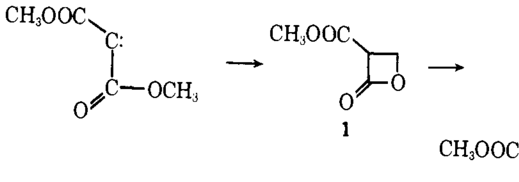
Gas-Phase Pyrolysis of Methyl Diazomalonate Wolff Rearrangement of Biscarbomethoxycarbene[1]

Sir:

Until rather recently, the Wolff rearrangement of carboalkoxycarbenes was a neglected reaction.[2] Attention has now turned to this process and mechanistic information has been forthcoming from Schenck and Ritter,[3] Westheimer and coworkers,[4,5] and most recently from Strausz and his collaborators.[6–11] The importance of oxirenes in the Wolff rearrangement of diazoacetates has been stressed[8,10,11] and intermediate alkoxyketenes have been trapped.[9] So far, however, the Wolff rearrangement of carboalkoxycarbenes has been observed only on photolysis, and the absence of the thermal reaction has been thrice noted.[9,10,11a]

We report here the preliminary results of our investigations of the gas-phase pyrolysis of methyl diazomalonate and demonstrate that the thermal Wolff rearrangement is an important process. Pyrolyses were conducted under vacuum by evaporating methyl diazomalonate through an empty quartz tube into a trap cooled to 77°K. Product analysis was by a combination of nmr spectroscopy and gas chromatography. The products of the pyrolysis were not interconverted under the reaction conditions.

At temperatures up to 260° methyl diazomalonate was recovered unchanged. At 280° methyl acrylate was by far the major product, although small amounts of methyl acetate and methyl vinyl ether were also visible. The source of the acrylate is very likely a reaction so far undetected in solution,[12–14] insertion into the carbon–hydrogen bond of the *O*-methyl group to give the *β*-lactone **1**, which cleaves to give carbon dioxide and methyl acrylate. Cleavages of *β*-lactones at elevated temperatures are known,[15] and stable lactones have been isolated from irradiations of *tert*-butyl diazoacetate and *tert*-amyl diazoacetate[16] as well as from the thiobenzophenone-sensitized decomposition of ethyl diazomalonate.[17] Lactams have been made from diazoamides as well.[18]



At higher temperatures methyl pyruvate appeared along with methyl acetate, and methyl vinyl ether became a major product. We attribute the formation of the ether to Wolff rearrangement to ketene **2**, followed by loss of carbon monoxide to give the new carbene **3**. Self-insertion followed by loss of carbon dioxide gives methyl vinyl ether. Again the easiest reaction for the carbene seems to be intramolecular carbon–hydrogen insertion. By 400° methyl acetate and methyl pyruvate were present in substantial amounts. The overall yield of products varies little from 420 to 540° and is *ca.* 65% based on carbene. Table I gives the product composition as a function of temperature.

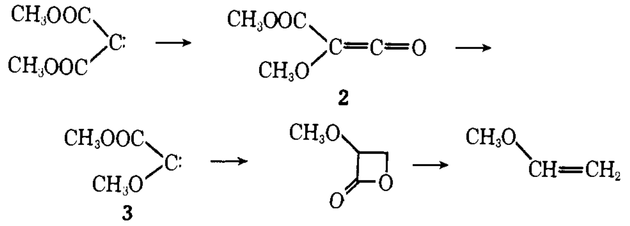
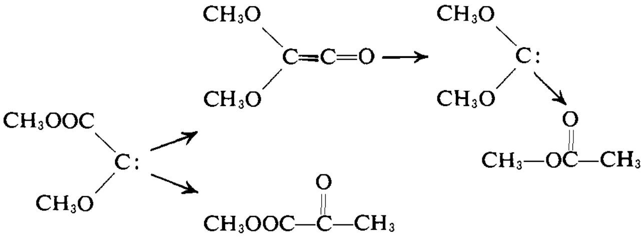


Table I. Variation of Products (%) of Methyl Diazomalonate Pyrolysis with Temperature

Temp, °C	Methyl pyruvate	Methyl acrylate	Methyl acetate	Methyl vinyl ether
280	0	92	3	5
300	0	72	8	20
330	6	51	12	31
360	3	38	7	52
390	7	29	8	56
420	7	32	8	52
450	6	35	8	51
480	7	29	9	54
500	6	30	8	57
540	8	30	9	53

Two high-temperature reactions of carbene **3** become apparent. These are further Wolff rearrangement to dimethoxyketene, which gives dimethoxycarbene and, ultimately, methyl acetate, and carbon–oxygen insertion to give methyl pyruvate. The formation of methyl acetate from dimethoxycarbene has been proposed previously.[19]



Thus the evidence for the thermal Wolff rearrangement of biscarbomethoxycarbene is very strong. In

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(2) For reviews, see W. E. Bachman and W. S. Struve, *Org. React.*, **1**, 38 (1942); F. Weygand and H. S. Bestmann, *Newer Methods Prep. Org. Chem.*, **3**, 451 (1964).

(3) G. O. Schenck and A. Ritter, *Tetrahedron Lett.*, 3189 (1968).

(4) J. Shafer, P. Baronowsky, R. Lausen, F. Finn, and F. H. Westheimer, *J. Biol. Chem.*, **241**, 421 (1965).

(5) H. Chaimovich, R. J. Vaughan, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **90**, 4088 (1968).

(6) O. P. Strausz, T. DoMinh, and H. E. Gunning, *ibid.*, **90**, 1660 (1968).

(7) I. G. Csizmadia, J. Font, and O. P. Strausz, *ibid.*, **90**, 7361 (1968).

(8) T. DoMinh, O. P. Strausz, and H. E. Gunning, *ibid.*, **91**, 1261 (1969).

(9) T. DoMinh and O. P. Strausz, *ibid.*, **92**, 1766 (1970).

(10) D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *ibid.*, **92**, 1768 (1970).

(11) G. Frater and O. P. Strausz, *ibid.*, **92**, 6654 (1970).

(11a) Note Added in Proof. See also J. Gelhaus and R. W. Hoffmann, *Tetrahedron*, **26**, 5901 (1970), who note the lack of Wolff rearrangement of 3 at 140°.

(12) M. Jones, Jr., A. Kulczycki, Jr., and K. F. Hummel, *Tetrahedron Lett.*, 183 (1967).

(13) M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *ibid.*, 1391 (1967).

(14) M. E. Hendrick, unpublished work.

(15) R. Wheland and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 6057 (1970).

(16) W. Kirmse and H. W. Bucking, *Tetrahedron Lett.*, 1833 (1967).

(17) J. A. Kaufman and S. J. Weininger, *Chem. Commun.*, 593 (1969).

(18) R. R. Rando, *J. Amer. Chem. Soc.*, **92**, 6706 (1970).

(19) D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *ibid.*, **88**, 582 (1966).

addition, a rough ordering of the relative ease of the intramolecular reactions of these carbenes is possible. Insertion into the carbon–hydrogen bonds of the neighboring *O*-methyl group is most favored, and Wolff rearrangement appears to be preferred to carbon–oxygen insertion, as **3** forms methyl acetate slightly faster than methyl pyruvate.

At temperatures at which products attributed to **2** appeared so did a white polymer. Formation of the polymer set in at about 280° and ceased by 360°. The material is not polyacrylate and has only methoxy signals in its nmr spectrum. It is tempting to speculate that it is poly-**2**, but so far all our attempts to isolate the monomer have been futile.

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Kinetics and Mechanism of Sulfur Dioxide Insertion into Carbon–Tin Bonds

Sir:

Although sulfur dioxide has been demonstrated to be a remarkably versatile inserting agent into carbon–metal bonds,[1] almost no information is available concerning the mechanistic details of these reactions.[2] We now wish to present the results of the first kinetic study of SO_2 insertion, which strongly supports the view that insertion into aryl carbon–tin bonds is an electrophilic sulfidestannylation.

The rates of insertion of a series of meta- and para-substituted phenyltrimethylstannanes in anhydrous methanol at 30° were measured by observing the decrease in intensity with time of the sharp $(CH_3)_3Sn$ resonance (*ca.* τ 10) of the starting compound, and the concomitant appearance of the lower field (by *ca.* 18 Hz at 60 MHz) $(CH_3)_3Sn$ resonance of the product. Details of such spectra and other physical properties of the insertion products have been previously described.[3]

For all compounds studied, clean second-order kinetics, first order in stannane and in SO_2, were observed for at least two half-lives, and for the parent compound phenyltrimethylstannane, at 30°, $k_2 = 1.97 \times 10^{-3}$ l. mol^{-1} sec^{-1}. From the temperature dependence of k_2, $\Delta S^{\ddagger} = -31$ eu and $\Delta H^{\ddagger} = 7.38$ kcal mol^{-1} were derived. The pronounced negative character of $\Delta S^{\ddagger}$ is expected for an insertion reaction, where considerable loss of vibrational and translational freedom occurs on passing to the transition state.[4] Solvent reorganization could contribute significantly to this term. The rate of SO_2 insertion can be directly compared with values for protodestannation[5,6] and halodestannation[7,8] in the same solvent, $CH_3COOH < SO_2 < HCl \ll I_2 \ll Br_2$, and on this basis SO_2 exhibits moderate electrophilic capability.

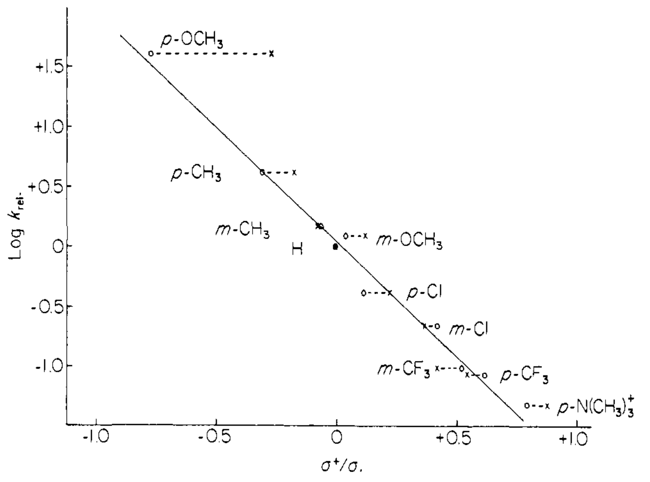

Figure 1. Plot of log k_{rel} *vs.* σ^+ (O) and σ (X).

For the meta- and para-substituted $Y\text{-}C_6H_4Sn(CH_3)_3$ (Y = *m*- and *p*-OCH_3, *m*- and *p*-CH_3, *m*- and *p*-Cl, *m*- and *p*-CF_3, and *p*-$N^+(CH_3)_3$) the rate is enhanced relative to the parent by net electron-donating substituents and retarded by net electron-withdrawing groups; log k_{rel} $(= k_{Y\text{-}C_6H_4Sn(CH_3)_3}/k_{C_6H_5Sn(CH_3)_3})$ correlates well with σ^+ ($r = 0.992$), as expected for an electrophilic aromatic substitution.[9] The correlation with σ ($r = 0.929$) (see Figure 1) is clearly of a lower order. The ρ value of -1.87 is similar to but significantly lower than those found for proto ($\rho = -2.17$)[6] and iodo[7] ($\rho = -2.54$) destannylations. The ρ value indicates a very moderate sensitivity to substituents and a low level of electron demand at the reaction site, with modest perturbation of the π-electron system. It would seem that the transition state for sulfidetrimethylstannylation would poorly approximate the classical σ intermediate for electrophilic aromatic substitution being more akin to starting state.

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(1) W. Kitching and C. W. Fong, *Organometal. Chem. Rev., Sect. A*, 5, 281 (1970).

(2) Wojcicki and coworkers have synthesized optically active π-$C_5H_5Fe(CO)_2CH(CH_3)C_6H_5$, $[\alpha]^{24}_{546}$ +77.3°, which yields, on reaction with SO_2, π-$C_5H_5Fe(CO)_2\cdot SO_2\cdot CH(CH_3)C_6H_5$, $[\alpha]^{24}_{546}$ −159°. This result could indicate a substantially stereospecific insertion, but whether inversion or retention is involved is not known: A. Wojcicki, J. J. Alexander, M. Graziani, J. E. Thomasson, and F. A. Hartmann, Abstracts, Symposium on Metal Carbonyls, Venice, Italy, Sept 1968.

(3) C. W. Fong and W. Kitching, *J. Organometal. Chem.*, 22, 95 (1970).

(4) For insertion of CO into $CH_3Mn(CO)_5$ to yield $CH_3COMn(CO)_5$, $\Delta S^{\ddagger} = -21$ cal deg^{-1} mol^{-1} has been reported: F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, 1, 31 (1962); but see also R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, 4, 331 (1970). We thank a referee for alerting us to this report.

(5) J. Nasielski, O. Buchman, M. Grosjean, and M. Jauquet, *J. Organometal. Chem.*, 19, 353 (1969).

(6) O. Buchman, M. Grosjean, and J. Nasielski, *Helv. Chim. Acta*, 47, 1679 (1964).

(7) O. Buchman, M. Grosjean, and J. Nasielski, *ibid.*, 47, 1695 (1964).

(8) P. Alcais and J. Nasielski, *J. Chim. Phys. Physicochim. Biol.*, 66, 95 (1969).

(9) We have elected to use $\sigma^+ = 0.80$ for *p*-$N^+(CH_3)_3$, which is the σ^n value, rather than the quoted [H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 80, 4979 (1958)] value, $\sigma^+ = 0.41$, which appears unreasonably low. (See J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 204.) A study of protodestannation of tricyclohexylarylstannanes [C. Eaborn and J. A. Walters, *J. Chem. Soc.*, 542 (1961)] indicates that $\sigma^+ = 0.7$ would be a better value. There appears no good reason why σ^+ should be drastically different from σ^n for $(CH_3)_3N^+$, although problems do arise for charged substituents. However, even using $\sigma^+ = 0.41$, an acceptable correlation ($r = 0.974$) is still obtained.