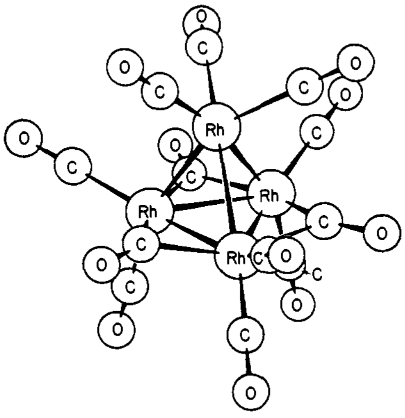
independent tetrahedron of rhodium atoms were to a first approximation interrelated by a mirror plane coincident with the c_b glide plane in the centrosymmetic monoclinic unit cell. Because of this additional pseudomirror plane, the rhodium atoms made no contribution to the calculated structure factors for $\{hkl\}$ with l odd, and the generated space group $P2_1/m$ (obtained from a halving of the c-axis length through omission of the l odd reflections) was used for both the initial least-squares refinement[13,14] of the rhodium atoms and the subsequent Fourier synthesis phased on the rhodium atoms only. Hence, this first approximation to an electron-density map contained mirror-image peaks in addition to any peaks which possibly represented actual carbon and oxygen atoms. From stereochemical considerations supplemented by knowledge of the structure of $Co_4(CO)_{12}$, initial carbonyl position were obtained. Since the contribution of these light atoms to the calculated structure factors destroyed the quasi-mirror symmetry imposed by the rhodium atoms, all further Fourier maps and least-squares refinements[13,14] were based on the original monoclinic $P2_1/c$ space group with the inclusion of all diffraction data. These atom-seeking procedures were reiterated twice before all 24 light atoms were located. Final unweighted discrepancy values[15] based on isotropic full-matrix least-squares refinement[13,14] were $R_1(F)_T = 0.10$ and $R_1(F^2) = 0.17$.

In contrast to the disordered crystalline structure of $Co_4(CO)_{12}$ for which coherent scattering interference must occur, our crystalline samples of $Rh_4(CO)_{12}$ conform to an incoherent twinning model. However, the derived molecular structure of $Rh_4(CO)_{12}$ possesses a configuration strikingly similar to that of $Co_4(CO)_{12}$. Its idealized structure (Figure 1) of C_{3v}-3m symmetry consists of four tetrahedrally arranged rhodium atoms in which an apical $Rh(CO)_3$ group is symmetrically coordinated by only Rh–Rh bonds to a basal $Rh_3(CO)_9$ fragment containing three identical $Rh(CO)_2$ groups located at the vertices of an equilateral triangle and linked in pairs to one another by both a bridging carbonyl group and a Rh–Rh bond. The twelve CO groups are disposed at corners of an icosahedron which encompasses the tetrahedron of rhodium atoms. Of particular interest is the dissimilarity of this molecular structure with that of $Ir_4(CO)_{12}$ for which the idealized tetrahedral molecule of T_d-$\bar{4}3m$ symmetry is stabilized by Ir–Ir bonds only (without bridging carbonyls).[4] This difference in structural type is the first proven case for corresponding metal carbonyls of the second- and third-row transition metal members of a group.



$Rh_4(CO)_{12}$

Figure 1. Molecular configuration of $Rh_4(CO)_{12}$.

The six Rh–Rh bonding distances in $Rh_4(CO)_{12}$ range from 2.70 to 2.80 A (individual esd, 0.01 A) with no apparent difference in length between the three carbonyl-bridged basal–basal Rh–Rh bonds and the three apical–basal Rh–Rh bonds. The weighted average Rh–Rh value of 2.73 A is 0.24 A longer then the average Co–Co bond length of 2.49 A (individual esd, 0.02 A) in $Co_4(CO)_{12}$ and 0.05 A longer than the average Ir–Ir bond length of 2.68 A (individual esd, 0.02 A) in $Ir_4(CO)_{12}$. It falls within the range of average Rh–Rh bond lengths observed in $[C_5H_5RhCO]_3$ (2.62 A),[16] $(C_5H_5)_2Rh_2(CO)_3$ (2.68 A),[16] rhodium metal (2.69 A),[17] and $Rh_6(CO)_{16}$ (2.78 A).[18] The average values for the other molecular parameters of $Rh_4(CO)_{12}$ are not unlike those in these other rhodium carbonyl complexes.

Acknowledgments. The use of CDC 1604 computers both at the University of Wisconsin Computing Center (made possible by financial support from NSF and WARF) and at the ORNL Computing Center is gratefully acknowledged. The authors are indebted to Drs. J. R. Einstein, W. R. Busing, and H. A. Levy of ORNL for helpful discussions.

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(13) The function minimized was $\Sigma w[|F(hkl)_o|^2 - s^2|F(hkl)_c|^2]^2$, where s is the adjusted scale factor.

(14) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1962.

(15) (a) For a twinned composite

$$R_1(F)_T = \frac{\Sigma\{||F(hkl)_{o'}| - s|F(hkl)_{c'}|| + ||F(\bar{h}kl)_{o'}| - s|F(\bar{h}kl)_{c'}||\}}{\Sigma\{|F(hkl)_{o'}| + |F(\bar{h}kl)_{o'}|\}}$$

(b) $$R_1(F^2) = \frac{\Sigma||F(hkl)_o|^2 - s^2|F(hkl)_c|^2|}{\Sigma|F(hkl)_o|^2}$$

(c) For X-ray photographic data the usual unweighted $R_1(F)$ value for an untwinned crystal is normally about one-half the unweighted $R_1(F^2)$ [*cf.* G. M. Brown, *Acta Cryst.*, 20, 921 (1966)]. The observed discrepancy factors are within an acceptable range for a successful structural determination and thereby signify that our incoherent twinning model must be essentially correct.

(16) O. S. Mills and E. F. Paulus, *Chem. Commun.*, 815 (1966).

(17) *Cf.* L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, p S9.

(18) E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 1202 (1963).

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A Novel Isomerization in the Diels–Alder Reaction of α-Pyrone and Bis(trimethylsilyl)acetylene

Sir:

Derivatives of α-pyrone have been used to prepare aromatic compounds *via* Diels–Alder reactions with acetylenedicarboxylic acid esters,[1] and we have used the

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(1) (a) K. Alder and H. F. Rickert, *Ber.*, **70**, 1354 (1937); (b) N. P. Shusherina, R. Ya. Levina, and V. M. Shostakovskii, *Zh. Obshch. Khim.*, **29**, 3237 (1959); (c) E. Wenkert, D. B. R. Johnston, and K. G. Dave, *J. Org. Chem.*, **29**, 2534 (1964).

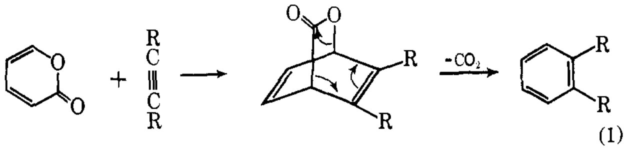
Table I. Comparison of the Isomeric Bis(trimethylsilyl)benzenes with the Main Product of the α-Pyrone + $Me_3SiC{\equiv}CSiMe_3$ Reaction

Compound	Physical state	Glpc retention time,[a] min	$n^{25}D$
ortho isomer	Liquid	11.2	1.5108 (lit.[e] 1.5111)
meta isomer	Liquid	4.5	1.4852 (lit.[e] 1.4867)
para isomer	Solid, mp 95.4–95.5° (lit.[d] 92–93°)	6.5	
Major product	Liquid	4.5	1.4870

	Infrared spectrum,[b] cm^{-1}	Ultraviolet spectrum, mμ (ε)[c]
ortho	3120 (w), 3080 (m), 3050 (m), 2990 (sh, m), 2960 (s), 2905 (m), 1450 (w), 1412 (m), 1300 (w), 1265 (s), 1250 (s), 1167 (w), 1120 (s), 1055 (m), 1040 (m), 1005 (sh, w), 925 (sh, w), 840 (s), 755 (s), 740 (s), 698 (m), 690 (sh, m), 680 (sh, m), 655 (m)	λ_{sh} 222 (9330); λ_{sh} 258 (268); λ_{max} 264 (447); λ_{max} 270 (654); λ_{max} 277.5 (570)
meta	3070 (w), 3040 (w), 3020 (w), 2965 (s), 2900 (w), 1400 (w), 1365 (m), 1305 (w), 1260 (m), 1250 (s), 1175 (vw), 1150 (sh, w), 1140 (w), 1110 (m), 860 (s), 840 (s), 788 (w), 750 (s), 690 (m)	λ_{sh} 252 (113); λ_{max} 258 (189); λ_{max} 264 (276); λ_{max} 269 (266); λ_{max} 275 (179)
para	3050 (m), 2990 (sh, w), 2960 (s), 2895 (w), 1405 (w), 1375 (s), 1345 (w), 1325 (w), 1255 (sh, m), 1245 (s), 1185 (w), 1140 (s), 1130 (s), 1110 (sh, w), 845 (sh, s), 835 (s), 805 (s), 750 (s), 690 (m), 630 (m)	λ_{max} 225 (16,700); λ_{max} 229 (14,500); λ_{sh} 250 (147); λ_{max} 258 (264); λ_{max} 264 (390); λ_{max} 270 (405); λ_{max} 276 (322)
Major product	Identical with that of the *meta* isomer	λ_{sh} 252 (116); λ_{max} 258 (191); λ_{max} 264 (276); λ_{max} 269 (264); λ_{max} 275 (175)

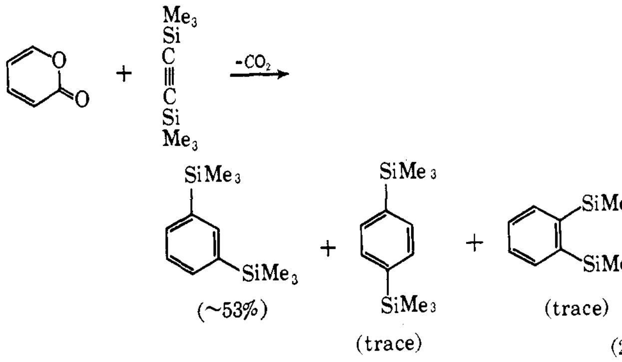
[a] F & M Model 700, 12-ft 20% LAC-728 on Chromosorb W column at 120°, 60-cc/min helium flow. [b] Perkin-Elmer 237B. *ortho* and *meta* isomers determined as liquid films, *para* isomer in CCl_4 (4000–2000 cm^{-1}) and Nujol (2000–625 cm^{-1}). [c] Cary 14, in *n*-hexane solution. [d] A. D. Petrov, E. A. Chernyshev, and L. Guan-lian, *Dokl. Akad. Nauk SSSR*, **132**, 1099 (1960). [e] Reference 5.

reaction of this diene with bis(trimethyltin)acetylene to prepare *o*-bis(trimethyltin)benzene.[2] In these examples the acetylene substituents occupied vicinal positions in the resulting benzene derivative, as might be expected in a process in which loss of carbon dioxide from the initial adduct and aromatization occur in a concerted fashion (eq 1). In view of this simple picture, the results presented in this communication are rather unexpected.



(1)

A solution of α-pyrone (11 mmoles) and bis(trimethylsilyl)acetylene (14.8 mmoles) in 2 ml of bromobenzene was heated at reflux (135–145°) under argon for 4.5 days. Distillation of the reaction mixture gave 1.3 g (53%) of liquid, bp 32° (0.1 mm), which glpc analysis showed to contain one major component in addition to trace quantities of three others. The major component gave the correct analysis for $C_{12}H_{22}Si_2$, but it was *m*-bis(trimethylsilyl)benzene rather than the expected *ortho* isomer (eq 2). Identification of the major product as the *meta* isomer is based upon comparison of its glpc retention time, refractive index, and infrared, nmr, and ultraviolet spectra with those of authentic samples of the three isomeric bis(trimethylsilyl)benzenes. These, all known compounds,[3] were prepared by the Barbier procedure.[4] Pertinent data are given in Table I. The minor products, presumed to be the *ortho* and *meta* isomers, were present in too small a quantity to permit their isolation, and their identification is based on glpc retention time only. It is important to note that the *ortho* isomer is thermally stable under the reaction conditions and does not undergo rearrangement to the *meta* isomer.



(2)

We suggest that the formation of *m*-bis(trimethylsilyl)benzene in this reaction is a consequence of the steric strain associated with the two vicinal, highly branched trimethylsilyl groups attached to sp^2 carbon atoms. At least three routes which lead ultimately to the observed product may be envisaged: (1) extrusion of carbon dioxide from the initial adduct I with formation of prismane II which then isomerizes to *m*-bis(trimethylsilyl)benzene; (2) extrusion of carbon dioxide from I with formation of the benzvalene III, isomerization of which would give the observed product; (3) extrusion of carbon dioxide from I with formation of *o*-bis(trimethylsilyl)benzene in a vibrationally excited ground state, followed by isomerization of the latter to the *meta* isomer *via* II and/or III. These routes are illustrated in Chart I. A diradical intermediate, IV,

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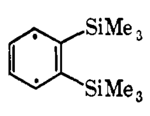
(2) A. B. Evnin and D. Seyferth, *J. Am. Chem. Soc.*, **89**, 952 (1967).

(3) H. A. Clark, A. F. Gordon, C. W. Young, and M. J. Hunter, *ibid.*, 73, 3798 (1951).

(4) R. G. Chaffee and H. N. Beck, *J. Chem. Eng. Data*, **8**, 453, 602 (1963).

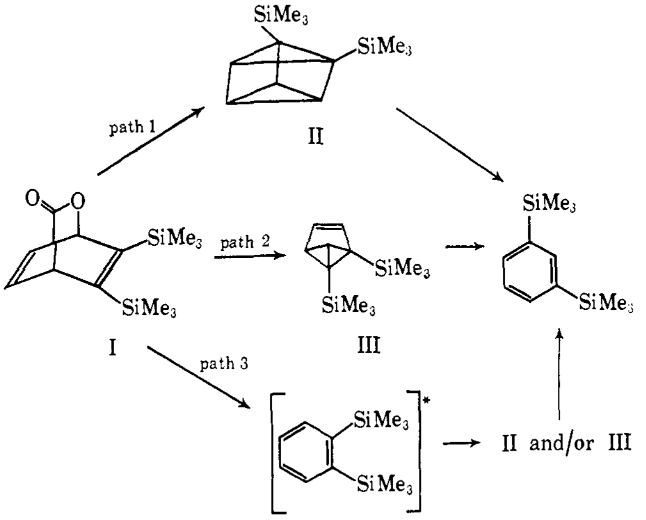
possibly could be involved in the formation of II and III. Since this reaction was carried out in solution,



IV

route 3 seems the least likely. However, route 3 is a formal analog of Burgstahler's photoisomerization of *o*-di-*t*-butylbenzene to a mixture of the *meta* and *para* isomers,[5] for which a prismane,[5] interconvertible Dewar structures,[6] and a benzvalene[6] have been suggested as intermediates. This analogy suggested that one might observe similar isomerization of *o*-bis(trimethylsilyl)-benzene upon irradiation. Such was the case: when 3.43 mmoles of this compound in 50 ml of diethyl ether was irradiated in a Rayonet photochemical reactor, a 12.4:1 mixture of *o*- and *m*-bis(trimethylsilyl)-benzene, as well as a trace amount of the *para* isomer, was present after a 24-hr reaction time. That such isomerization did occur (presumably *via* II and/or III) suggests that the paths we list above for the thermal Diels-Alder reaction are possible and even plausible routes to the observed *meta* isomer.

Chart I



There remains the problem of why α-pyrone and $Me_3SnC\equiv CSnMe_3$ react to give *o*-bis(trimethyltin)-benzene, while in the corresponding reaction of $Me_3SiC\equiv CSiMe_3$ the *meta* isomer is produced. In this connection it is noteworthy that attempts to photoisomerize *o*-bis(trimethyltin)benzene thus far have been unsuccessful. Perhaps then the excited state of this molecule is less sterically strained than is that of its silicon analog, and this in turn may have some implications with respect to the thermal Diels-Alder reaction of bis(trimethyltin)acetylene and its silicon analog with α-pyrone. In general, steric effects associated with Me_3M^{IV} groups decrease with increasing size of M^{IV}: C > Si > Ge > Sn. However, other factors may be of importance in the excitation of these *ortho*-disubstituted benzenes.

Further studies of α-pyrones and 5,5-dimethoxytetrachlorocyclopentadiene[7] with $Me_3M^{IV}C\equiv CM^{IV}Me_3$ compounds (M^{IV} = C, Si, Ge, Sn, Pb) are being carried out with the aim of determining which factors are of importance with respect to the question of isomerization *vs.* absence of isomerization in these Diels-Alder reactions, as are more detailed investigations of o-$(Me_3M^{IV})_2C_6H_4$ compounds and their photochemical transformations.

Acknowledgments. The authors are grateful to the National Science Foundation for generous support of this work (Grant GP 6466X). This work was supported in part by Public Health Service Fellowship 5-F1-GM-20, 099 (to A. B. E.).

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[5] (a) A. Burgstahler and P.-L. Chien, *J. Am. Chem. Soc.*, **86**, 2940 (1964); (b) A. Burgstahler, P.-L. Chien, and M. O. Abdel-Rahman, *ibid.*, **86**, 5281 (1964).

[6] L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *ibid.*, **87**, 675 (1965).

(7) Note the reaction of this compound with bis(trimethyltin)acetylene, which gives 1,2-bis(trimethyltin)tetrachlorobenzene: D. Seyferth and A. B. Evnin, *ibid.*, **89**, 1468 (1967).

(8) National Institutes of Health Predoctoral Fellow, 1963-1966.

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On the Mechanism of the Photochemical Decomposition of Cyclobutanone in the Gas Phase[1]

Sir:

The photochemical decomposition of cyclobutanone in the gas phase yields ethylene and ketene or cyclopropane, propylene, and CO,[2,3] and only a negligible amount of the expected rearrangement product (3-butenal?) has been detected.[4,5] Recently a pressure-dependence study of the ratio of propylene to cyclopropane led to the conclusion that propylene is a secondary product arising from the unimolecular decomposition of an excited cyclopropane,[6,7a] and a theoretical model for internal energy distribution in the photochemical excitation and the unimolecular decomposition processes has been developed.[7b] As far as the photochemical intermediate responsible for the observed decomposition products is concerned, it has been suggested to be an acyl diradical of the type $\dot{C}H_2-CH_2-CH_2-\dot{C}O$.[2,3,8]

We have shown that the benzene-photosensitization technique[9,10] can be very useful for a mechanistic diagnosis of the gas-phase photochemical reactions of 4-pentenal[11] and cyclopentanone.[12] The singlet-singlet

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(1) This research has been supported by a National Science Foundation grant (GP 6924).

(2) S. W. Benson and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **64**, 80 (1942).

(3) F. E. Blacet and A. Miller, *ibid.*, **79**, 4327 (1957).

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(5) See, for a review of the photochemistry of cyclic ketones, R. Srinivasan, *Advan. Photochem.*, **1**, 84 (1963).

(6) R. G. Klemm, D. N. Morrison, P. Gilderson, and A. T. Blades, *Can. J. Chem.*, **43**, 1934 (1965).

(7) (a) R. J. Campbell, E. W. Schlag, and B. W. Ristow; (b) R. J. Campbell and E. W. Schlag, private communication, to be published.

(8) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 2758 (1960). The trimethylene diradical, an assumed decomposition product of this acyl diradical intermediate, has been reported to react with excess ethylene to yield C_5 olefins as trapped products, but attempts to confirm this result have so far failed (see ref 6 and 7a).

(9) (a) H. Ishikawa and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **84**, 1502 (1962); *J. Chem. Phys.*, **37**, 583 (1962); (b) W. A. Noyes, Jr., and I. Unger, *Advan. Photochem.*, **4**, 49 (1966).

(10) R. B. Cundall, F. J. Fletcher, and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964).

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(12) E. K. C. Lee, *ibid.*, **71**, 2804 (1967).