Insufficient data are available for evaluating the energetics of reactions 3 and 4, but it is quite reasonable to assume that the free energy change for reaction 3 is determined primarily by the difference in the O–H bond dissociation energy for phenol and the substituted phenol. Similarly, the main contribution to $\Delta G°$ for reaction 4 is expected to be the difference in the electron affinity of $C_6H_5O\cdot$ and $XC_6H_4O\cdot$. Enhanced gas-phase acidity will result, therefore, when the substituent decreases the O–H bond dissociation energy and increases the electron affinity of the substituted phenoxy radical.

In general the substituent would be expected to cause only small changes in the phenolic O–H bond dissociation energy. But considering the large magnitude of the intramolecular ion dipole and ion-induced dipole interactions,[1b] one would expect larger differences in the electron affinity of the substituted phenoxy radicals. Within this degree of approximation, the data in Table I can be analyzed in terms of the effect of the substituent on the electron affinity of the substituted phenoxy radicals. The enhanced acidity produced by halogen substituents is best explained by a large electron withdrawing inductive effect which provides internal stabilization for the halophenoxide ions. This effect is decreased somewhat the ortho and para positions due most probably to electron-donating resonance forms involving the p orbitals of the halogens. Alkyl substituents can stabilize the phenoxide substrate by an ion-induced dipole polarization interaction which increases with the size of the alkyl group and its proximity to the negative charge on oxygen. Brauman and Blair have shown this to be the predominant effect determining the intrinsic acidity of aliphatic alcohols.[1] Several members of the phenol series show, however, that alkyl groups can also *destabilize* negative charge. Hybridization effects of this type have also been observed in the acidity of alkynes and carboxylic acids.[1,10]

A more complete discussion of these substituent effects within the context of gas-phase acidity data for a broader set of substituted phenols is planned. In particular, the influence of ortho substituents and the distinction between hyperconjugation and hybridization effects will be considered.

Acknowledgment. We wish to thank the National Science Foundation (GP-38170X) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

(10) R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, **95**, 4050 (1973).

(11) Alfred P. Sloan Fellow, 1973–1975.

(12) President's Undergraduate Research Fellow at the University of California, Irvine, 1972–1973.

Robert T. McIver, Jr.,*[11] Jeffrey H. Silvers[12]
Department of Chemistry, University of California
Irvine, California 92664

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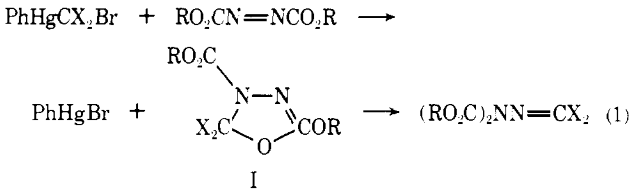
Synthesis of Heterocyclic Systems *via* 1,4-Addition Reactions of Phenyl(bromodichloromethyl)mercury Derived Dichlorocarbene

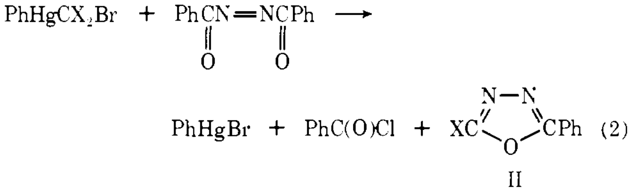
Sir:

Recently we have reported concerning the reaction of phenyl(trihalomethyl)mercury compounds with azodicarboxylate esters, which appears to take the course shown in eq 1.[1] Tentative ir and nmr spectroscopic evidence for the formation of 1,3,4-oxadiazoline intermediates (I) was available for several such reactions.

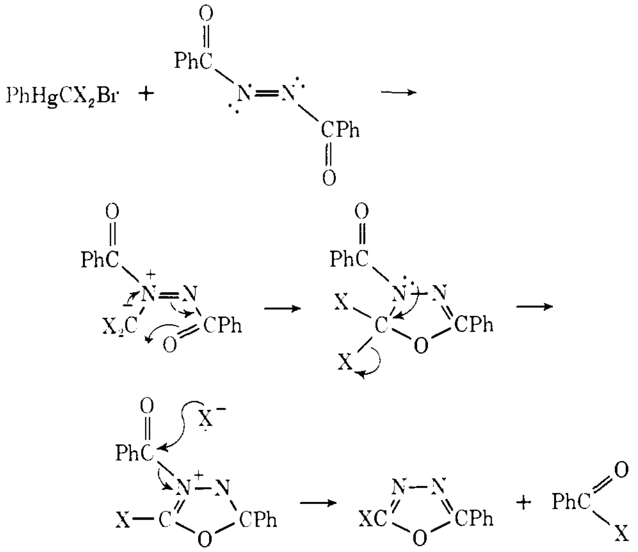


It was expected that such formal 1,4 addition of CX_2 might be possible with other α,β-unsaturated systems, and we report here concerning the preparation of an oxadiazole and an oxazole by similar processes.

A carbon tetrachloride solution of phenyl(bromodichloromethyl)mercury and azodibenzoyl (5 mmol each) was stirred at room temperature under nitrogen for 8 days and then heated at 80° for 1 hr. Two products, identified as benzoyl chloride (66%) and 2-chloro-5-phenyl-1,3,4-oxadiazole (II, X = Cl) (54%), mp 76–78° (lit.[2] mp 75°), were obtained. An ir spectroscopic study of the reaction revealed the intervention of an intermediate with an ir band at 1610 cm^{-1}, presumably a C=N frequency. When $PhHgCBr_3$ was the mercurial used in this reaction, benzoyl bromide and 2-bromo-5-phenyl-1,3,4-oxadiazole (II, X = Br), mp 107–109°, were obtained, the latter in 80% yield. A plausible mechanism for formation of the heterocyclic products is shown in Scheme I.



Scheme I



1,4 addition of CX_2 also can occur with an –N=C-C=O system. The reaction of $PhHgCCl_2Br$ with $EtO_2CN{=}C(CO_2Et)_2$ or $MeO_2CN{=}C(CO_2Et)_2$ in ben-

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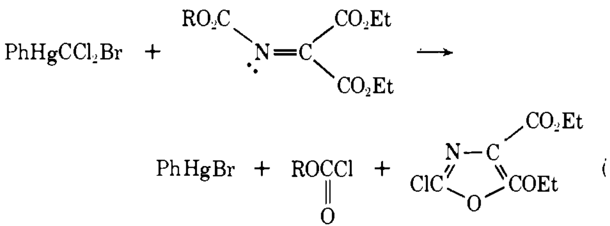
(1) D. Seyferth and H. Shih, *J. Amer. Chem. Soc.*, **94**, 2508 (1972).

(2) C. Ainsworth, *Can. J. Chem.*, **43**, 1607 (1965). The nmr and ir spectra of II (X = Cl) are identical with those reported here.

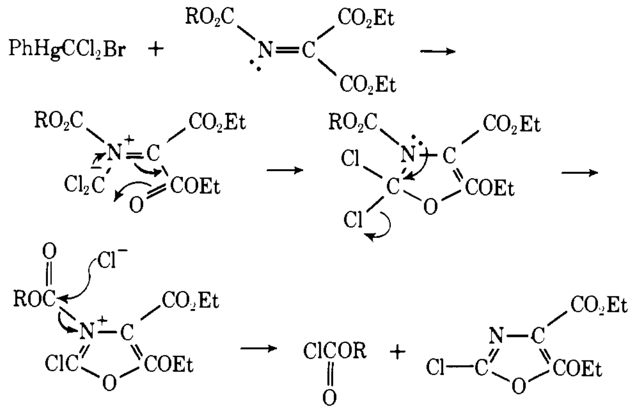
zene at 80° gave the same heterocyclic product (III, a liquid, $n^{25}\text{D}$ 1.4833) in each case (eq 3) in 20–35% yield.


(3)

III

Spectral studies suggested that III was 2-chloro-4-carboethoxy-5-ethoxy-1,3-oxazole, as indicated. Its proton nmr spectrum showed signals due to two non-equivalent OEt groups and its ir spectrum indicated the presence of C=O, C=C, and C=N functions (bands at 1720, 1620, and 1535 cm^{-1}, respectively). A spectroscopic study of this reaction with R = Me after 4 days at room temperature clearly indicated the presence of an intermediate by its ir absorption at 1630 cm^{-1} ($\nu_{C=C}$). Although the intermediate was not isolated, in view of the isolation of alkyl chloroformate and III as well as the spectral evidence, it is reasonable to explain this reaction also in terms of 1,4(N,O) addition of CCl_2 (Scheme II).

Scheme II



Such 1,4 addition does not appear to occur with $-C=CC=O$ systems. We had observed simple C=C addition of $PhHgCCl_2Br$ derived CCl_2 with methyl acrylate and mesityl oxide[3] and in the present work examined the reaction of $PhHgCCl_2Br$ with diethyl fumarate. In this case, only diethyl 3,3-dichlorocyclopropane-1,2-dicarboxylate was obtained.[4]

Since the presence of a terminal nitrogen atom seems to facilitate 1,4 addition of CX_2 to α,β-unsaturated systems, it seems reasonable to propose that the initial interaction between the substrate and CX_2 (or possibly with $PhHgCX_2Br$ rather than with free CX_2) occurs at the nitrogen atom and that this is followed by ring closure as indicated in Schemes I and II. This 1,4 addition of CX_2 to $-N=NC=O$ and $-N=CC=O$ systems should be capable of further generalization and may find application in the synthesis of heterocyclic systems containing halogen which are difficult to prepare by other routes.

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[3] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

[4] Formal 1,4 addition of CF_2 to a steroidal α,β-unsaturated ketone was reported by P. Hodge, J. A. Edwards, and J. H. Fried, *Tetrahedron Lett.*, 5175 (1966).

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Dietmar Seyferth,* Houng-min Shih
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
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Rotational Diffusion Anisotropy in Near Ellipsoidal Molecules

Sir:

While the symmetrical top formulation[1,2] of dipole–dipole spin relaxation has already received attention in carbon-13 studies,[3–7] Woessner's elegant theoretical treatment of an allipsoidal tumbler has not yet been utilized to interpret carbon-13 relaxation data. To be precise, this formulation requires that the D_{2h} symmetry group of an ellipsoid obtain and that the molecule possess three uniquely different carbon atoms with attached protons whose C–H vectors manifest linearly independent sets of directional cosines. These conditions allow diagonalization of the rotational diffusion tensor and provide sufficient data to specify the three diagonal components. Unfortunately, these conditions are so restrictive as to eliminate any extensive application of the theory, and, therefore, we have approximated ellipsoidal symmetry with molecules of slightly lower symmetry. Investigators should be aware that rotational diffusional tensors of asymmetric tops cannot in general be diagonalized and, therefore, the approximation of ellipsoidal symmetry, which is involved here, may at times be severe. In the hydrocarbon molecules considered, the approximation was felt to be reasonable, however, as no larger electric dipoles exist, heavy atoms are not present to shift greatly the center of mass from the effective epicenter of diffusional rotation, and each molecule is near ellipsoidal in shape.

Nuclear Overhauser enhancements (NOE) and relaxation time data were obtained by methods previously reported from this laboratory.[3–7] The T_1 and NOE values obtained for norbornane, cyclopentene, and *trans*-decalin are given in Table I along with the dipolar relaxation time, T_{1D}, which may be calculated from these two values. A sizable spin–rotation constant for the ethylenic carbon in cyclopentene and the relative small size of this molecule are expected to give a significant spin–rotation contribution, and it is felt that this best explains the reduced NOE value recorded for the ethylenic carbon.[8] Collins, Alger, and Grant[8] also observed similar features in the methylethylenes

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[7] D. M. Grant, E. P. Black, K. A. Christensen, J. R. Lyerla, Jr., and R. J. Pugmire, 13th ENC, Asilomor, Calif., 1972.

[8] S. W. Collins, T. D. Alger, and D. M. Grant, to be submitted for publication.