TABLE I

CARBONYL STRETCHING FREQUENCIES FOR SOME LOWER METAL CARBONYLS

| Normal carbonyl | Observed frequencies upon irradiation in 1:4 isopentane-methylcyclohexane glass | Assignments |
|---|---|---|
| $W(CO)_6$ | 2092 (w), 1952 (s), 1924 (m) | as $W(CO)_5$, $C_{4v}$ symmetry |
| $Mo(CO)_6$ | 2093 (w), 1960 (s), 1922 (m) | as $Mo(CO)_5$, $C_{4v}$ symmetry |
| $Mo(CO)_6$ | 2007 (s), 1995 (s) | as $Mo(CO)_5$, $D_{3h}$ symmetry |
| $Cr(CO)_6$, | 2088 (w), 1955 (s), 1928 (m) | as $Cr(CO)_5$, $C_{4v}$ symmetry |
| $Fe(CO)_5$ | 1990 (s), 1980 (w), 1946 (s) | |

Band intensities: w = weak, m = medium, s = strong.

more CO groups by ligands such as ethers, nitriles and olefins. Further work, utilizing improved equipment, has led to significant information concerning a transition between structures for such species. We also have obtained evidence for the photoproduction of two new species, $Mo(CO)_5$ and $Cr(CO)_5$.

Carefully purified 1:4 isopentane–methylcyclohexane solutions 0.01 $M$ in the normal hexacarbonyl ($Cr(CO)_6$, $Mo(CO)_6$ or $W(CO)_6$) were cooled under an inert atmosphere with liquid nitrogen in an infrared cold cell with NaCl windows. Through use of this cell it was possible to irradiate the metal carbonyl-containing glasses and to record their spectra for the carbonyl-stretching region of the infrared (2200–1700 cm.$^{-1}$) at $-180°$. The cell temperature was measured through use of an iron–constantan thermocouple. The spectrum of the irradiated $Mo(CO)_6$ glass was also recorded as the glass was slowly warmed to the fluid state. Results are shown in Table I.

The spectra obtained in frozen glasses for the carbonyl-stretching region of the infrared for these group VI lower carbonyls are consistent as to number, position and intensity of bands to those predicted by group theoretical considerations for pentacoördination of $C_{4v}$ symmetry.[5] The bands observed for $W(CO)_5$ were at slightly higher frequencies than were those reported in the earlier communication.[1]

We have been able to discount the possibility that these lower carbonyl complexes may actually involve the replacement of a carbonyl group by a dissolved gas or solvent molecule. A sample of $W(CO)_6$ was sublimed under high vacuum onto a cold-finger and was exposed to ultraviolet radiation at $-196°$. A yellow-brown product was produced. After the irradiation was stopped, this product was treated in vacuo with acetonitrile to yield $W(CO)_5(CH_3CN)$.

As the glass containing $Mo(CO)_5$ was warmed to the fluid state there occurred a rapid conversion from the three carbonyl bands characteristic of the square pyramidal carbonyl configuration to two bands of approximately equal intensity (Table I). The glass softens at between $-165°$ and $-160°$, while this transition occurs at about $-155°$. The latter spectrum is consistent with $D_{3h}$ symmetry and is quite similar[6] to that of $Fe(CO)_5$, which has been proven[7] to be trigonal bipyramidal. We suppose that in the glass the $Mo(CO)_5$ molecule is unable to assume the more expected trigonal bipyramidal configuration. Evidence for the restriction of molecular motion in the glass which could enable the $Mo(CO)_5$ molecule to retain $C_{4v}$ symmetry in preference to $D_{3h}$ comes from the similarity of position and shape between the stretching band due to trapped CO in our work and that reported by Ball[8] for clathrate complexes in which the presence of the CO Q branch indicates that the CO molecules are unable to rotate freely in the cage. For these clathrate complexes the

CO band is reported at 2133 cm.$^{-1}$, while we observe the free CO stretch at 2135 cm.$^{-1}$. These characteristic CO stretching bands are observed for each lower carbonyl produced, and disappear as the carbonyl reverts substantially (about 70%) to its parent.

We also have observed, in similar experiments with $Fe(CO)_5$, three bands (Table I) which we believe to be the carbonyl stretching frequencies of an intermediate iron carbonyl species. Work on this aspect of the problem is continuing.

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## A RADIATION-INDUCED PREPARATION OF TROPYLIUM BROMIDE[1]

*Sir:*

Our interest in the significance of ionic reactions in radiation chemistry led us to explore a direct radiation-induced route to the formation of the ionic salt, tropylium bromide. One of the most useful preparative methods involves the primary generation of a carbonium ion which subsequently reacts with cycloheptatriene by hydride ion transfer. Thus triphenylmethyl bromide and cycloheptatriene react in a strong ionizing solvent such as liquid sulfur dioxide,[2] and Friedel–Crafts catalysts are also known to promote the formation of the tropylium ion by a similar mechanism.[3] We reasoned that if ionizing radiation produces the $t$-butyl carbonium ion from the fragmentation of the $t$-butyl bromide parent ion,[4] a way would then be open for the preparation of tropylium bromide without the agency of ionizing solvent or added catalyst; this prospect seemed

$$t\text{-}C_4H_9Br^- \longrightarrow t\text{-}C_4H_9^- + Br\cdot$$

$$t\text{-}C_4H_9^+ + C_7H_8 \longrightarrow iso\text{-}C_4H_{10} + C_7H_7^+$$
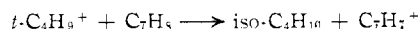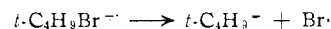
all the more inviting in view of recurring evidence[5] that alkyl bromides undergo dissociative electron capture, even in the liquid state.

$$RBr + e^- \longrightarrow R\cdot + Br^-$$
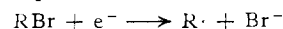
As envisaged, a tropylium cation and a bromide anion would be formed upon the radiolysis of $t$-butyl bromide containing cycloheptatriene; it is the purpose of this Communication to report that tropylium bromide is indeed produced under these conditions.

(1) This research is supported by A.E.C. Contract No. AT-(40-1)-2968.

(2) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson. *J. Am. Chem. Soc.*, **79**, 4557 (1957).

(3) K. M. Harmon and A. B. Harmon, *ibid.*, **83**, 865 (1961), and references therein.

(4) Our initial choice of $t$-butyl bromide was dictated by the ease of formation of branched carbonium ions from the dissociation of excited parent molecule-ions as revealed by mass spectra. This point, and its relevance to liquid phase studies, is discussed in some detail elsewhere; cf. Williams, *Trans. Faraday Soc.*, **57**, 755 (1961), and *Quart. Rev.*, in press.

(5) W. Van Dusen, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 3648 (1962), and references therein.

(5) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(6) The CO stretching frequencies for $Fe(CO)_5$ are found at 2023 (s) and 1997 (s) cm.$^{-1}$.

(7) A. W. Hanson, *Acta Cryst.*, **15**, 930 (1962).

(8) D. F. Ball and D. C. McKean, *Spectrochim. Acta*, **18**, 933 (1962).

Mixtures containing varying proportions of *t*-butyl bromide and cycloheptatriene[6] were prepared in sealed tubes by conventional vacuum technique; both reagents were dried rigorously by passage down silica gel columns into the vacuum apparatus. After irradiation at ambient temperature in a cobalt-60 gamma source[7] to doses in the range from $1.0 \times 10^{21}$ to $7.0 \times 10^{21}$ e.v. g.$^{-1}$, those mixtures containing *t*-butyl bromide in excess of a 1:1 mole ratio were found to have solid material deposited in the tube; the liquid was decanted and a yellow solid isolated quantitatively by washing and centrifuging with dry ether. Recrystallization from dry ethanol gave a bright yellow solid (*Anal.* Calcd. for $C_7H_7Br$: C, 49.16; H, 4.13; Br, 46.72. Found: C, 49.02; H, 4.05; Br, 47.03) with m.p. 202°, which dissolved immediately in water and formed a precipitate of silver bromide with aqueous silver nitrate.[8] Conclusive identification of the product was afforded by its infrared spectrum in a KBr disk (absorption bands at 6.75 μ (very strong); 3.3 μ (s), 14.7 μ (s); 3.2 μ (m), 3.45 μ (m), 6.1 μ (m), 7.9 μ (m), 8.2 μ (m), 9.55 μ (m)), its ultraviolet spectrum in 96% sulfuric acid ($\lambda_{min}$ 244 mμ, $\lambda_{max}$ 216 mμ, 273.5 mμ, 279.5 mμ), and its ultraviolet and visible spectrum in methylene chloride ($\lambda_{min}$ 253 mμ, $\lambda_{max}$ 276 mμ, 400 mμ), which agreed with published information on tropylium bromide.[3,8,9]

The *G*-value (molecules per 100 e.v.) for the formation of tropylium bromide is greatest at high ratios of *t*-butyl bromide to cycloheptatriene; when this initial mole ratio was held at 10:1, the *G*-values for $C_7H_7^+$-$Br^-$ formation in separate experiments were determined to be 1.34, 1.43, 1.58 and 1.59 for total irradiation doses in the range from $1.5 \times 10^{21}$ e.v. g.$^{-1}$ to $3.6 \times 10^{21}$ e.v. g.$^{-1}$. Expressed as mole % yield, we have obtained up to *ca.* 25% conversion of the initial cycloheptatriene in the mixture. There is no reason why the irradiations could not be carried through to even higher mole % yields, but the onset of progressive secondary decomposition of solid tropylium bromide by the gamma radiation makes prolonged irradiation somewhat unrewarding in terms of the purity of the product.

Examination of the mother liquor by vapor phase chromatography (v.p.c.) revealed that two major volatile components had been formed whose retention times coincided with those for isobutane and isobutene. An infrared spectrum of this volatile fraction taken in a gas cell was partly masked by the spectrum of some accompanying *t*-butyl bromide,[10] but the differential spectrum before and after pumping off the more volatile components revealed sufficient detail[11] to be in accord with the v.p.c. assignments. The yield of isobutane has consistently exceeded that of isobutene by a factor of five to six, and *G* (isobutane) was found to be 2.3 when *G* ($C_7H_7^+Br^-$) was 1.59 for the same mixture. Bearing in mind that no isobutane has been reported in the radiolysis of *t*-butyl bromide alone,[12] it is clear that the formation of tropylium bromide and isobutane in about comparable yields is consistent with our projected ionic mechanism. However, it is also pertinent

to consider whether the products may not arise through free-radical reactions. If a homolytic mechanism applies, it must account for the formation of $C_7H_7Br$ from $C_7H_7\cdot$, where the latter is assumed to be the product of hydrogen atom abstraction from $C_7H_8$.[13] Now, the only reactions which seem thermochemically feasible are the following[14]:

$$C_7H_7\cdot + Br\cdot \longrightarrow C_7H_7Br$$
$$C_7H_7\cdot + Br_2 \longrightarrow C_7H_7Br + Br\cdot$$
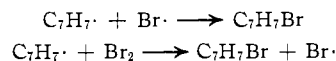
Since the latter reaction depends upon the prior dimerization of bromine atoms, both of these processes would depend on the ability of bromine atoms to remain unscavenged by species other than $C_7H_7\cdot$. However, the reaction

$$Br\cdot + C_7H_8 \longrightarrow HBr + C_7H_7\cdot$$
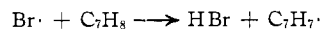
is highly exothermic by virtue of the greater bond dissociation energy of HBr (88 kcal./mole)[15] relative to $C_7H_7$-H (*ca.* 53 kcal./mole).[16] Indeed, the analogous reaction in which triphenylmethane functions as the "active hydrogen" donor has been used to convert bromine atoms to HBr in radiolysis studies.[5] In our system, we would expect some addition of bromine atoms to the cycloheptatriene as well, and the sum of these effects must surely be to allow few bromine atoms to react with cycloheptatrienyl radicals.[17] On the other hand, no problem is posed in going from $C_7H_7^+$ to $C_7H_7^+Br^-$ by ionic combination, for it is hard to envisage $Br^-$ undergoing a competitive reaction.

Our observation that only very low yields of tropylium bromide obtain when cycloheptatriene is present in excess is also difficult to reconcile with a radical mechanism, for it is probable that $C_7H_7\cdot$ radicals are produced directly by energy deposition in cycloheptatriene.[18] Instead, we submit that our finding lends support to the prior suggestion that the reaction involves indirect action on cycloheptatriene, and also conforms to the expectation that an ionic reaction should be sensitive to the dielectric constant of the system.

Further studies have established that $C_7H_7^+Br^-$ is also formed in comparable yields when 10 mole % solutions of cycloheptatriene in isopropyl bromide, and in isobutyl bromide, are irradiated with gamma rays; in each case, the corresponding alkane is also a

(6) This material was generously supplied by the Shell Chemical Company. It was decolorized by passage over alumina, and distilled under nitrogen immediately before use; analysis of the distillate revealed less than 5% toluene as the major impurity.

(7) We thank Dr. Hochanadel for the use of this facility at the Oak Ridge National Laboratory.

(8) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

(9) K. M. Harmon, F. E. Cummings, D. A. Davis and D. J. Diestler, *ibid.*, **84**, 3349 (1962).

(10) W. Zeil, H. Buchert, H. Heel and H. Pförtner, *Z. Elektrochem.*, **64**, 769 (1960).

(11) Comparison with A. P. I. Catalog of Infrared Spectra, No. 439 and 378.

(12) W. S. Wilcox, *Radiation Res.*, **10**, 112 (1959).

(13) Evidence is lacking on this point, and we would expect the occurrence of some addition of *t*-$C_4H_9\cdot$ to the triene. A referee has suggested that *t*-butylcycloheptatriene may be formed in this system. We intend to look for this possible product.

(14) Alternate possibilities involving the reactions of $C_7H_7\cdot$ with HBr and *t*-$C_4H_9$Br are endothermic. Moreover, the formation of H· and *t*-$C_4H_9\cdot$, respectively, would set up a chain, and this is obviated by the magnitude of the *G*-values.

(15) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 670.

(16) We estimate D ($C_7H_7$-H) as that of a "normal" C–H bond dissociation energy (*ca.* 94 kcal./mole) less the difference in stabilization energy between $C_7H_7\cdot$ [J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952), calculate the delocalization energy of $C_7H_7\cdot$ to be 2.54 β or *ca.* 50 kcal./mole, taking β (resonance integral) to be 20 kcal./mole] and that of $C_7H_8$ [R. B. Turner in "Theoretical Organic Chemistry," Butterworths, London, 1959, p. 71, gives the stabilization energy of cycloheptatriene as 9.0 kcal./mole].

(17) The referees have disclosed to us that tropylium bromide is formed by the homolytic bromination of cycloheptatriene through the use of N-bromosuccinimide (NBS) (H. J. Dauben, Jr., and D. L. Pearson, Abstracts, 126th National Meeting, American Chemical Society, New York, N. Y., 1954; D. L. Pearson, Ph. D. thesis, University of Washington, 1955, *Dissertation Abstr.*, **15**, 978 (1955)). A failure to obtain tropylium bromide in this manner (H. L. Dryden, Jr., and B. E. Burgert, *J. Am. Chem. Soc.*, **77**, 5633 (1955)) is attributed to the subsequent reaction of tropylium bromide with NBS. A referee also points out, and we concur, that the occurrence of homolytic bromination by means of NBS is impertinent to this Communication. In the generally accepted mechanism of NBS bromination (C. Walling "Free Radicals in Solution," Wiley, New York, 1957, p. 381), the allylic radical abstracts a bromine atom from NBS, but it is clear from our discussion that no parallel step is available in the present system.

(18) G. Juppe and A. P. Wolf, *J. Am. Chem. Soc.*, **83**, 337 (1961), found bitropyl as a product from the radiolysis of cycloheptatriene alone.

major product. Our work is continuing in order to define the scope of this reaction, and to assess the implications for the mechanisms of other radiation-induced reactions in organic media.

**Acknowledgment.**—We thank Professors W. H. Fletcher and A. D. Melaven for the use of spectroscopic apparatus.

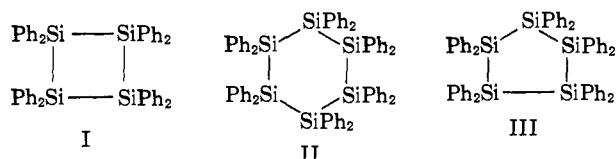DEPARTMENT OF CHEMISTRY      DONALD H. MARTIN
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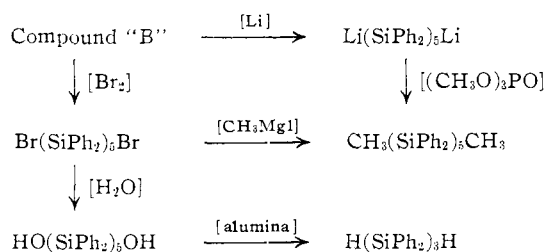RECEIVED JANUARY 11, 1963

## DECAPHENYLCYCLOPENTASILANE

*Sir:*

The reaction of dichlorodiphenylsilane with sodium[1,2] or lithium[2b,3] produces several perphenylated cyclosilanes. One of them, designated Compound "B" by Kipping,[1a] was first proposed to be octaphenylcyclotetrasilane (I)[1a,b]; and, more recently, to be dodecaphenylcyclohexasilane (II).[3] Both of these proposals were based on molecular weight determinations; the

$$Ph_2Si-SiPh_2$$
$$|\qquad\quad|$$
$$Ph_2Si-SiPh_2$$
$$I$$

(structure II)

$$Ph_2Si-SiPh_2$$
$$|\qquad\quad|$$
$$Ph_2Si-SiPh_2$$
$$III$$

former on values determined cryoscopically in benzene and camphor[1a,b] and the latter on values determined cryoscopically in perylene.[3] It now has been shown that both proposals were in error and that Compound "B" is decaphenylcyclopentasilane (III). Derivatives of this compound, which had previously been designated as hexasilanes,[3,4] are in fact 1,5-disubstituted-decaphenylpentasilanes.

Chemical proof for the structure of decaphenylcyclopentasilane has been obtained by two different means starting with decaphenylcyclopentasilane. In a recent publication,[5] it has been shown that the $\alpha,\omega$-dihydroxy derivative of Compound "B" (decaphenylcyclopentasilane), when chromatographed on basic alumina, provides 1,1,2,2,3,3-hexaphenyltrisilane. This reaction indicates that the dihydroxy compound was a pentasilane and that Compound "B" is the cyclopentasilane.

Compound "B" $\xrightarrow{[Li]}$ Li(SiPh$_2$)$_5$Li

$\downarrow$ [Br$_2$]             $\downarrow$ [(CH$_3$O)$_3$PO]

Br(SiPh$_2$)$_5$Br $\xrightarrow{[CH_3MgI]}$ CH$_3$(SiPh$_2$)$_5$CH$_3$

$\downarrow$ [H$_2$O]

HO(SiPh$_2$)$_5$OH $\xrightarrow{[alumina]}$ H(SiPh$_2$)$_3$H

The lithium cleavage products of Compound "B" were examined to throw more light on the structure of the cyclic polysilane. It was found that when the cyclosilane was allowed to react with lithium in tetrahydrofuran for 2 hr., the cleavage was essentially com-

plete. Formation of derivatives, using trimethyl or tri-*n*-butyl phosphate[6] or chlorotrimethylsilane, led to derivatives of the corresponding 1,5-disubstituted compounds, in yields approaching 83%. The constitutions of these compounds were established by elemental analysis and by proton magnetic resonance spectra determinations to obtain aliphatic to aromatic hydrogen atom ratios. 1,5-Dimethyldecaphenylpentasilane was also obtained in high yield from the reaction of methylmagnesium iodide with 1,5-dibromodecaphenylpentasilane.

Molecular weight determinations have been obtained for decaphenylcyclopentasilane (molecular weight 911) by three different methods which gave consistent results. Ebullioscopic determinations in toluene[7] using octaphenylcyclotetrasilane as a standard gave a value of 921 ± 7 (four determinations). An X-ray diffraction study and density determination of decaphenylcyclopentasilane, crystallized from benzene–ethanol, provided a value of 983, in good agreement with a value of 989 calculated for decaphenylcyclopentasilane plus one molecule of benzene, which was subsequently shown to be present. The molecular weight was also determined in benzene using a "vapor phase osmometer"[8] at several concentrations. Extrapolation to zero concentration gave a value of 912, in excellent agreement with the theoretical value of 911 for decaphenylcyclopentasilane.

Experimental details for the reactions and data presented here and for other polysilanes derived from decaphenylcyclopentasilane will be forthcoming.

**Acknowledgments.**—The authors wish to express their gratitude to Drs. C. A. Glover, H. W. Patton and W. D. Kennedy, of the Tennessee Eastman Co., for the ebullioscopic and X-ray determinations. This research was supported in part by the United States Air Force under Contract AF 33(616)-6463 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

(6) H. Gilman and B. J. Gaj, *ibid.*, **26**, 247 (1961).

(7) C. A. Glover and R. R. Stanley, *Anal. Chem.*, **33**, 447 (1961).

(8) Mechrolab, Inc., Mountain View, Calif.

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RECEIVED JANUARY 28, 1963

## THE REDUCTIONS OF *cis*- AND *trans*--Co(NH$_3$)$_4$(N$_3$)$_2$$^+$ AND Co(NH$_3$)$_5$N$_3$$^{+-}$ BY Fe$^{++}$

*Sir:*

We have measured spectrophotometrically the rates of reduction of *cis*- and *trans*-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$ and Co(NH$_3$)$_5$N$_3$$^{++}$ by Fe$^{++}$ in aqueous perchlorate solutions (no other anions present) at 25°. The results, summarized in Table I, show that the reduction of the *cis* complex is acid-independent for (H$^+$) varying from 0.072 to 0.219 $M$, whereas that of the *trans* complex is, under the same conditions, strongly acid-dependent. The rate laws (time in minutes) are given by the equations 11.1(Fe$^{++}$) (*cis*-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$) and [4.4 + 82 (H$^+$)](Fe$^{++}$) (*trans*-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$). The reduction of Co(NH$_3$)$_5$N$_3$$^{++}$ is acid-independent and obeys the rate law 0.52(Fe$^{++}$)(Co(NH$_3$)$_5$N$_3$$^{++}$).

Because of the substitution–lability of Fe(III), it cannot be ascertained whether these reactions proceed *via* a bridged or outer-sphere activated complex.[1] However, assuming that bridged activated complexes are operative, reasonable explanations can be advanced for the present observations.

(1) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

(1) (a) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830 (1921); (b) F. S. Kipping, *ibid.*, **123**, 2590 (1923); (c) **125**, 2291 (1924); (d) 2719 (1927).

(2) (a) H. Gilman, D. J. Peterson, A. W. Jarvie and H. J. S. Winkler, *J. Am. Chem. Soc.*, **82**, 2076 (1960); (b) A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson and H. Gilman, *ibid.*, **83**, 1921 (1961).

(3) (a) H. Gilman, D. J. Peterson, A. W. Jarvie and H. J. S. Winkler, *Tetrahedron Letters*, **23**, 5 (1960); (b) H. J. S. Winkler, A. W. P. Jarvie, D. J. Peterson and H. Gilman, *J. Am. Chem. Soc.*, **83**, 4089 (1961).

(4) (a) A. W. P. Jarvie and H. Gilman, *Chem. Ind.* (London), 1271 (1960); (b) A. W. P. Jarvie, H. J. S. Winkler and H. Gilman, *J. Org. Chem.*, **27**, 614 (1962); (c) H. J. S. Winkler and H. Gilman, *ibid.*, **27**, 254 (1962).

(5) G. R. Chainani, S. Cooper and H. Gilman, *ibid.*, in press.