tween efficiencies and rates might be expected. Therefore we determined the relative *rates* of migration using absorption and fluorescence data according to eq 2,

$$\frac{k_r}{k_{r_0}} = \frac{\Phi_r}{\Phi_{r_0}}\frac{\Phi_{f_0}}{\Phi_f}\frac{k_f}{k_{f_0}} \tag{2}$$

where $k_r \equiv$ rate constant for cyclopropane formation, $\Phi_r \equiv$ quantum yield for cyclopropane formation, $k_f \equiv$ rate constant for fluorescence, and $\Phi_f \equiv$ quantum yield for fluorescence. The results of these determinations are listed in Table I.

It is immediately clear that the polar substituents exert dramatic effects on the rate of cyclopropane formation. Such effects are most pronounced at the styryl migration terminus as may be seen by comparing **1a**, **d**, and **e**. Decreasing the electron density at the migration terminus (**1a**) greatly enhances the rate of migration. Conversely, increasing the electron density at C-2 (**1e**) drastically lowers the rate. On the other hand, substituent effects on the migrating group are not nearly so large but are still quite evident. It is seen that both a *p*-methoxy (**1b**) and a *p*-cyano (**1c**) increase the rate of rearrangement of a phenyl group relative to the unsubstituted compound **1d**.

The pattern of substituent effects observed for **1a**, **d**, and **e** is seen to be strikingly analogous to that predicted for ground-state phenyl migration from one carbon atom to an adjacent carbon center, where the migration is predicted to become less favorable as the migration terminus goes from cationic to radical-like to anionic.[13] The excited state migration appears to be sensitive to the same effects of charge density. In the cases **1b**, **c**, and **d**, one would expect the migration terminus to show predominantly odd-electron character. (The excitation is initially largely localized in the nonpolar styryl portion of the molecule.) The relative migratory aptitudes observed are indeed consistent with and support this view.[14] Indeed the pattern observed is quite similar to that seen in other photochemical reactions where odd-electron reaction centers seem to be involved.[7] The faster rate of migration of a *p*-methoxyphenyl (**1b**) as compared to a *p*-cyanophenyl (**1c**) may be an indication that polar effects play a role here also.

While this is the only study of which we are aware of ring substituent effects on the di-π-methane rearrangement, it is perhaps relevant to point out that polar solvent effects have been noted previously by Zimmerman and Samuelson.[15] Thus, the efficiency of rearrangement of 4,4-diphenyl-1-methylenecyclohexene to cyclopropane was twice as great in methanol as in cyclohexane. These separate observations may be related.

It is interesting and gratifying that the observed substituent effects appear to be easily and logically interpreted as has been found to be the case for excited state transformations of ketones[7] and recently for cyclopropanes.[8] With this encouragement we are expanding our investigation of structure–reactivity relationships in olefin photochemistry.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Received December 1, 1971

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(13) H. E. Zimmerman and A. Zweig, *J. Amer. Chem. Soc.*, **83**, 1196 (1961).

(14) For a discussion of the assumptions involved see ref 7. The situation regarding energy localization and correlation of excited-state and ground-state reactivities is quite analogous in the two cases.

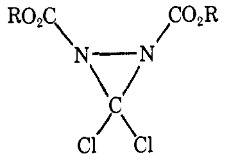
(15) H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **91**, 5307 (1969).

New Reactions of Phenyl(trihalomethyl)mercury Compounds. Dihalocarbene Addition to Azodicarboxylate Esters

Sir:

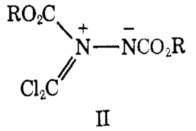
We describe here the novel course of the first reported reaction of dihalocarbenes with compounds containing an N=N bond, the azodicarboxylate esters. Recent studies in these laboratories have shown that the phenyl(trihalomethyl)mercury reagents react not only with compounds containing C=C and C≡C bonds,[1] but also with compounds containing C=N,[2,3] C=S,[3,4] and C=O[5] bonds. We have extended these studies to compounds containing N=N bonds.

When a mixture of 20 mmol of $PhHgCCl_2Br$ and 26 mmol of $EtO_2CN{=}NCO_2Et$ in benzene solution was stirred and heated under nitrogen for 3 hr, the orange color of the reaction mixture gradually was discharged and phenylmercuric bromide (98% yield) precipitated. The filtered benzene solution was shown by glc to contain a single product (87% yield), which was isolated by distillation (bp 88° (0.24 mm), $n^{25}D$ 1.4730). Its analysis (C, H, N, Cl) indicated the composition $C_7H_{10}O_4N_2Cl_2$. In its mass spectrum (at 70 eV) the largest fragment corresponded to $C_7H_{10}O_4N_2Cl^+$, most probably the $(M - Cl)^+$ species. Addition of CCl_2 to the azodicarboxylate ester thus had been achieved, and a similar reaction was observed with $MeO_2CN{=}NCO_2Me$ to give a product of composition $C_5H_6O_4N_2Cl_2$ in good yield. These products, however, were *not* the expected diaziridines I. The ir spectrum

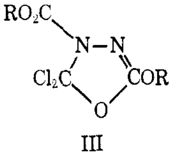


I

of the $EtO_2CN{=}NCO_2Et$-derived product showed, in addition to the ester carbonyl bands at 1805 and 1770 cm⁻¹, a band at 1590 cm⁻¹ assignable to a C=N stretching vibration. This product also showed absorption in the ultraviolet region, $\lambda_{max}^{cyclohexane}$ 238 nm (ε 1655). Three structures isomeric with I were given further consideration: II, III, and IV. Structures II and



II



III

$(RO_2C)_2NN{=}CCl_2$

IV

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(1) D. Seyferth, *Accounts Chem. Res.*, **5**, 65 (1972).

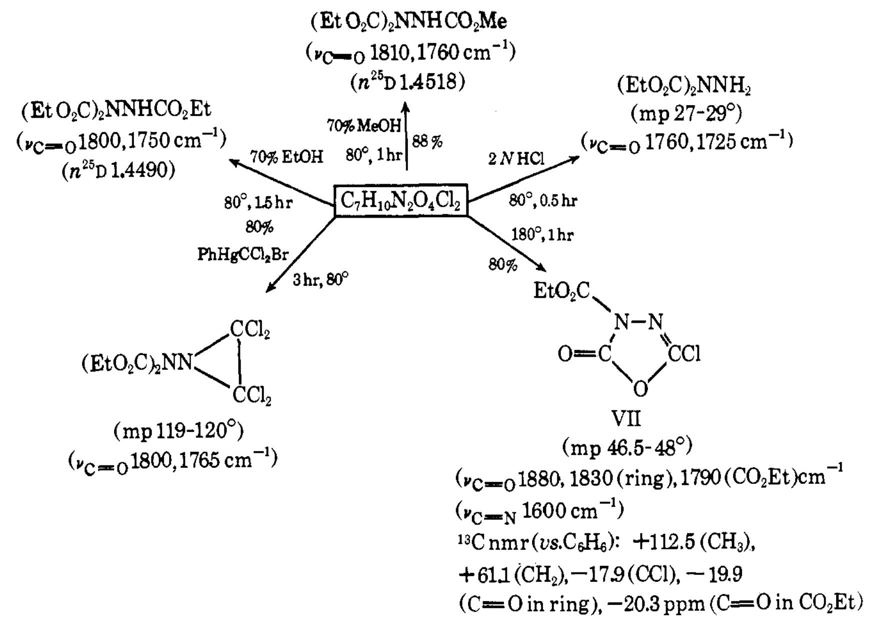
(2) D. Seyferth and W. Tronich, *J. Organometal. Chem.*, **21**, P3 (1970).

(3) D. Seyferth, R. Damrauer, H. Shih, W. Tronich, W. E. Smith, and J. Y.-P. Mui, *J. Org. Chem.*, **36**, 1786 (1971).

(4) D. Seyferth and W. Tronich, *J. Amer. Chem. Soc.*, **91**, 2138 (1969).

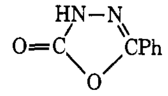
(5) D. Seyferth and W. Tronich, *J. Organometal. Chem.*, **18**, P8 (1969).

Chart I



III could be ruled out on the basis of the ^{1}H nmr spectra of both products (R = Me and Et), which showed only single resonances due to equivalent CO_2Et or CO_2Me groups.[6]

Further evidence supported IV as the structure of the isolated products. For compounds of type $RN{=}CCl_2$, where R is a rather electronegative group (Cl, CH_3SO_2, $Cl_2C{=}N$, CF_3), $\nu_{C=N}$ is observed between 1560 and 1610 cm^{-1},[8] and our observed $\nu_{C=N}$ of 1590 cm^{-1} falls within this range. The ^{13}C nmr spectrum ($CHCl_3$ solvent) of the $MeO_2CN{=}NCO_2Me$-derived product (Bruker HFX-10 connecting with a Digilab NMR/FTS-3 data system) showed *one* upfield (from benzene) signal at +74.1 ppm (CH_3) and two downfield signals at −21.1 (C=O) and −17.5 ppm (=CCl_2), in agreement with structure IV. Chemical studies which are summarized in Chart I also provide confirmation of the spectroscopic data which support structure IV for the product of the $EtO_2CN{=}NCO_2Et$–$PhHgCCl_2Br$ reaction. The solvolysis reactions indicated are characteristic of imidoyl dichlorides,[9] and the reactions with methanol and 2 *N* HCl suggest that both CO_2Et groups in the compound in question are geminal rather than vicinal. The addition of CCl_2 to the C=N bond of $RN{=}CCl_2$ compounds is a known reaction.[2] The pyrolysis product, VII, is readily rationalized in terms of the known chemistry of hydrazonoyl halides. For instance, the thermolytic conversion of $EtO_2CNHN{=}C(Cl)Ph$ to VIII has been described.[10]



VIII

The products isolated from the $RO_2CN{=}NCO_2R$–$PhHgCCl_2Br$ reactions cannot be those formed initially, and to obtain further information concerning the reaction course, we followed the progress of the slow reaction between this organomercury reagent and $MeO_2CN{=}NCO_2Me$ at room temperature in CCl_4 solution by means of nmr (^{1}H and ^{13}C) and ir spectroscopy. The ^{1}H nmr spectra in Figure 1 are illustrative.

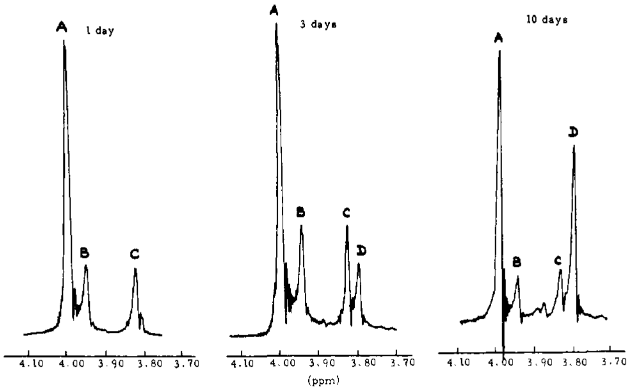


Figure 1. ^{1}H nmr spectra (60-MHz) of the reaction mixture of $PhHgCCl_2Br$ + $MeO_2CN{=}NCO_2Me$ at room temperature in CCl_4.

The resonance A is due to the CH_3 protons of the starting azo compound. After 1 day, two new signals,

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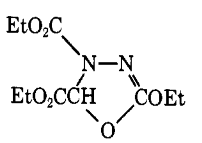
[6] That it was a matter of equivalent CO_2R groups, not of accidentally coincidental chemical shifts of nonequivalent alkoxy groups, was suggested by the nmr spectra of two model compounds for the most likely product structures, V and VI, synthesized by the procedure



V

$(EtO_2C)_2NN{=}CHCO_2Et$

VI

of Fahr, *et al.*[7] In the spectrum of V three different ethoxy group resonances were observed; in the spectrum of VI only two ethoxy group resonances in a 2:1 ratio were apparent.

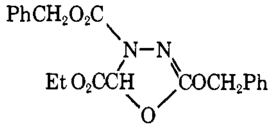
[7] E. Fahr, K. Königsdorfer, and F. Scheckenbach, *Justus Liebigs Ann. Chem.*, **690**, 138 (1965).

[8] (a) E. Kühle, B. Anders, and G. Zumach, *Angew. Chem.*, **79**, 663 (1967); (b) W. P. Trompen, J. Geevers, and J. Th. Hackmann, *Recl. Trav. Chim., Pays-Bas*, **90**, 463 (1971); (c) H. Hagemann, D. Arlt, and I. Ugi, *Angew. Chem.*, **81**, 572 (1969); (d) R. C. Dobbie and H. J. Emeleus, *J. Chem. Soc. A*, 933 (1966).

[9] E. Kühle, *Angew. Chem.*, **81**, 18 (1969).

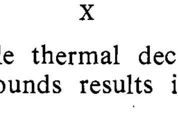
[10] T. Bacchetti, *Gazz. Chim. Ital.*, **91**, 866 (1961).

B and C, are observed. These continue to increase in area, but another signal, D, due to the CH_3 groups of $(CH_3O_2C)_2NN{=}CCl_2$, the final product, appears as the reaction progresses and grows at the expense of B and C. Clearly, an intermediate with nonequivalent OMe groups is formed initially and rearranges at room temperature to the final product. Similar information was obtained from the ^{13}C nmr spectra of such reaction mixtures; the intermediate showed *two* different *C*OMe and CH_3 carbon resonances (−25.8 and −23.1 ppm; +70.9 and +72.2 ppm, *vs.* C_6H_6). In an experiment where ir spectroscopy was applied, it was seen that the formation of the intermediate correlated with the growth of a band at 1640 cm^{-1} ($\nu_{C=N}$). This band disappeared with time with concomitant formation of a new band at 1580 cm^{-1} ($\nu_{C=N}$ of $(MeO_2C)_2NN{=}CCl_2$). Although we have not yet been able to isolate these intermediates, the most likely structure which accounts for the data presented is III. The facile rearrangement of III to IV finds precedent in the thermal isomerization of IX to $(PhCH_2O_2C)_2NN{=}CHCO_2Et$.[7]


IX

The reactive species which interacts with the azodicarboxylate ester could be either $PhHgCCl_2Br$ or CCl_2 formed in its decomposition. That it is the latter is made likely by the observation that decarboxylation of CCl_3CO_2Na in the presence of $EtO_2CN{=}NCO_2Et$ in refluxing 1,2-dimethoxyethane also gave IV (R = Et) in 69% yield. In terms of the final products obtained, there is a striking similarity between the reactions of azodicarboxylate esters with dihalocarbenes and diazoalkanes.[7,11] However, we wish to emphasize that quite different reactions are involved. In the case of the latter reagents, direct attack of the diazoalkane *as a carbon nucleophile* at an azo ester nitrogen atom (rather than a carbene mechanism) was established.[7] With the dihalocarbenes, we no doubt are dealing with an initial attack by these *as electrophiles* at nitrogen. It may well be that II is a transitory, nonobservable intermediate formed in the initial attack by CCl_2 at a nitrogen atom of the azodicarboxylate ester. None of our evidence speaks in favor of the formation of I as a stable intermediate, but it cannot be excluded as a transitory intermediate.

Similar reactions between azodicarboxylate esters and $PhHgCClBr_2$ and $PhHgCBr_3$ have been observed, but the $(RO_2C)_2NN{=}CClBr$ and $(RO_2C)_2NN{=}CBr_2$ products formed are less stable thermally than $(RO_2C)_2NN{=}CCl_2$. Thermolysis of the dibromide gives X


X

in good yield, while thermal decomposition of the chlorobromo compounds results in a 10:1 mixture of VII and X. This new route to the difficult-to-prepare 2-halo-1,3,4-oxadiazolin-5-ones may well find useful application in synthetic chemistry.

Our studies of reactions of phenyl(trihalomethyl)mercury compounds with azo compounds are continuing. In the case of azobenzene, a completely different reaction course is observed. Depending upon the reagent stoichiometry, the major product is either $PhN{=}CCl_2$ (azobenzene in excess) or 1-phenyl-2,2,3,3-tetrachloroaziridine (mercurial in excess). Such reactions with azoarenes, however, are not clean reactions, and the yields of these products under optimum conditions do not exceed 40–50%.

Acknowledgments. The authors are grateful to the U.S. Air Force Office of Scientific Research for generous support of this research (Grants AF-AFOSR-70-1971 and AF-AFOSR-72-2204) and to Dr. D. D. Traficante for assistance in obtaining ^{13}C nmr spectra.

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Carbon-13 Fourier Transform Nuclear Magnetic Resonance Study of Some Porphyrins. Evidence for a Preferred Delocalization Pathway

Sir:

The application of Fourier transform techniques[1] for the observation of ^{13}C in natural abundance has extended the range of accessible biological systems.[2,3]

Porphyrins are a class of compounds which are extremely important, both from biological and theoretical standpoints, but whose natural abundance ^{13}C spectra would be difficult to observe by continuous-wave methods. The understanding of porphyrin ring currents through proton magnetic resonance studies is frequently complicated somewhat by the dependence of proton chemical shifts on aggregation and solvation effects.[4] This complication is not expected to arise with ^{13}C nmr studies because ^{13}C chemical shifts are largely determined by the paramagnetic screening term.[5] Any through-space screening is likely to be of only minor importance, making ^{13}C chemical shifts ideally suited for probing the electronic structure of the porphyrin ring. Here we report ^{13}C chemical shift data which strongly support the concept that the main pathway of electron delocalization is the inner 16-membered ring of the porphyrin skeleton.[4c,4d,6]

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