a quartz vessel with irradiation from a Hanovia No 616A medium pressure mercury arc source. ^h B.p. 86° (0.05 mm.), *n*_D²⁰ 1.4600, [R₂NCH₂CH=]₂-dipicrate m.p. 144-145°. ⁱ Obtained by LiAlH₄ reduction of the unusually reactive adduct Vc initially isolated; b.p. 62° (0.02 mm.), *n*_D²⁰ 1.5006. ^j Obtained by acetylation of the trifluoroacetate salt of the corresponding chloro adduct V, cf. text; b.p. 77.5° (1.5 mm.), *n*_D²⁰ 1.4466. ^k B.p. 92.5-93.5° (2 mm.), *n*_D²⁰ 1.4908-1.4917. ^l B.p. 86.5-88° (3 mm.), *n*_D²⁰ 1.4926-1.4940.

avoiding prior isolation of the chloro adduct in a separate, tedious basification step.

In contrast to the free radical addition of Ia to butadiene, only ionic chlorination was observed when this chloroamine was treated under nitrogen with the monoolefin 1,1-diphenylethylene; 1-chloro-2,2-diphenylethylene was isolated in 65% yield (Table I, entry 9). Further evidence of the dual ability, thereby defined, of a chloroamine in strongly acidic media to provide cationic chlorine or to undergo radical addition to a diene was sought when N-chlorodiethylamine was treated with norbornadiene under nitrogen (Table I, entry 10). Approximately equal yields of neutral and of basic products were obtained. The former, isolated by dilution of the reaction mixture with water, consisted mainly (>90%) of 3-acetoxy-5-chloronorbornene (VI) along with a small amount of the isomeric 2-endo-acetoxy-3-exo-chloro-5-norbornene (VII); the latter, liberated on basification of the diluted solution, consisted of 3-chloro-5-diethylaminonorbornene (VIII) and the isomeric *exo*-2-diethylamino-*syn*-7-chloro-5-norbornene (IX) in the approximate ratio VIII/IX = 2/3. The structure of compound IX strongly indicates the basic products to have resulted from an ionic reaction involving the skeletal rearrangements presumably observed previously⁶ in carbonium ion reactions of norbornadiene. When the reaction was carried out in the presence of air, the products VI-IX were obtained in the same yields as under nitrogen, which strongly supports the supposition of an ionic pathway.

Each of the compounds VI-IX was obtained pure by g.l.c. The proof of structure has been unambiguously carried out for each product, principally by thorough n.m.r. analysis; the details of this reaction and characterization of the products will be described in a forthcoming paper.

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The Preparation of Dihalomethyl Derivatives of Carbon, Silicon, and Germanium by the Action of Phenyl-(trihalomethyl)mercurials on C-H, Si-H, and Ge-H Linkages

Sir:

The high reactivity of phenyl(trihalomethyl)mercurials in reactions with olefins of low reactivity toward dihalocarbenes generated by action of bases on trihalomethide ion sources¹ suggested to us that phenyl(trihalomethyl)mercury compounds might release CX₂ to other types of substrates which are known to react with carbenes. The insertion of methylene itself into C-H bonds is well known.² However, only a few isolated cases of dihalocarbene insertion into C-H linkages have been reported,^{3,4} and the yields of insertion products were only low to moderate. The insertion of methylene

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(2) E. Chinopoulos, *Chem. Rev.*, **63**, 235 (1963).

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TABLE I

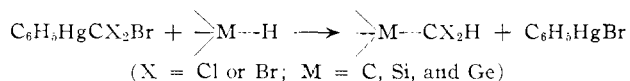
DIHALOMETHYL DERIVATIVES OF CARBON, SILICON, AND GERMANIUM PREPARED BY THE PHENYL(TRIHALOMETHYL)MERCURIAL ROUTE

Reactant	Product ^c (% yield)	B.p., °C. (mm.) or m.p.	δ H of CX ₂ H ^b
(C ₆ H ₅) ₃ SiH ^a	(C ₆ H ₅) ₃ SiCCl ₂ H ^d (90)	M.p. 151-152	6.0 (singlet)
(C ₆ H ₅) ₃ SiH ^a	(C ₆ H ₅) ₃ SiCBr ₂ H ^e (89)	M.p. 154-156	5.72 (singlet)
(C ₂ H ₅) ₃ SiH ^a	(C ₂ H ₅) ₃ SiCCl ₂ H ^d (79)	97-99 (25)	5.44 (singlet)
(C ₆ H ₅) ₂ SiH ₂ ^a	(C ₆ H ₅) ₂ Si(CCl ₂ H)H ^{d,f} (77)	118-119 (0.4)	5.70 (doublet, <i>J</i> = 2.5 c.p.s.)
(C ₆ H ₅) ₂ SiH ₂ ^a	(C ₆ H ₅) ₂ Si(CCl ₂ H) ₂ ^{d,g} (83)	M.p. 100-102	6.08 (singlet)
(C ₆ H ₅) ₃ GeH ^a	(C ₆ H ₅) ₃ GeCCl ₂ H ^d (88)	M.p. 154-155	5.95 (singlet)
C ₆ H ₅ CH ₂ CH ₃ ^b	C ₆ H ₅ CH(CH ₃)(CCl ₂ H) ^d (35)	63-65 (0.8)	5.80 (doublet, <i>J</i> = 5.5 c.p.s.)
C ₆ H ₅ CH(CH ₃) ₂ ^b	C ₆ H ₅ C(CH ₃) ₂ (CCl ₂ H) ^d (58)	83-84 (1.5)	5.97 (singlet)
cyclo-C ₆ H ₁₂ ^b	cyclo-C ₆ H ₁₁ CCl ₂ H ^d (32)	59-60 (3)	5.60 (doublet, <i>J</i> = 4.0 c.p.s.)
C ₆ H ₅ CH ₂ CH ₃ ^b	C ₆ H ₅ CH(CH ₃)(CBr ₂ H) ^e (6.5)	G.l.c. sample	5.88 (doublet, <i>J</i> = 4.5 c.p.s.)

^a Benzene used as a solvent. ^b Excess of substrate used as solvent. ^c All products had satisfactory analyses. ^d From reaction of C₆H₅HgCCl₂Br. ^e From reaction of C₆H₅HgCBr₂. ^f Mercurial to silane ratio used = 1. ^g Mercurial to silane ratio = 3. ^h In p.p.m. downfield from tetramethylsilane (Varian A60 n.m.r. spectrometer).

(via diazomethane) into Si-H bonds was disclosed recently,⁵ but no dichlorocarbene insertions into Si-H containing substrates have been reported to date. In the latter case the Si-H linkage would not survive the strongly basic conditions usually used in generating the dihalocarbene, nor, for that matter, would the product containing the Si-CX₂H unit be expected to be stable in the presence of base.

We report here the insertion of CCl₂ and CBr₂ units into C-H, Si-H, and Ge-H bonds. The general procedure involves heating C₆H₅HgCCl₂Br⁶ or C₆H₅HgCBr₂⁷ with the substrate at ca. 80° until all of the mercurial has been utilized⁸ (ca. 2-4 hr.).



Silanes and triphenylgermane react rapidly with these mercurials to give >Si-CX₂H derivatives and (C₆H₅)₃GeCCl₂H in very good yields (see Table I). An experiment in which 0.03 mole each of cyclohexane and triethylsilane were allowed to compete for 0.01 mole of phenyl(bromodichloromethyl)mercury gave 7,7-dichlorobicyclo[4.1.0]heptane and dichloromethyltriethylsilane in yields of 54 and 40%, respectively, a finding which demonstrates the high reactivity of the Si-H linkage toward such mercurials. A similar competition reaction between the less reactive triethylvinylsilane and triethylsilane resulted in the exclusive formation of dichloromethyltriethylsilane; no 1,1-dichloro-2-triethylsilylcyclopropane⁹ could be detected.

Product yields in analogous insertions into C-H bonds were not as high, but still were considerably better than those reported for the sodium trichloroacetate-derived dichlorocarbene insertions by Fields.³ When ethylbenzene or cumene was heated to 85° with C₆H₅HgCCl₂Br an exothermic reaction commenced. Work-up of these reaction mixtures gave β,β-dichloroisopropylbenzene (35%) and β,β-dichloro-*t*-butylbenzene (58%), respectively. Yields of these products using the sodium trichloroacetate procedure were 17 and 33%, respectively. While such insertions into benzylic C-H bonds are not too surprising, the reaction of C₆H₅HgCCl₂Br with an excess of cyclohexane at reflux for 2.5 hr., which gives dichloromethylcyclohexane in 32% yield, is noteworthy. Two other major products were encountered in this reaction: tetrachloroethylene

(26%) and cyclohexyl bromide (22%). The former compound results in high yield in the controlled thermal decomposition of C₆H₅HgCCl₂Br in the absence of a reactive substrate. The latter may provide a clue to the mechanism of the insertion into C-H bonds, and this question will be the subject of further investigation.

The insertion reaction of C₆H₅HgCX₂Br compounds (X = Cl and Br) has valuable, and in some cases, unique, preparative utility, and the full scope of this reaction, in particular with regard to application to other metal- and metalloid-hydrogen insertions, is under active investigation. Experiments relating to the mechanism of these reactions are in progress. Further details concerning these and related experiments will be given at a later date. Pertinent data concerning the products mentioned above are given in Table I.

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 RECEIVED JUNE 28, 1963

Chemical Applications of Sensitivity Enhancement in Nuclear Magnetic Resonance and Electron Spin Resonance¹

Sir:

It has long been known that the effective sensitivity of a measurement being taken in a noise background can be enhanced by extending the measuring period. If the noise background is gaussian random and the integration period is *T*, the signal-to-noise improvement is proportional to \sqrt{T} . The increasing precision and stability of modern spectrometers makes it possible and worthwhile to exploit this potential sensitivity enhancement to a greater extent than is current chemical practice. It is completely practical to raise the sensitivity of existing spectrometers by a factor of 2 to 50. A sensitivity increase of 10 for the CH₂ and CH₃ n.m.r. peaks of 0.2% ethylbenzene in CCl₄ is shown in Fig. 1. There are now several combinations of commercially available electronic units that may be easily applied to achieve sensitivity enhancement by time integration at prices that are roughly 10-40% the cost of magnetic resonance spectrometers.

This situation provides opportunity for a great variety of chemical applications. As an analytical

(1) Supported in part by a grant from the Petroleum Research Fund of the American Chemical Society.

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(8) Thin layer chromatography serves excellently in following the course of these reactions.

(9) Prepared by the reaction of C₆H₅HgCCl₂Br with triethylvinylsilane in a separate experiment; b.p. 54-56° at 0.8 mm.; *n*_D²⁰ 1.4735.