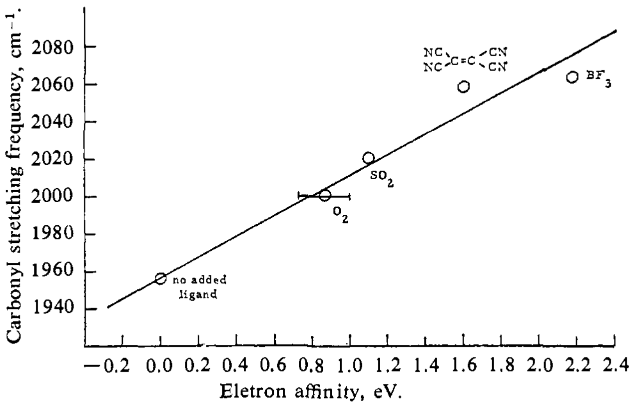

Figure 1. Carbonyl stretching frequencies of $[IrCOCl(PPh_3)_2]$ and its adducts *vs.* electron affinity of added ligand. Except for the BF_3 adduct all infrared data are taken from the literature.[10,12] The molecular electron affinities for O_2, SO_2, and BF_3 are those reported by V. I. Vedeneyev, *et al.*, "Bond Energies, Ionization Potentials and Electron Affinities," Arnold, London, 1966. For TCNE the value is from G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

$[IrClCO(P(C_6H_5)_3)_2]$ and its bis(boron trifluoride) adduct.[7] However, formation of the 1:1 complex in solution is clearly indicated by titrations in which composition of the benzene solution is monitored by infrared or near-ultraviolet spectroscopy. At a composition of $1.2BF_3$:1Ir complex the 1968-cm^{-1} band of the parent complex has disappeared and a single new CO stretching frequency has taken its place at 2067 cm^{-1}. When the reaction is followed under experimentally more favorable conditions (dilute solution at 387 mμ), the mole ratio at the end point is much closer to 1:1 ($1BF_3$ per 1.021). The molecular weight of the 1:1 adduct, as indicated by cryoscopy in benzene solution, is 900 *vs.* the formula weight of 848. Thus, although a 1:1 complex is formed in solution, it appears to disproportionate upon removal of solvent.

In view of the molecular weight and CO stretching frequency, the two most likely modes of attachment of BF_3 to the Ir complex for 1:1 adduct are (1) simple Ir–B donor–acceptor interaction or (2) oxidative insertion of the Ir atom into a B–F bond.[8]

The former possibility is favored because (1) there is evidence against oxidative insertion in the case of the 2:1 adducts (*i.e.*, no trigonally bonded boron is present), (2) the parent complex, **1**, can be regenerated by treating the adduct with mild bases such as acetone or amines, and (3) $B(C_6F_5)_3$, which is similar in acidity to BF_3[9] but for which insertion is unlikely, forms a weak adduct with $[IrClCO(P(C_6H_5)_3)_2]$. This adduct displays a CO stretching frequency similar to that of the BF_3 adduct. (Furthermore, the more stable $[IrClCO(P(C_2H_5)_2C_6H_5)_2]\cdot B(C_6F_5)_3$ yields a ^{19}F nmr spectrum which is characteristic of a simple $B(C_6F_5)_3$ adduct and not an insertion product.) Since the CO stretching frequencies are nearly identical for the 1:1 and 2:1 adducts, it is probable that the second molecule of BF_3 is not attached directly to Ir, but the true nature of the 2:1 adduct is not clear.

In Figure 1 the carbonyl stretching frequencies of several molecular adducts and the uncoordinated iridium(I) complex are plotted as a function of the electron affinity of the added molecule.[10] There is a roughly linear dependence of the stretching frequency upon the electron affinity indicating that the electron density around the iridium atom decreases in a smooth continuous fashion rather than in discrete discontinuous jumps between the formal oxidation states I, II, and III.

It has been pointed out[11–13] that O_2, $C_2(CN)_4$, and SO_2 can form bonds to iridium in which two types of interactions can occur. These are weak donation from filled π orbitals in O_2 and $C_2(CN)_4$ or the nonbonding electron pair on the sulfur atom in SO_2, and moderately strong acceptance of electron density from the metal by a π-bonding interaction of filled metal d orbitals and antibonding orbitals on the ligand molecules. In the case of the boron trifluoride adduct, the only possible interaction is σ donation from iridium to boron. The correlation of the carbonyl stretching frequencies with molecular electron affinities for the added molecules, including BF_3, suggests that all of the molecular adducts considered here may be viewed as Lewis salts in which the metal primarily serves as a donor. Accordingly, much of the chemistry of the Ir(I) adducts can be described in terms of the strongest electron acceptor (Lewis acid) forming the most stable complex. Thus, the uptake of O_2 and of SO_2 by $[IrClCO(P(C_6H_5)_3)_2]$ is reversible, while BF_3 uptake is not. Similarly, C_2F_4 is more strongly[14] held than C_2H_4. However, some caution is necessary in the inference of Lewis acid strengths from known or estimated electron affinities, or even from acidity toward radically different reference bases. For one thing the three-center bonds formed between the oxygen-like acids and the metal are different in detail from the two-center boron–metal bond. Also differences may occur in the geometry of the first coordination sphere and in the degree of reorganization of the acid. Therefore, comparisons of stabilities with electron affinities or of frequencies with electron affinities are only potentially meaningful for large differences.[15]

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(7) Solvent removal was performed on the vacuum line which allowed a check of all volatiles removed from the reaction mixture. This experiment demonstrated that no BF_3 was evolved from the 1:1 mixture.

(8) G. Schmid, W. Arloth, and H. Nöth, *Angew. Chem. Intern. Ed. Engl.*, 6, 696 (1967).

(9) A. G. Massey and A. G. Park, *J. Organometal. Chem.* (Amsterdam), **5**, 218 (1966).

(10) It is to be emphasized that upon interaction with the iridium complex, cleavage of the added molecule does not occur for any of the cases cited in Figure 1.

(11) L. Vaska and S. S. Bath, *J. Am. Chem. Soc.*, **88**, 1333 (1966).

(12) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Science*, **155**, 709 (1967).

(13) W. H. Baddley, *J. Am. Chem. Soc.*, **88**, 4545 (1966).

(14) R. Cramer and G. W. Parshall, *ibid.*, **87**, 1392 (1965).

(15) Supported by the National Science Foundation through Grant GP-6676.

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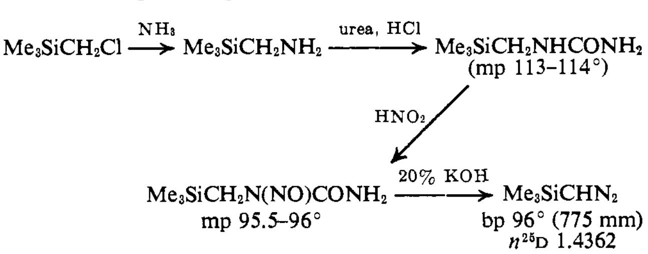
Trimethylsilyldiazomethane and Trimethylsilylcarbene

Sir:

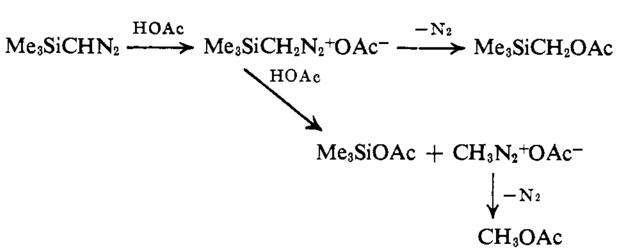
A recent report on "trimethylstannyldiazomethane"[1] mentioned in passing that trimethylsilyldiazomethane had been prepared by the reaction of diazomethyllithium with trimethylchlorosilane.[2] However, no reactions of this compound or physical data other than a boiling point were reported.

We have prepared trimethylsilyldiazomethane by a less hazardous route.[3] We report our results at the present time since we find that this unusually stable diazoalkane serves as a useful reagent for the introduction of trimethylsilyl groups into organic molecules by its reactions as a diazoalkane and by reactions of the carbenoid species derived from it. The preparation of trimethylsilyldiazomethane is described by the reaction sequence given. This sequence is analogous

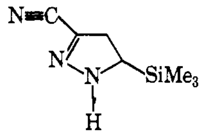


to the preparation of diazomethane *via* N-nitroso-N-methylurea.[4] The final step proceeds smoothly at room temperature, but no matter whether it is carried out in the presence or absence of an organic solvent, hexamethyldisiloxane is formed as a side product. In a typical preparation, 0.119 mole of N-nitroso-N-trimethylsilylmethylurea was suspended in 87 ml of benzene, and 41 ml of 20% KOH solution was added. The mixture was stirred rapidly and cooled when necessary to maintain the mixture at room temperature. A greenish yellow solution of trimethylsilyldiazomethane in benzene resulted. The yield of the diazo compound was 56%; in addition, hexamethyldisiloxane was formed in 23% yield. Trimethylsilyldiazomethane, a greenish yellow liquid, is very stable thermally and can, in fact, be distilled at atmospheric pressure and can be analyzed and isolated in analytical purity by gas–liquid partition chromatography (glpc) using General Electric Co. SE-30 or XF-1150 columns at room temperature, with detector and injection blocks at ~100°. The N–N stretching vibration of its diazo group, 2070 cm^{-1}, is very similar to that of diazomethane (2074 cm^{-1} in solution, 2108 cm^{-1} in the gas phase) and acyl-substituted diazomethanes (2100–2087 cm^{-1}). In contrast, alkyl- and aryldiazomethanes show this absorption at lower frequency (2049–2020 cm^{-1}).[5] Thus the shift of the acyl- and trimethylsilyldiazomethane N–N stretching frequency to shorter wavelength can be rationalized in terms of increased contributions of $R\bar{C}HN^+{\equiv}N$ to the total resonance description of the molecules. In the case of the silyl derivative, this may possibly be a result of $d\pi$–$p\pi$ stabilization of the carbanionic center adjacent to silicon in $Me_3Si\bar{C}HN^+{\equiv}N$. The proton α to the diazo group in trimethylsilyldiazomethane is seen at τ 7.77 as a singlet in its nmr spectrum in benzene solution, the Me_3Si protons as a singlet at τ 10.02 (*vs.* internal TMS).

Experiments in which a benzene solution of trimethylsilyldiazomethane was stirred at room temperature for 2 hr with water and 20% aqueous KOH indicated considerable hydrolytic stability of this reagent. This suggests that trimethylsilyl group cleavage occurred before or during formation of the diazoalkane. As expected, trimethylsilyldiazomethane reacts with acids, but the protolysis reaction is complicated by trimethylsilyl cleavage. Thus a reaction of this diazoalkane with water-free acetic acid in benzene at room temperature gave not only the expected trimethylsilylmethyl acetate but also equimolar amounts of methyl acetate and trimethylsilyl acetate; the yield accounting of trimethylsilyl groups was almost quantitative. This may be understood in terms of loss of the trimethylsilyl group from the intermediate trimethylsilylmethyldiazonium ion. Such cleavage is not unexpected in terms of known organosilicon chemistry, and the previous report[6] of the loss of the trimethylsilyl group upon treatment of trimethylsilylmethylamine with nitrous acid represents a closely related situation.



Trimethylsilyldiazomethane in decalin solution underwent 1,3-dipolar addition to acrylonitrile, giving a moisture-sensitive, white crystalline solid, mp 55.4–57.6°, in 73% yield, whose analytical data indicated the composition $C_7H_{13}N_3Si$. Its infrared spectrum showed (among others) bands at 3400 and 3350 (s, N–H), 2963 (s), 2905 (m), 2215 (s, C≡N), 1676 (w), 1630 (w), 1540 (s), 1252 (s, Me_3Si), 1028 (s), and 860 (s, Me_3Si) cm^{-1}. These data are compatible with a conjugated, 2-pyrazoline structure, I. Other reactions with 1,3-dipolarophiles are under investigation. Of greater interest to us has been the carbenoid reactivity of trimethylsilyldiazomethane as demonstrated by its use in the synthesis of Me_3Si-substituted cyclopropanes.



I

While a benzene solution of trimethylsilyldiazomethane was quite stable at 80°, its addition to a benzene suspension of cuprous chloride at room temperature caused vigorous evolution of nitrogen in an exothermic reaction that required moderation by external cooling. The major products of this decomposition were identified as *cis*- and *trans*-1,2-bis(trimethylsilyl)ethylenes by comparison of their spectral properties and refractive indices with those reported for these com-

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(1) M. F. Lappert and J. Lorberth, *Chem. Commun.*, 836 (1967).

(2) See, however, a conflicting report concerning this reaction: O. J. Scherer and M. Schmidt, *Z. Naturforsch.*, **20b**, 1009 (1965).

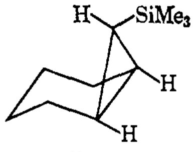
(3) Diazomethyllithium, as the dry solid, is explosive: E. Müller and W. Rundel, *Chem. Ber.*, **90**, 1299 (1957).

(4) W. E. Bachmann and W. S. Struve, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 461.

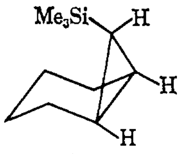
(5) P. Yates, B. L. Shapiro, N. Yoda, and J. Fugger, *J. Am. Chem. Soc.*, **79**, 5756 (1957).

(6) R. J. Fessenden and F. J. Freenor, *J. Org. Chem.*, **26**, 1681 (1961).

pounds by Chvalovský, *et al.*[7] Such CuCl-catalyzed decomposition of Me_3SiCHN_2 in benzene in the presence of an excess of cyclohexene gave as the major product (in 65% yield) *anti*-7-trimethylsilylnorcarane (II). Three minor products were the other 7-trimethylsilylnorcarane isomer (III) (7%), *trans*-1,2-bis(trisilyl)ethylene (13%), and the *cis* isomer (9%). All products were isolated as pure materials by glpc. The identification of the 7-trimethylsilylnorcarane isomers was based on their analyses and their infrared and nmr spectra. Particularly the latter were of value: in the nmr spectrum (in CCl_4) of II, the Me_3Si group appeared as a singlet at τ 10.09 and the cyclopropane proton *gem* to the trimethylsilyl group as a triplet at τ 10.69 (J = 7 cps). In III these resonances were seen at τ 9.88 and 10.41 (triplet, J = 10 cps). In support of these assignments we may note that previous work has established that in norcaranes the 7-proton *syn* to the $-(CH_2)_4-$ bridge is more highly shielded than is the proton which is *anti* to the tetramethylene bridge and, furthermore, that the magnitude of *cis* coupling between vicinal protons in cyclopropanes is greater than that of *trans* coupling.[8] The CuCl-catalyzed decomposition of trimethylsilyldiazomethane in the presence of an excess of *cis*-4-methyl-2-pentene gave, in addition to *trans*- and *cis*-1,2-bis(trimethylsilyl)ethylenes, the two isomers of 1-methyl-2-isopropyl-3-trimethylsilylcyclopropane. Further carbenoid reactions of trimethylsilyldiazomethane are under investigation.



II, n^{25}_D 1.4561



III, n^{25}_D 1.4734

In conclusion, it should be noted that trimethylsilylcarbene has been proposed as an intermediate previously: in the $Me_3SiCHCl_2$ + Na–K gas phase reaction (which gave $Me_2HSiCH{=}CH_2$),[9] in the rather complicated reaction of Me_3SiCH_2Cl with lithium,[10] and in the reaction of Me_3SiCH_2Cl with *n*-butyllithium.[11] The latter reaction was carried out in the presence of cyclohexene, but no 7-trimethylsilylnorcarane was obtained. More recently, a brief report concerning trimethylsilylcarboethoxycarbene has appeared.[12]

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(7) (a) J. Knížek, M. Horak, and V. Chvalovský, *Collection Czech. Chem. Commun.*, **28**, 3079 (1963); (b) J. Cudlín, J. Schraml, and V. Chvalovský, *ibid.*, **29**, 1476 (1964).

(8) (a) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962); (b) G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4985 (1962); (c) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963); (d) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963); (e) G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **87**, 4270 (1965).

(9) P. S. Skell and E. J. Goldstein, *ibid.*, **86**, 1442 (1964).

(10) J. W. Connolly and G. Urry, *J. Org. Chem.*, **29**, 619 (1964).

(11) I. A. D'yakonov, I. B. Repinskaya, and G. V. Golodnikov, *Zh. Obshch. Khim.*, **35**, 199 (1965).

(12) U. Schöllkopf and N. Rieber, *Angew. Chem.*, **79**, 906 (1967).

(13) National Institutes of Health Postdoctoral Fellow, 1967–1968.

(14) Postdoctoral Research Associate, 1963–1964.

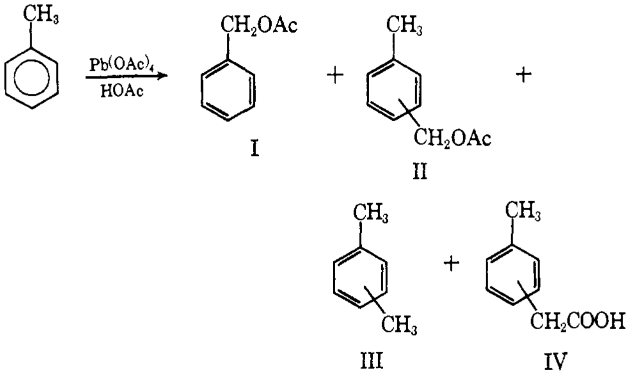
(15) National Science Foundation Trainee, 1967–1968.

Oxidation by Metal Salts. I. The Reaction of Lead Tetraacetate with Toluene

Sir:

Despite many investigations of the oxidation of alkylaromatics by lead tetraacetate, the mechanisms of these processes are not fully understood, and some conflicting theories and interpretations are current in the literature.[1] In particular, the formation of products in which the $-CH_2OAc$ group has been added to the aromatic ring has been observed in a few instances[2] and the mechanism of their formation has not been adequately explained. We wish to report our studies on the oxidation of toluene by lead tetraacetate and present a general mechanism which explains the production of these adducts and predicts the conditions conducive to their formation.

The oxidation of toluene with lead tetraacetate in refluxing acetic acid containing anhydrous potassium acetate under a nitrogen atmosphere[3] yielded two major products, benzyl acetate (I) and methylbenzyl acetate (II) (mixture of isomers, predominantly *ortho*), along with minor amounts of xylenes (III) and tolylacetic acids (IV).



In a typical experiment in which 21.7 mmoles of lead tetraacetate was added to a solution of toluene (15-fold excess) in acetic acid, the following product yields were obtained: benzyl acetate (7.04 mmoles), methylbenzyl acetates (4.95 mmoles), xylenes (1.91

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(1) Reviewed by R. Criegee in "Oxidation in Organic Chemistry," Part A, K. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, p 277.

(2) (a) L. F. Fieser, R. C. Clapp, and W. H. Daudt, *J. Am. Chem. Soc.*, **64**, 2052 (1942); (b) J. Jadot and M. Neuray, *Bull. Soc. Roy. Sci. Liege*, **29**, 138 (1960); (c) D. I. Davies, *J. Chem. Soc.*, 2351 (1963); (d) J. M. Davidson and C. Triggs, *Chem. Ind.* (London), 1361 (1967).

(3) In the presence of oxygen, the reaction times increased and the yields of products based on lead tetraacetate consumed decreased, as would be expected in a radical chain process. These observations are in accord with those reported by Davidson and Triggs.[2d]