a zero-field parameter with matrix.[10] The 50% decrease in E with increasing temperature contrasted with the 12% decrease in D also supports the conclusion that nonzero E's arise from environmental perturbations of an $E = 0$ system. At the higher temperatures, lattice expansion should allow the guest methylene to assume its preferred geometry. In anthracene as a host it was observed that $E \cong 0$ for all temperatures ($-196°$ to $+160°$C) with $E < 0.0003$ cm^{-1} in the upper half of the range. Thus the deviation from collinearity at the central carbon atom is not more than 9°.[1]

The one structure which is at all reasonable for $E = 0$ is I. This is the analog of the structure originally postulated for diphenylmethylene by Skell,[11] but which differs from those observed for that species.[3–5] Structure I for 9,9′-dianthrylmethylene may be rationalized by noting that there is extensive delocalization of the unpaired electrons into the anthryl portions. The extensive π bonding converts the methylene carbon into the central atom of a linear allene. The substituents at either end of the central three-carbon-atom group then lie in perpendicular planes.

Evidence for this extensive delocalization of the unpaired electrons is found in the low D's observed with I. Methylene should have $D_{\mathrm{CH_2}} \approx 0.76$ cm^{-1},[12] while 9-anthrylmethylene has $D = 0.3008$.[6] When one electron is delocalized, D should be proportional to the unpaired spin density of that electron remaining at the carbene carbon; $\rho \sim 0.30/0.76$. If each electron is delocalized into one anthryl residue, we should have $D = \rho^2 D_{\mathrm{CH_2}} \approx (0.30/0.76)^2(0.76) = 0.118$ cm^{-1}, as compared to the observed value (at 4°K) of 0.113.

The linear decrease of D with temperature (Figure 3) may be rationalized by considering the molecule to lie in a two-dimensional harmonic oscillator well. The long (z) axis of the molecule wobbles with increasing temperature. Because of the large mass of I, these oscillatory states are closely spaced, and a classical approximation is appropriate. A linear decrease with T is then predicted. The point at 4°K could lie below the line because of zero-point motion.

The stability of I, the free methylene, is due to the rigidity of the environment and not to an intrinsic lack of reactivity. Solid solutions of I when prepared in viscous glass matrices, such as 2-methyltetrahydrofuran and methylcyclohexane, are stable for many hours at 77°K. On warming with a consequent thawing of the matrix, the signals disappeared irreversibly.

(10) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Chim. Phys.*, **61**, 1663 (1964).

(11) R. M. Elter, H. S. Skovrovek, and P. S. Skell, *J. Amer. Chem. Soc.*, **81**, 1008 (1959).

(12) E. Wasserman, V. J. Kuck, R. S. Hutton, E. D. Anderson, and W. A. Yager, *J. Chem. Phys.*, **54**, 4120 (1971); *ibid.*, **55**, 2593 (1971).

(13) (a) Bell Laboratories; (b) Rutgers University; (c) we gratefully acknowledge financial support, in part, from the Petroleum Research Fund, administered by the American Chemical Society.

E. Wasserman,*[13a,b] **V. J. Kuck,**[13a]
W. A. Yager,[13a] **R. S. Hutton**[13a]
Bell Laboratories
Murray Hill, New Jersey 07974
Rutgers University, School of Chemistry
New Brunswick, New Jersey 08903

F. D. Greene, V. P. Abegg, N. M. Weinshenker[13c]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received July 20, 1971

Furan Formation in the Sensitized Photolysis of Methyl Diazomalonate in Acetylenes[1]

Sir:

Although the copper-catalyzed addition of diazo compounds to acetylenes constitutes an important technique for the synthesis of cyclopropenes,[2–4] studies of the reactions of carbenes with acetylenes have focused on the relative contributions of addition and insertion reactions,[5–7] or have dealt with succeeding transformations of the initially formed cyclopropenes.[8] We have recently reported the formation of indenes from the reaction of diphenylcarbene with acetylenes, a reaction characterized by a remarkable steric dependence.[9] It was of considerable interest to ascertain whether or not this closure to an adjacent unsaturation is a characteristic reaction of triplet carbenes. Biscarbomethoxycarbene can be generated in both the singlet and triplet states,[10–12] and thus seemed an excellent test case. Also the products of the desired reaction, alkyl 2-methoxy-3-carbomethoxyfurans, represent a hitherto unreported substitution pattern for the furan nucleus, giving the reaction obvious synthetic appeal.

The direct photolysis of methyl diazomalonate in 2-butyne afforded the expected cyclopropene **2a**, in 36% yield. Only trace amounts of other products, assumed to be insertion products, were detectable by vpc. Similarly 1-hexyne and 4-octyne afforded **2b** and **2c**, respectively, in comparable yields. The cyclopropenes were identified by elemental analysis and spectra, which agreed well with those of known tri- and tetrasubstituted cyclopropenes.[13]

In sharp contrast, sensitization of the photolysis in 2-butyne with an equimolar amount of benzophenone gave as the major product the furan **3a**, in 43% yield, accompanied by only 9% **2a**. Acetylenes **1b–d** gave entirely analogous results, with the slight variations in the relative yields of furans and cyclopropenes noted in Table I.

Table I. Relative Yields of **2** and **3** from Decompositions of Methyl Diazomalonate in **1**

Acetylene	Decomposition mode	% **2**	% **3**
1a	Direct photolysis	>99	<1
1a	Ph_2CO, photolysis	16	84
1b	Direct photolysis	>99	>1
1b	Ph_2CO, photolysis	10	90
1c	Direct photolysis	>99	>1
1c	Ph_2CO, photolysis	25	75
1c	$CuSO_4$, reflux	>99	>1
1d	Ph_2CO, photolysis	<1	<99

(1) Generous support of this work by the National Science Foundation through Grants GP-12759 and GP-30797X is gratefully acknowledged.

(2) V. Dave and E. W. Warnhoff, *Org. React.*, **18**, 217 (1970).

(3) F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964).

(4) R. Fuks and H. G. Viehe in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969.

(5) M. Vidal, F. Massot, and P. Arnaud, *C. R. Acad. Sci., Ser. C*, **268**, 423 (1969).

(6) H. Lind and A. J. Deutschman, Jr., *J. Org. Chem.*, **32**, 326 (1960).

(7) W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).

(8) H. Dürr, L. Schrader, and H. Seidl, *Chem. Ber.*, **104**, 391 (1971).

(9) M. E. Hendrick, W. J. Baron, and M. Jones, Jr., *J. Amer. Chem. Soc.*, **93**, 1554 (1971).

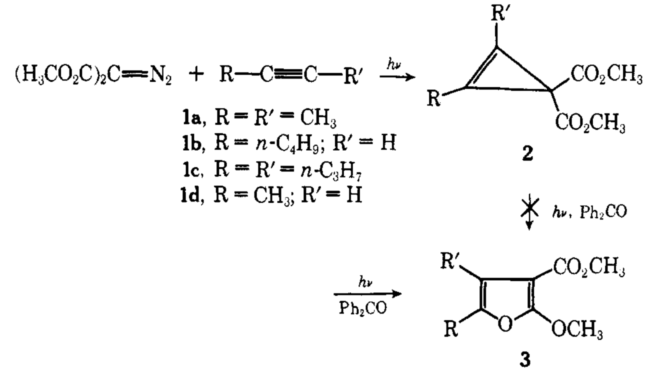
(10) M. Jones, Jr., A. Kulczycki, Jr., and K. F. Hummel, *Tetrahedron Lett.*, 183 (1967).

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

(12) T. C. Neil, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1964.

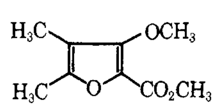
(13) G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 53 (1966).

The furans were primary products of the reaction, as irradiation of authentic cyclopropenes **2a–c** in the presence of benzophenone gave no detectable isomerization to the furans, but resulted only in slow disappearance of the cyclopropenes and formation of a polymeric gum.

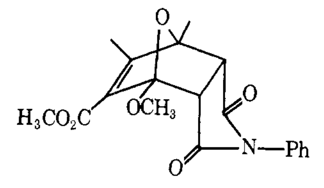


1a, R = R′ = CH_3
1b, R = n-C_4H_9; R′ = H
1c, R = R′ = n-C_3H_7
1d, R = CH_3; R′ = H

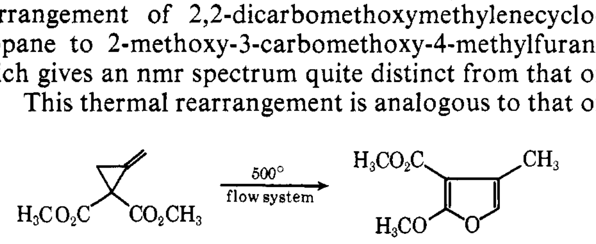
The furans were identified by elemental analysis and spectra. For example, compound **3a** gave the following ^{1}H nmr spectrum: δ 3.97 (s, 3 H), 3.67 (s, 3 H), 2.08 (q, J = 0.7 Hz), 2.00 (q, J = 0.7 Hz). This observed methyl–methyl homoallylic coupling can only be explained by a structure bearing both methyl groups on a double bond,[14] thus reducing the possibilities to the two furans **3a** and **4**. Isomer **4** can be eliminated on the basis of the ir spectrum of **5**, the Diels–Alder adduct with N-phenylmaleimide. This shows a carbonyl absorption at 1705 cm^{-1}, as anticipated for an α,β-unsaturated ester. In **3b** and **3d**, the orientation of the alkyl groups is revealed by the nmr spectra, which exhibit multiplets at δ 6.1, in good agreement with the published values for furan 3-H, but not 2-H, absorptions.[15] A second proof of this orientation is afforded by the thermal rearrangement of 2,2-dicarbomethoxymethylenecyclopropane to 2-methoxy-3-carbomethoxy-4-methylfuran, which gives an nmr spectrum quite distinct from that of **3d**. This thermal rearrangement is analogous to that of 2,2-diphenylmethylenecyclopropane,[16] and a similar rearrangement has been uncovered in the thermal addition of Feist's ester to dimethyl acetylenedicarboxylate.[17]



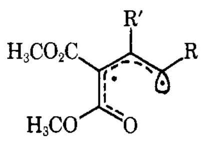
4



5



The course of the triplet carbene reaction can best be ascribed to a cyclization of the diradical **6**. The contrast between this reaction and the addition of triplet biscarbomethoxycarbene to olefins, which fails to give dihydrofurans,[10–11] is most likely due to the additional 27 kcal/mol strain energy of cyclopropene relative to cyclopropane.[13] It is interesting to note that the substitution of bulky groups on the acetylene results in increased closure to cyclopropene but not nearly so dramatically as in the case of diphenylcarbene.[9] This reaction, as are all diazo compound photolyses, is haunted by the specter of reactions of excited diazo compounds. Recently phenylcarbene[18] and 4,4-dimethylcyclohexadienylidene[19] have been shown to possess properties (*i.e.*, relative rate factors and insertion product compositions) independent of precursor. This hints that the photolysis of diazo compounds may generally involve free carbenes.[20]



6

Furan formation has been observed in the CuSO$_4$-catalyzed addition of ethyl diazoacetate to 4-octyne[21] and attributed[22] to a catalyzed rearrangement of the initially formed cyclopropenes. Interestingly, the catalyzed decomposition of methyl diazomalonate in refluxing 4-octyne, using amounts of CuSO$_4$ more than sufficient to induce the rearrangement in the acetate series, afforded only the cyclopropene **2c**. This dichotomy cannot at this moment be fully understood. It may involve the necessity of an α hydrogen, or may be as simple as a stringent steric requirement, which the larger malonate violates. Heterocyclic products have also been detected as in the thermal and catalytic decompositions of other diazo compounds in nitriles and acetylenes,[23–25] but the photolytic decompositions yield no more than traces of the 1,3-dipolar cycloaddition products, and no sensitization experiments have been reported.

We are currently working to determine the scope of this reaction, both with respect to the nature of the diazo compound, and the orientation resulting from unsymmetrical dialkylacetylenes.

Acknowledgment. The author wishes to acknowledge Professor Maitland Jones, Jr., for support of this work and comments on the manuscript, and Dr.

---

(14) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, pp 325–328.

(15) F. A. Bovey, "Nmr Data Tables for Organic Compounds," Vol. 1, Interscience, New York, N. Y., 1967.

(16) M. Jones, Jr., M. E. Hendrick, J. C. Gilbert, and J. R. Butler, *Tetrahedron Lett.*, 845 (1970).

(17) A. C. Day, C. G. Scales, O. J. R. Hodder, and C. K. Prout, *Chem. Commun.*, 1228 (1970).

(18) R. L. Smith, A. Manmade, and G. W. Griffin, *Tetrahedron Lett.*, 663 (1970).

(19) R. H. Levin and M. Jones, Jr., *Tetrahedron*, 27, 2031 (1971).

(20) An alternative mechanism would involve sensitized photolysis of an intermediate pyrazole. Although this cannot be rigorously excluded, the fact that pyrazoles are not formed by methyl diazomalonate and 2-butyne in the dark, coupled with the considerably faster nitrogen evolution on sensitization (pyrazoles are not found when the direct photolyses are stopped short of completion), mitigates against this possibility.

(21) M. I. Komendantov, I. A. D'yakonov, I. Gokhanova, and R. R. Kostikov, *Zh. Org. Khim.*, **1**, 209 (1965), and references therein.

(22) M. I. Komendantov, I. A. D'yakonov, and T. S. Smirnova, *ibid.*, **2**, 559 (1966).

(23) R. Huisgen, G. Binsch, and L. Ghosez, *Chem. Ber.*, **97**, 2628 (1964).

(24) R. Huisgen, H. Sturn, and G. Binsch, *ibid.*, **97**, 2864 (1964).

(25) R. Huisgen, G. Binsch, and H. König, *ibid.*, **97**, 2884 (1964).

J. C. Barborak and Mr. S. F. Martin for helpful comments.

(26) National Science Foundation Predoctoral Fellow, 1967–1971; address correspondence to: Abteilung für Chemie, Ruhr Universität Bochum, 463 Bochum-Querenburg, West Germany.

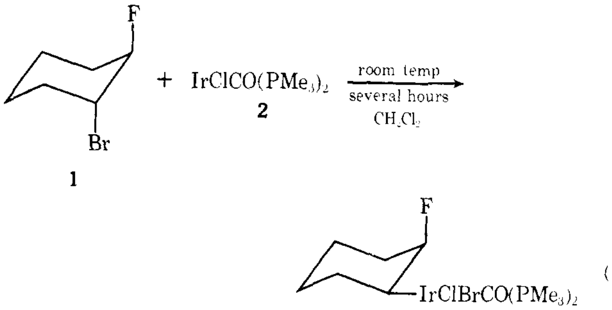
Michael E. Hendrick[26]
Department of Chemistry, Princeton University
Princeton, New Jersey 08540
Received July 15, 1971

A Reinvestigation of the Claimed Oxidative Addition of *trans*-1-Bromo-2-fluorocyclohexane to *trans*-IrClCO(PMe$_3$)$_2$

Sir:

Recently there has been appreciable interest in the stereochemical course of the oxidative addition of alkyl halides to low-valent transition-metal complexes. Because both inversion[1] and retention[2] of configuration at carbon have been reported in reactions with square planar Ir(I) complexes, interest in the reactions of iridium compounds has been especially keen.

Osborn, *et al.*,[1] reported that the addition of *trans*-1-bromo-2-fluorocyclohexane[3] (**1**) to *trans*-IrClCO-(PMe$_3$)$_2$[4] (**2**) occurs with inversion of configuration (eq 1).



(1)

Structural and stereochemical assignments were made spectroscopically (ir and ^{19}F nmr) on reaction mixtures without isolation of products. In the present study, this work (eq 1) has been reinvestigated and in fact it has been found that no reaction occurs at all under the reported or much more severe reaction conditions.

At the time the claimed addition was reported, studies in our laboratory with acyclic halides and Ir(I) complexes indicated such a low order of reactivity that reaction of **1** with **2** (eq 1) would be very surprising. The absence of well-characterized products[1] on which to base the claimed reaction, the low reactivity of Ir(I) observed in our studies, and the current interest in these transformations prompted a reinvestigation of the study.

Under vacuum, *trans*-1-bromo-2-fluorocyclohexane (**1**) (0.25 mmol) in 0.3 ml of CD$_2$Cl$_2$[5] was transferred to an equimolar amount of *trans*-IrClCO(PMe$_3$)$_2$ (**2**) in an nmr tube[5] containing a capillary of TMS as standard and the tube was sealed. A proton nmr spectrum was taken immediately after addition of the reactants and the region containing signals from the residual hydrogens of CD$_2$Cl$_2$ (δ = 5.88) and the protons α to bromine at C-1 (δ 4.54, broad singlet) and α to fluorine at C-2 (δ 5.0, J = 48 Hz, doublet) of the cyclohexyl derivative was time averaged and recorded. The nmr tube was then kept at room temperature for 166 hr and the nmr spectrum recorded periodically.

After 166 hr the reaction mixture still showed the yellow color of the starting Ir(I) complex. During the period of standing: (a) the relative areas of the signal of the residual hydrogens of CD$_2$Cl$_2$ and the signals of the protons of **1** α to bromine and α to fluorine remained constant; (b) the position of the methyl protons of the two PMe$_3$ groups (δ 2.17, J = 4 Hz, triplet) of the starting Ir(I) complex remained unchanged; and (c) no new signals appeared. The nmr tube was then opened; all volatiles were removed under vacuum and collected in a trap. Methyl iodide in CD$_2$Cl$_2$ was added to the dry, yellow Ir complex remaining in the nmr tube. After several minutes the MeI adduct of **2** was formed in 98.5% yield (2PMe$_3$, δ 2.40, J = 4 Hz; IrMe, δ 1.66, J = 6 Hz; ir (CH$_2$Cl$_2$) CO 2030 cm^{-1}). Examination of the volatiles by glpc analysis showed only starting material **1** and solvent.

An attempt was also made to bring about reaction of **2** with *cis*-1-bromo-2-fluorocyclohexane[6] (**3**), but no reaction occurred even after 336 hr at room temperature. (In CD$_2$Cl$_2$, the reaction mixture exhibited: PMe$_3$, δ 2.20, J = 4 Hz, triplet; H$_\alpha$ to bromine at C-1, δ 4.97, broad singlet; H$_\alpha$ to fluorine at C-2, δ 5.10, J = 78 Hz, doublet; external TMS.)

In the claimed observation of reaction 1, the carbonyl-stretching band of **2** at 1935 cm^{-1} was reported to disappear after the addition of **1** while a new band appeared at 2020 cm^{-1}. In our experiments utilizing ordinary ir cells, similar conversions occurred within a few hours. Addition of a controlled amount of oxygen (air) to **2** in the absence of **1** also brings about the observed spectral change in the carbonyl stretching region. Presumably, the reported[1] observations of such a change result from the presence of oxygen. The previous workers also reported the resonance at +88.3 ppm in the ^{19}F spectrum decreases while a new signal centered at +64.2 ppm appears (CF$_3$CO$_2$H as external reference). While we observed the signal at +88.3 ppm, no change in its intensity nor the appearance of a new signal at +64.2 ppm was observed.

An attempt was made to ascertain the reason for the previously reported spectral changes. 1-Fluorocyclohexene (**4**), which could be an impurity in the *trans*-1-bromo-2-fluorocyclohexane (**1**), produced no new products with **2** or with HIrCl$_2$CO(PMe$_3$)$_2$ (**5**) at 25° in CD$_2$Cl$_2$. Chloroform is an impurity in commercial CD$_2$Cl$_2$ and reacts rapidly with **2**. An attempt was made to use unpurified CD$_2$Cl$_2$ to initiate the reported reaction (eq 1) but no oxidative addition of **1** occurred.

While the stereochemistry at carbon for oxidative addition of alkyl halides to Ir(I) complexes may be inversion, it remains to be proven.

Pearson and Muir[2] reported that the addition of optically active CH$_3$CHBrCOOC$_2$H$_5$ to *trans*-IrClCO-(PMePh$_2$)$_2$ occurs with retention of configuration at

---

(1) J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970).

(2) R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970).

(3) A. Bowers, L. C. Ibanes, E. Denot, and R. Becerra, *ibid.*, **82**, 4001 (1960).

(4) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1887 (1968).

(5) All samples were carefully degassed before transfer. Carbon and hydrogen analyses and spectroscopic analyses were correct for all reported compounds. Commercial CD$_2$Cl$_2$ was freed from CDCl$_3$ by vpc before use.

(6) G. Wittig and U. Mayer, *Chem. Ber.*, **96**, 336 (1963).