Table I. Analyses of Compounds Prepared

Compound	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
$[Ir(en)_2(H_2O)Cl](ClO_4)_2$	8.51	8.66	3.21	3.24	9.92	9.99
$[Ir(en)_2BrCl]ClO_4$	9.11	9.12	3.06	2.89	10.63	10.70
$[Ir(en)_2ICl]ClO_4$	8.36	8.54	2.81	2.89	9.76	9.94
$[Ir(en)_2IBr]ClO_4 \cdot H_2O$	7.55	7.57	2.85	2.72	8.80	8.86
$[Rh(en)_2BrCl]ClO_4$	10.97	10.74	3.68	3.68	12.79	12.50
$[Rh(en)_2(ONO)Cl]ClO_4$	11.89	11.64	3.99	3.96	17.33	17.21

trans-$[Rh(en)_2(H_2O)Cl]^{2+}$ was prepared *in situ* by irradiating an aqueous solution of *trans*-$[Rh(en)_2Cl_2]ClO_4$. *trans*-$[Rh(en)_2BrCl]ClO_4$ was isolated in 80% yield by treatment of this solution with silver ion and bromide ion in the manner above. The ultraviolet spectra of both of these compounds agree with those published.[3b,c]

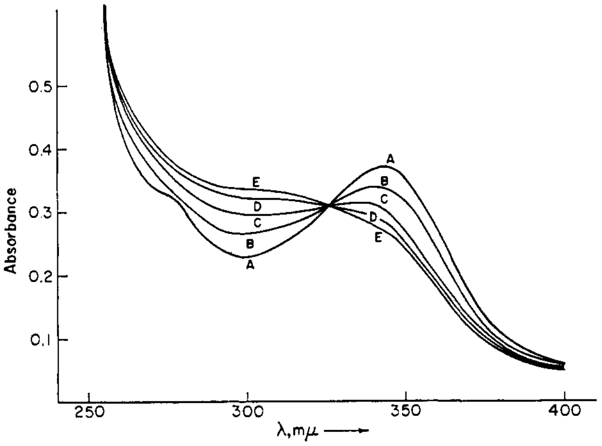


Figure 1. Spectral changes during the photoaquation of *trans*-$[Ir(en)_2Cl_2]^+$ in water at 25°. [Complex] = 0.0250 *M*. Curves A–E correspond to irradiation periods of 0, 500, 1500, 3500, and 7500 sec, respectively.

trans-$[Rh(en)_2(ONO)Cl]ClO_4$ was prepared from a photochemically produced solution of *trans*-$[Rh(en)_2(H_2O)Cl]^{2+}$ by a method similar to that reported[5] previously for the synthesis of nitrito complexes. After irradiation of a solution of *trans*-$[Rh(en)_2Cl_2]^+$ and precipitation of the chloride ion as AgCl, the solution was acidified with $HClO_4$, cooled in an ice bath, and treated with excess $NaNO_2$. After 20 min the light yellow crystals were collected on a filter, washed with cold water, ethanol, and ether, and air-dried. At this low reaction temperature, the nitrito linkage isomer was isolated in 60% yield. The nitrito isomer rearranges to the more stable nitro isomer with a half-life of about 10 min at room temperature in water solution. The nitrito isomer also rearranges in the solid state with the following changes in infrared spectra (cm^{-1}): *trans*-$[Rh(en)_2(ONO)Cl]ClO_4$, 1435 (s), 828 (m); *trans*-$[Rh(en)_2(NO_2)Cl]ClO_4$ (rearranged), 1410 (s), 1415 (s), 832 (m), 812 (m); *trans*-$[Rh(en)_2(NO_2)Cl]ClO_4$ (prepared by thermal replacement of Cl^- in *trans*-$[Rh(en)_2Cl_2]^+$), 1410 (s), 1415 (s), 822 (m), 803 (m). The shifts of 10 cm^{-1} in the 800-cm^{-1} region of the same chloronitro compounds are apparently due to differing crystalline environments, since one was isolated from aqueous solution and the other prepared by a solid-state reaction.

All complexes were determined to be *trans* isomers by their characteristic infrared spectra.[6]

Extensive application has been made of the photochemical syntheses of organometallic compounds.[7] More use should be made of this approach for the syntheses of Werner complexes, particularly complexes of the platinum metals which are often otherwise difficult to prepare.

Acknowledgment. This work was supported by the U. S. Atomic Energy Commission under Grant No. At(11-1)-1087.

---

[5] F. Basolo and G. S. Hammaker, *Inorg. Chem.*, 1, 1 (1962).

[6] M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960).

[7] E. O. Fischer, J. P. Kögler, and P. Kuzel, *Chem. Ber.*, **93**, 3006 (1960); W. Strohmeier and K. Gerlach, *Z. Naturforsch.*, **15b**, 413 (1960); R. S. Nyholm, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.*, 5916 (1963).

Robert A. Bauer, Fred Basolo
Chemistry Department, Northwestern University
Evanston, Illinois 60201

Received February 28, 1968

Bis(trimethylsilyldichloromethyl)mercury, a New and Useful Reagent in Synthetic Organosilicon Chemistry

Sir:

Much work has been devoted in the past 6 years to organomercury compounds of types $PhHgCX_3$, $PhHgCHX_2$, and $(XCH_2)_2Hg$, which are capable of transferring CX_2, CHX, and CH_2, respectively, to olefins and other substrates.[1,2] However, thus far no functional carbene reagents of this type have been prepared. We report here the first such reagent, an organomercury compound which transfers Me_3SiCCl to olefins and Si–H compounds.

The recently reported trimethylsilyldichloromethyllithium[3] reacted with mercuric bromide at −135° in a solvent mixture containing tetrahydrofuran, methylal, diethyl ether, and pentane to give bis(trimethylsilyldichloromethyl)mercury, a white crystalline solid, mp 151–153°, in moderate (~35%) yield. Use of a deficiency of the lithium reagent resulted in formation of Me_3SiCCl_2HgBr, mp 132–135°.

A reaction was carried out in which a solution of 4.9 mmoles of $(Me_3SiCCl_2)_2Hg$, 5.2 mmoles of diphenylmercury,[4] and 0.1 mole of cyclohexene in 25 ml of

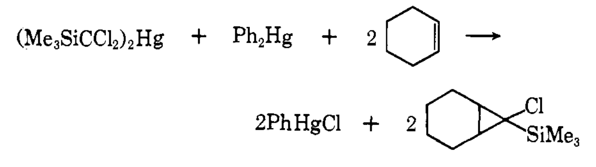
---

[1] D. Seyferth in "Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research. IX. Organometallic Compounds," Robert A. Welch Foundation, Houston, Texas, 1966, pp 89–135 (review).

[2] D. Seyferth and R. B. King, "Annual Surveys of Organometallic Chemistry," Elsevier Publishing Co., Amsterdam: Vol. 1, 1965, pp 44–45; Vol. 2, 1966, pp 55–56; Vol. 3, 1967, pp 66–69.

[3] D. Seyferth, F. M. Armbrecht, Jr., and E. M. Hanson, *J. Organometal. Chem.* (Amsterdam), 10, P25 (1967).

n-decane was heated at reflux (118°, with stirring, under nitrogen). Thin layer chromatography[5] was used to monitor the gradual consumption of the organomercury compounds. After 10 days less than 5% of the starting mercurials remained. Filtration from phenylmercuric chloride (82%) and 0.074 g of metallic mercury gave a filtrate which was analyzed by glpc (F & M Model 5750; DC-200 oil column; 40–190° program). The major products were trimethyl(dichloromethyl)silane (15.5%) and 7-chloro-7-trimethylsilylnorcarane (I) (62%). An analytical sample of the latter had n^{25}D 1.4797, and its infrared and nmr spectra were in agreement with this structure. The Me_3Si group appeared as a sharp singlet 0.017 ppm downfield from TMS (Varian A-60), suggesting the presence of a single isomer, probably the one in which the trimethylsilyl group is *anti* with respect to the tetramethylene unit. Several minor components with slightly higher retention time were present as well. Thus the main reaction which occurred may be summarized by eq 1.



(1)

I

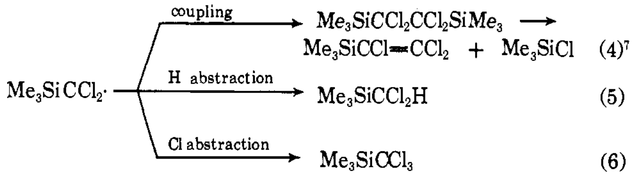
This reaction also was carried out in chlorobenzene solution (8 days at 119°) to give I in 63% yield and phenylmercuric chloride in 95% yield. Bis(trimethylsilyldichloromethyl)mercury did not react with cyclohexene at 83° during a 7-day heating period. Reaction of the $(MeSiCCl_2)_2Hg$–Ph_2Hg system with cyclooctene in chlorobenzene solution carried out in similar fashion for 7 days at 125–135° gave 9-chloro-9-trimethylsilylbicyclo[6.1.0]nonane (II), mp 40–42°, in 73% yield, as well as phenylmercuric chloride (98%). The nmr spectrum of II showed the Me_3Si group at 0.15 ppm and the cyclopropyl hydrogens centered at 0.82 ppm.

Another characteristic reaction of phenyl(trihalomethyl)mercurials is their insertion of CX_2 into the Si–H bond of silanes to give $Si–CX_2H$ compounds.[1] The $(Me_3SiCCl_2)_2Hg$–Ph_2Hg reagent reacts similarly. When a mixture of 5 mmoles each of these mercury compounds and 0.1 mole of triethylsilane in chlorobenzene solution was heated at 126° under nitrogen for 3 days, subsequent glpc analysis of the volatile components indicated the formation of the insertion product, $Et_3SiCHClSiMe_3$, n^{25}D 1.4675, in 42% yield. Its nmr spectrum ($CHCl_3$) showed the Me_3Si group at 0.185 ppm, the –C*H*Cl– proton as a sharp singlet at 2.6 ppm, and the Et_3Si group as a complex multiplet centered at 0.8 ppm downfield from TMS. The presence of a further product, triethylchlorosilane (5.64 mmoles), the absence of phenylmercuric chloride, and the isolation of 4.95 mmoles of diphenylmercury and of 4.97 mg-atoms of metallic mercury showed that the phenylmercuric chloride formed had been reduced by the triethylsilane (which was present in large excess) (eq 2). The formation of triethylchlorosilane in a quantity greater than expected on the basis of eq 2 found an explanation when another minor (7.3%) product, $Et_3SiCH_2SiMe_3$, was identified. Apparently, at these temperatures, some C–Cl reduction of the insertion product by triethylsilane had occurred. Longer reaction times resulted in a much greater extent of such reduction; thus, in one case carried out similarly, a reaction time of 6 days resulted in formation of $Et_3SiCH_2SiMe_3$ in 80% yield.

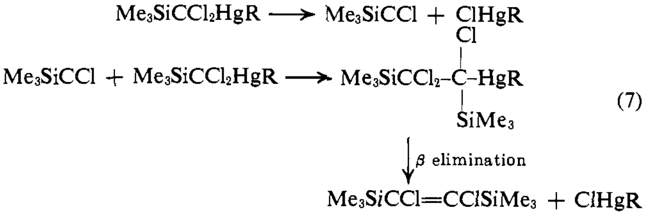
$$\begin{array}{l} PhHgCl + Et_3SiH \longrightarrow Et_3SiCl + [PhHgH] \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad 0.5Ph_2Hg + 0.5Hg + 0.5H_2 \end{array} \quad (2)$$

The thermolysis of bis(trimethylsilyldichloromethyl)mercury at higher temperatures also was investigated. A mixture of products resulted when this mercurial was heated in an oil bath at 220° in the absence of substrate. There was obtained the expected (formally) carbene-derived product, $Me_3SiCCl{=}CClSiMe_3$, mp 48–49° (Me_3Si groups as a sharp singlet at 0.32 ppm), in 14% yield, but the major products were trimethylchlorosilane (34%) and trimethyl(trichlorovinyl)silane[6] (40%). Trimethyl(dichloromethyl)silane and trimethyl(trichloromethyl)silane also were obtained in yields of 2.5 and 4.5%, respectively, and metallic mercury also was produced. These products suggest a predominant homolytic cleavage at this temperature (eq 3–6). In confirmation of this, when the pyrolysis was carried out at 220° in a good hydrogen donor medium, diphenylmethane, the principal product (73% yield) was trimethyl(dichloromethyl)silane. In this case, $Me_3SiCCl{=}CCl_2$ and $Me_3SiCCl{=}CClSiMe_3$ also were formed, but in much lower yield, 13 and 4%, respectively. It is likely, but by no means certain, that 1,2-dichloro-1,2-bis(trimethylsilyl)ethylene was formed by the process shown in eq 7. The insertion of CCl_2 into alkyl–mercury bonds is a known reaction,[8] and it is believed that the formation of

$$(Me_3SiCCl_2)_2Hg \xrightarrow{\Delta} 2Me_3SiCCl_2\cdot + Hg \quad (3)$$



$$\begin{array}{ll} Me_3SiCCl_2\cdot \xrightarrow{\text{coupling}} Me_3SiCCl_2CCl_2SiMe_3 \longrightarrow & \\ \qquad Me_3SiCCl{=}CCl_2 + Me_3SiCl & (4)^{7} \\ Me_3SiCCl_2\cdot \xrightarrow{\text{H abstraction}} Me_3SiCCl_2H & (5) \\ Me_3SiCCl_2\cdot \xrightarrow{\text{Cl abstraction}} Me_3SiCCl_3 & (6) \end{array}$$



$$\begin{array}{l} Me_3SiCCl_2HgR \longrightarrow Me_3SiCCl + ClHgR \\ Me_3SiCCl + Me_3SiCCl_2HgR \longrightarrow Me_3SiCCl_2\text{–}\overset{\displaystyle Cl}{\underset{\displaystyle SiMe_3}{C}}\text{–}HgR \\ \qquad\qquad \downarrow \beta \text{ elimination} \\ Me_3SiCCl{=}CClSiMe_3 + ClHgR \end{array} \quad (7)$$

---

(4) Added to effect utilization of both Me_3SiCCl_2 groups. Note our previously reported $(BrCH_2)_2Hg$–Ph_2Hg CH_2 transfer system: D. Seyferth, M. A., Eisert, and L. J. Todd, *J. Am. Chem. Soc.*, **86**, 121 (1964).

(5) D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.* (Amsterdam), **4**, 127 (1965).

(6) (a) E. T. McBee, C. W. Roberts, and G. W. A. Puerkhauer, *J. Am. Chem. Soc.*, **79**, 2326 (1957); (b) D. Seyferth, R. J. Cross, and B. Prokai, *J. Organometal. Chem.* (Amsterdam), 7, P20 (1967).

(7) Similar thermal β elimination from haloethylsilanes has been noted previously, *e.g.*, $Cl_3SiCF_2CF_2Cl \xrightarrow{220°} SiFCl_3 + CF_2{=}CFCl$: R. N. Haszeldine and R. J. Markow, *J. Chem. Soc.*, 962 (1956).

(8) J. A. Landgrebe and R. D. Mathis, *J. Am. Chem., Soc.*, **86**, 524 (1964).

tetrachloroethylene in the thermolysis of $PhHgCCl_2Br$ in the absence of a substrate capable of trapping CCl_2 occurs by such a route.[1]

We report our results at the present time because the $(Me_3SiCCl_2)_2Hg$ reagent adds two new, potentially useful species to the arsenal of synthetic organosilicon chemistry: trimethylsilylchlorocarbene and the trimethylsilyldichloromethyl radical. Our recent report of Me_3SiCH transfer to olefins *via* CuCl-catalyzed reactions of trimethylsilyldiazomethane also should be noted in this connection.[9] Our efforts in this area are continuing.

All new compounds reported in this communication had satisfactory analyses, and known compounds were identified by means of their infrared or nmr spectroscopic properties.

Acknowledgments. The authors are grateful to AFOSR(SRC)-OAR, U. S. Air Force (Grant No. AFOSR-68-1350), for generous support of this research. This investigation was supported in part by Public Health Service Fellowship 5-F1-GM-28,934 (to E. M. H.).

(9) D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Am. Chem. Soc.*, **90**, 1080 (1968).

(10) National Institutes of Health Predoctoral Fellow, 1965–present.

Dietmar Seyferth, Earle Marie Hanson[10]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

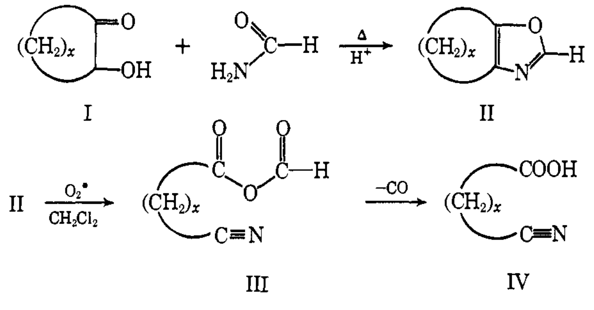
Received February 15, 1968

The Reaction of Oxazoles with Singlet Oxygen. II.[1] A Novel Method for the Preparation of ω-Cyano Acids

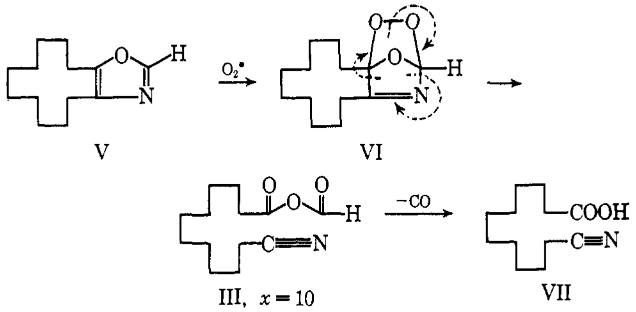
Sir:

We have previously described the conversion of oxazoles to triamides by dye-photosensitized autoxidation in methanol.[1] We now wish to report that, in inert solvents such as methylene chloride, the reaction of singlet oxygen with 4,5-condensed oxazoles of type II takes a different course, providing a useful method for the preparation of ω-cyano acids.

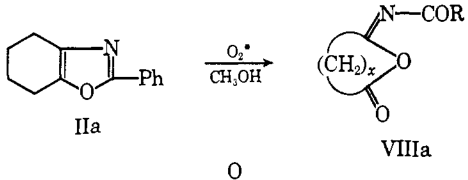
The fused-ring oxazoles were readily prepared from the acyloins (I) by condensation with formamide in acidic medium.[2] Systems studied included II, x = 4, 5, 6, and 10, based on their ready availability. In a typical oxidation, the oxazole II, x = 4 (4 g), was irradiated in CH_2Cl_2 (1000 ml) with a 275-W sunlamp[3] for 12–14 hr while dry oxygen was bubbled through the stirred solution. Methylene blue was used as a sensitizer. After evaporation of the solvent at room temperature a crude product was obtained showing sharp nitrile (2250 cm^{-1}) and anhydride absorption (1785 and 1765 cm^{-1}) in the ir. The nmr spectrum exhibits a characteristic sharp singlet at τ 0.9 (formyl hydrogen). The anhydride thus obtained readily liberated CO during work-up to yield the nitrile acid IV (x = 4).[4] The structure of the product was shown by ir (broad OH absorption near 3100 cm^{-1}, $C{\equiv}N$ at 2250 cm^{-1}, and C=O at 1705 cm^{-1}) and nmr spectra (singlet at τ −1.4 (carboxylic proton) and two multiplets centered at τ 7.6 and 8.5). Hydrolysis of IV, x = 4, yielded adipic acid. The yields in the conversions II → IV (x = 4, 5, 6, and 10) were 80–90%.

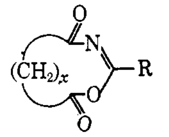


As illustrated in the case of oxazole V, formed from cyclododecanone, the reaction appears to proceed through the intermediate transannular peroxide, VI, which then undergoes rearrangement[5] to form the cyano anhydride III, x = 10. Loss of CO from this mixed anhydride of formic acid[6] leads to VII, the observed product. Further evidence for the participation of singlet oxygen in this reaction was provided by the thermal reaction of V with 9,10-diphenylanthracene peroxide[7] (19 hr in boiling toluene) which yielded the nitrile acid VII (75%).[8]



Oxazoles of type II substituted in the 2 position (CH_3, C_6H_5) also undergo the same rearrangement, yielding cyano anhydrides which may react further by hydrolysis or alcoholysis to form the corresponding ω-cyano acids or esters. By-products in these reactions are N-acylimino anhydrides VIIIa or VIIIb. The





---

(1) For the first paper in this series see H. H. Wasserman and M. B. Floyd, *Tetrahedron Suppl.*, 7, 551 (1966).

(2) H. Bredereck and R. Gompper, *Chem. Ber.*, **87**, 726 (1954).

(3) The reaction also proceeds with a 150-W floodlamp, but at a much slower rate.

(4) Satisfactory C, H, and N analyses were obtained for all new compounds.

(5) D. W. Kurtz and H. Shechter (*Chem. Commun.*, 689 (1966)) have observed that benzonitrile and benzoic anhydride are among the products formed in the photolysis of 2,4,5-triphenyloxazole in oxygen. An analogous mechanism has been suggested by these authors to explain their results.

(6) G. F. Fanta, *J. Org. Chem.*, **29**, 981 (1964).

(7) H. H. Wasserman and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 3073 (1967).

(8) H. H.Wasserman and J. Cooper, to be published.