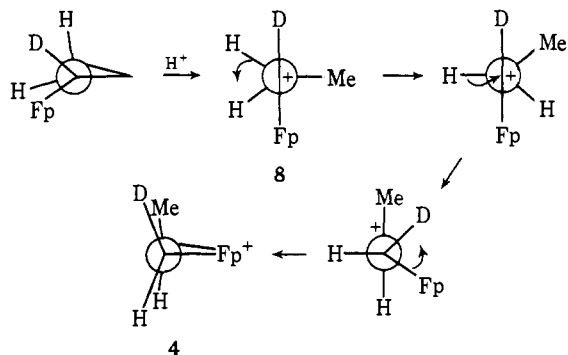


cation **6** exclusively⁹ and not **7**. This product may be accounted for by a mechanism involving initial formation of cationic metal-carbene complex **8**¹⁰ through cleavage of C₁-C₂, and the rapid rearrangement of this ion through minimum energy conformational changes as depicted below. The alternative cleavage of C₂-C₃



cannot be assisted by the metal atom owing to the orthogonality of C-C and Fp-C bonds which precludes a concerted process.

The cationic metal-carbene complex may be trapped through the reaction of **1** with uncharged electrophiles. Thus, treatment of **1** with SO₂ in benzene gives a mixture of stereoisomeric sultines (**9**):⁷ mp 74-76°; ir (KBr) 1945, 2000 (C≡O), 1120 cm⁻¹ (OSO);¹¹ nmr (CD₃NO₂) τ 3.90 (d, 0.4, CHOSO) 4.49 (t, 0.6, CHOSO), 4.99, 5.02 (2 s, 5, Cp), 6.5-7.6 (m, 4, CH₂). Reaction of SO₂ with **1-d** gave **9-d**. Analogously, treatment of **1** with tetracyanoethylene (TCNE) gave the cycloaddition product **10**:^{7,12} mp 119-121°; ir (KBr) 1965, 2021 (C≡O), 2250 cm⁻¹ (C≡N); nmr (CD₃NO₂) τ 4.66 (s, 5, Cp), 6.8-8.0 (m, 5, CH, CH₂).

These products evidently arise through collapse of the dipolar intermediate **11** whose formation, like that of **8**, proceeds through metal-assisted electrophilic cleavage of C₁-C₂. Rearrangement of **11** (E = SO₂) through hydrogen migration to **12** proceeds competitive with its collapse to **9**, as is evidenced by the formation of a small amount of the metal allyl sulfone (**13**),⁷ identical with the product obtained from **3** and SO₂.

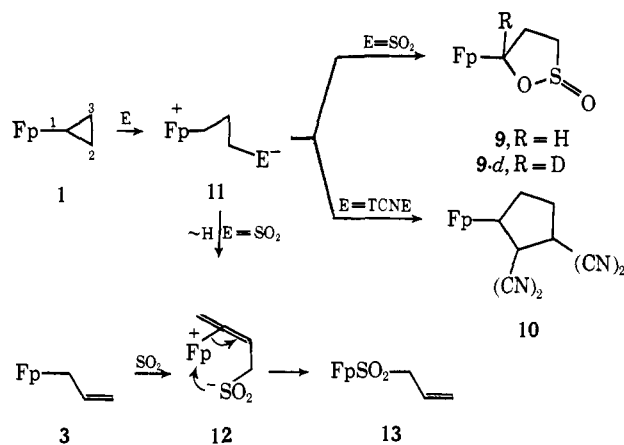
The reaction of SO₂ with the norcarane metal complex **2**⁷ illustrates the delicate balance between these competing reaction paths. This reaction yields only the metal allyl sulfone (**16**):⁷ mp 149° dec; ir(KBr)

(9) The stereochemistry at the methylene group of the product is evident from its nmr spectrum (CD₃NO₂), which exhibits doublet absorption at τ 6.03 (*J* = 8 Hz), but fails to show doublet absorption at 6.43 (*J* = 15 Hz) present in the undeuterated complex.

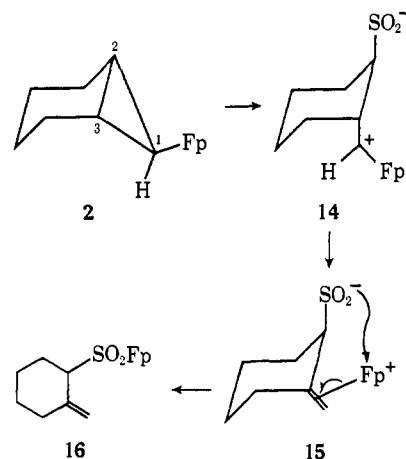
(10) This is ample precedent for such an ion: H. J. Beck, E. O. Fischer, and C. G. Kreiter, *J. Organometal. Chem.*, **26**, C41 (1971); L. Knauss and E. O. Fischer, *ibid.*, **31**, C68 (1971), and references cited therein; F. A. Cotton and C. M. Lukehart, *J. Amer. Chem. Soc.*, **93**, 2672 (1971); K. Ofele, *Angew. Chem., Int. Ed. Engl.*, **7**, 900 (1968); P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **93**, 4597 (1971); M. Sakai, H. Yamaguchi, and S. Masamune, *Chem. Commun.*, 486 (1971); P. W. Jolly and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 5044 (1966).

(11) The parent 1,2-oxathiolane 2-oxide and 1,2-oxathiane 2-oxide exhibit ir absorption at 1105 and 1125 cm⁻¹, respectively: D. N. Harp, T. G. Gleason, and D. K. Ash, *J. Org. Chem.*, **36**, 322 (1971).

(12) This product is isomeric with the product mp 193-196° dec obtained from the cycloaddition reaction of the allyl complex **3** and TCNE.



2026, 2060 (C≡O), 1042, 1175 cm⁻¹ (SO₂); nmr (C₂-D₆SO) τ 4.67 (s, 5, Cp), 4.87 (m, 2, =CH₂), 6.45 (m, 1, CH), 7.7-8.9 (m, 8, CH₂). The stereochemistry of **2** is such that edge attack by the electrophile from either side of the cyclopropane ring on C₁-C₂ is blocked. The alternative reaction path involving corner attack¹³ of the electrophile at C₂ results in inversion at this center and formation of the trans ion **14** which, owing to its stereochemistry, preferentially rearranges to **15** and thence to the observed product.



Acknowledgment. This work was supported by grants from the National Science Foundation (GP-27991X), National Institutes of Health (GM-16395), and the Army Research Office (70-G88).

(13) R. T. Lalonde, J. Ding, and M. A. Tobias, *J. Amer. Chem. Soc.*, **89**, 6651 (1967). For leading references to the question of edge and corner electrophilic attack on cyclopropane rings, see J. B. Hendrickson and R. K. Boeckman, *ibid.*, **93**, 4491 (1971).

A. Cutler, R. W. Fish
W. P. Giering, M. Rosenblum*

Department of Chemistry, Brandeis University
Waltham, Massachusetts 02154
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Direct Evidence for the Reaction of Monomeric Silicon Difluoride with 1,3-Butadiene¹

Sir:

Silicon difluoride, the best characterized structural analog to carbenes, is also the least prone to undergo

(1) This research was supported by AEC Contract No. AT-(40-1)-3898.

reactions in monomeric form.²⁻⁵ It is extraordinarily stable and quite unreactive in the gas phase.^{6,7} Virtually all reactions of SiF₂ reported to date have been initiated by the cocondensation at -196° with reactants.^{2-5,8-11} Under those conditions, all the observed reactions are generally attributable to secondary reactions of (SiF₂)_x polymeric species. While the monomer has been suggested as the reacting species for some condensed-phase^{9,10} as well as gas-phase reactions,¹² there is still as yet no unequivocal evidence for its participation.²

We wish to report the definite formation of monomeric SiF₂ by the nuclear recoil technique and to report its reaction with 1,3-butadiene. Previously, this reaction had been carried out by the cocondensation technique,³ the major product being *c*-C₄H₆Si₂F₄. This presumably resulted from the reaction of the (SiF₂)₂ dimer. Since the nuclear recoil technique produces labeled silicon in a concentration far too low to permit dimerization,^{13,14} the observed reactions *must* be due to a ³¹Si-containing species in its monomeric form. The detection of 1,1-difluorosilacyclopent-3-ene-³¹Si (DFSCP*) as a reaction product in the present case is a definite indication of a ³¹SiF₂ precursor. The analogous 1,4 additions to conjugated dienes of dimethylsilylene¹⁵ and methylene¹⁶⁻¹⁸ have previously been observed. Presumably the monomeric ³¹SiF₂ is produced by successive fluorine abstractions by ³¹Si atoms in the reaction system.

A vapor-phase mixture of phosphorus trifluoride and 1,3-butadiene was subjected to irradiation by fast neutrons which were produced by the ⁹Be(d,n)¹⁰B nuclear transmutation with a 20-MeV deuteron beam. Silicon atoms were formed from the nuclear reaction ³¹P(n,p)³¹Si.¹³ Product analysis was accomplished by standard radio-gas chromatographic techniques.¹⁹ Identification of DFSCP* was performed by coinjection of authentic samples²⁰ on two columns of different elution characteristics. Quantitative yields of the product were measured by monitoring the radioactivity of ³¹Si.

Preliminary data are presented in Table I. Experi-

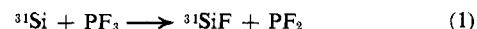
- (2) P. P. Gaspar and B. J. Herold in "Carbene Chemistry," W. Kirmse, Ed., 2nd ed, Academic Press, New York, N. Y., 1971.
 (3) J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, **4**, 145 (1971).
 (4) J. C. Thompson and J. L. Margrave, *Science*, **155**, 669 (1965).
 (5) P. L. Timms, *Prep. Inorg. React.*, **4**, 59 (1968).
 (6) P. L. Timms, R. A. Kent, T. C. Ehler, and J. L. Margrave, *J. Amer. Chem. Soc.*, **87**, 2824 (1965).
 (7) P. L. Timms, T. C. Ehler, and J. L. Margrave, *Nature (London)*, **207**, 186 (1965).
 (8) D. Solan and P. L. Timms, *Inorg. Chem.*, **7**, 2157 (1968).
 (9) P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave, *J. Amer. Chem. Soc.*, **88**, 940 (1966).
 (10) K. G. Sharp and J. L. Margrave, *Inorg. Chem.*, **8**, 2655 (1969).
 (11) J. L. Margrave, K. G. Sharp, and P. W. Wilson, *J. Amer. Chem. Soc.*, **92**, 1530 (1970).
 (12) D. C. Pease, U. S. Patent 3,026,173 (March 20, 1962).
 (13) P. P. Gaspar, S. Allan Bock, and W. C. Eckleman, *J. Amer. Chem. Soc.*, **90**, 6914 (1968).
 (14) For general information on the nuclear recoil technique, see, for example, R. Wolfgang, *Progr. React. Kinet.*, **3**, 97 (1965).
 (15) W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968).
 (16) V. Franzen, *Chem. Ber.*, **95**, 571 (1962).
 (17) B. Gzybowska, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4402 (1961).
 (18) H. M. Frey, *Trans. Faraday Soc.*, **58**, 516 (1962).
 (19) J. K. Lee, E. K. C. Lee, B. Musgrave, Y.-N. Tang, J. W. Root, and F. S. Rowland, *Anal. Chem.*, **34**, 741 (1962).
 (20) T. H. Chao, S. L. Moore, and J. Laane, *J. Organometal. Chem.*, **33**, 157 (1971).

Table I. Formation of 1,1-Difluorosilacyclopent-3-ene-³¹Si from the Reaction of Monomeric ³¹SiF₂ with 1,3-Butadiene

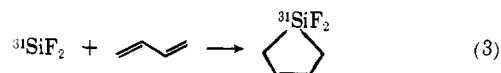
Expt	Composition, Torr			Specific yield ^a	Rel specific yield ^b
	PF ₃	1,3-Butadiene	O ₂		
1	422	407		1.65 ± 0.08	(100)
1	653	147		1.44 ± 0.09	87 ± 8
1	736	90		1.80 ± 0.09	109 ± 8
2	463	194		2.68 ± 0.14	(100)
2	355	210	30	2.31 ± 0.10	86 ± 7

^a Total decay corrected activity of product per unit PV of precursor ³¹PF₃. Units are counts/(Torr cc). ^b Since the irradiation conditions for each experiment are not easily reproducible, results are normalized within each set, where a number of samples are exposed to an equivalent neutron flux.

ment 1 shows the results for three samples with varying relative amounts of reactants. As the 1,3-butadiene to phosphorus trifluoride ratio changes from 8.6 to 1.0, the specific yield of the product is essentially unchanged. (The specific yield of DFSCP* is 30% relative to the ³¹SiH₄ yield from recoil ³¹Si reaction with SiH₄.¹³ In addition, three minor products are observed which together amount to only 4.5% of that in DFSCP*.) In these experiments, phosphorus trifluoride served as the source of both ³¹P and F atoms. The resulting hot ³¹Si atoms are likely to undergo stepwise fluorine abstractions (1 and 2). The ³¹SiF₂ thus



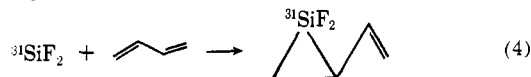
formed will undergo an apparent 1,4 addition to 1,3-butadiene to give the final product as shown in (3).



The insensitivity of the DFSCP* yield to relative amounts of 1,3-butadiene indicates that reactions 1 and 2 are both efficient in comparison with abstraction of hydrogen from the olefin, and that (3) is efficient in comparison with further fluorine abstraction by ³¹SiF₂.

Experiment 2 was designed to reveal the spin state of the reacting ³¹SiF₂. It is well established that SiF₂ has a singlet ground state.² Since the present results indicate that the addition of radical scavenger (O₂) has no significant effect upon the specific product yield, it appears that the ³¹SiF₂ reacts as a singlet.

In the analogous addition of methylene to 1,3-butadiene, cyclopentene results from the radical addition reaction of triplet methylene.¹⁶ Singlet methylene, rather, gives predominantly the 1,2-addition product, vinylcyclopropane,¹⁷ in contrast to the 1,4-addition product observed here for singlet ³¹SiF₂. However, since it has been shown that excited vinylcyclopropane isomerizes to cyclopentene¹⁸ with an activation energy of 49.6 kcal/mol, we suggest that the apparent 1,4 addition of ³¹SiF₂ may, in fact, be a 1,2 addition (4) followed by isomerization (5) to give the observed



product. It is likely that none of the 1,1-difluoro-2-vinylsilacyclopropane- ^{31}Si survives as a final product because of its inherent instability and because of the excess energy deposited during its formation. Attempts thus far to synthesize a silacyclopropane have failed, 21 presumably due to excessive ring strain introduced by the silicon atom. Skell and Goldstein 22 observed vinylsilanes rather than silacyclopropanes under conditions which should have produced the latter.

The resulting 1,1-difluoro-2-vinylsilacyclopropane- ^{31}Si from (4) is likely to be excited. 23 Even though being formed by two successive fluorine abstraction reactions, the reacting $^{31}\text{SiF}_2$ might still retain part of the original excitation of the hot ^{31}Si atom. Some energy could also have been released during the formation of two extra silicon-carbon bonds. Nevertheless, the major reason that (5) is expected to go to completion is the instability of the reactant rather than its excitation.

Between the two mechanisms (a) direct 1,4 addition by singlet $^{31}\text{SiF}_2$ and (b) 1,2 addition followed by isomerization, we favor the latter process. However, it is impossible to rule out the possibility that SiF_2 , being larger than its carbene analog, might have the right geometry to participate in a direct 1,4 addition process.

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(21) C. H. Yoder and J. J. Zuckerman, *Prep. Inorg. React.*, **6**, 100 (1971).

(22) P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, **86**, 1442 (1964).

(23) F. S. Rowland, "Proceedings of the International School of Physics, 'Enrico Fermi' Course XLIV-Molecular Beam and Reaction Kinetics," Ch. Schlier, Ed., Academic Press, New York and London, 1970.

Y.-N. Tang,* G. P. Gennaro, Y. Y. Su
Department of Chemistry, Texas A & M University
College Station, Texas 77843

Received March 9, 1972

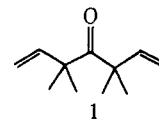
The Photochemistry of an Acyclic Bis β,γ -Unsaturated Ketone

Sir:

The photochemistry of β,γ -unsaturated ketones is currently a topic of lively interest. Direct irradiation of acyclic compounds results in α cleavage to an acyl and an allyl radical. $^{1-4}$ When the structure allows it, γ -hydrogen abstraction 2,3 and cis-trans isomerization of the double bond 1,5 are also observable. Triplet photosensitization of an acyclic β,γ -unsaturated ketone 4 led to oxa-di- π -methane rearrangement, a reaction now familiar in cyclic compounds. 6

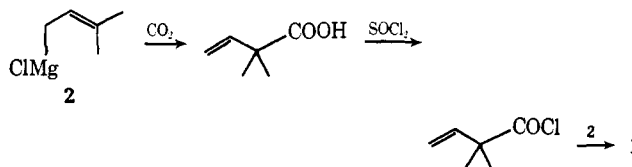
We report here a study of the first acyclic bis β,γ -unsaturated ketone, 3,3,5,5-tetramethylhepta-1,6-dien-

- (1) H. Morrison, *Tetrahedron Lett.* 3653 (1964).
- (2) N. C. Yang and D. Thap, *ibid.*, 3671 (1966).
- (3) E. F. Kiefer and D. A. Carlson, *ibid.*, 1617 (1967).
- (4) W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *J. Amer. Chem. Soc.*, **92**, 1786 (1970).
- (5) D. O. Cowan and A. A. Baum, *ibid.*, **92**, 2153 (1970).
- (6) R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *ibid.*, **93**, 3957 (1971), and references cited therein.



4-one (1). Although this work was originally undertaken to determine the fate of allylic radicals 7 produced by decarbonylation, 8 the photochemistry of the ketone itself has proven to be intriguing. The dimethyl groups in 1 serve to stabilize it against positional isomerization and to distinguish the ends of the allylic radicals formed.

The synthesis of 1 was based upon the preferential reaction of allylic Grignard reagents at the more hindered end. 9 Thus, carbonation of the Grignard reagent 2 derived from 1-chloro-3-methyl-2-butene 10 gave



2,2-dimethyl-3-buten-1-yl carboxylic acid. Reaction of its acid chloride with more Grignard reagent provided 1, a clear oil (bp 75° (18 mm)). 11 The ir spectrum of 1 showed bands at 1696 (C=O), 1635 (C=C), 918, and 988 cm^{-1} (terminal vinyl), while the nmr spectrum in CCl_4 appeared as follows: δ 1.28 (s, 12 H), 5.13 (m, 4 H), 6.22 (q, 2 H). The mass spectrum gave a molecular ion at m/e 166 and a base peak at 69 (C_5H_9^+). The uv spectrum of 1 revealed an enhanced $n-\pi^*$ transition in hexane at λ_{max} 292 nm (ϵ 100).

Irradiation of 0.1 M 1 in toluene at 313 nm gave a 90% yield of CO and the three possible allylic radical recombination products. Designating the dimethyl end of the radical as the head (h) end, one can identify these products as hh, ht, and tt. They were formed in relative yields of 14, 27, and 59%, virtually the same distribution as observed from the analogous azo compound. 7 The formation of all three products in amounts characteristic of free radicals rules out an appealing seven-membered cyclic decomposition mechanism, which would produce only the tt product. The CO quantum yield from 1 was 0.30, less than half that of di-*tert*-butyl ketone ($\Phi = 0.62$) 12 and of dibenzyl ketone ($\Phi = 0.70$). 8 Since cis-trans isomerization is known in related systems 1,5 it is likely that the relatively low efficiency of decarbonylation is caused by degenerate isomerization of the double bonds of 1. In fact decarbonylation of the saturated analog of 1 in toluene occurs with a substantially higher efficiency 13 ($\Phi = 0.50$).

When 1 was irradiated to low conversions, the presence of a new product was noted by vpc. Moreover, this material was formed to the complete exclusion of

(7) P. S. Engel and D. J. Bishop, *ibid.*, **94**, 2148 (1972).

(8) P. S. Engel, *ibid.*, **92**, 6074 (1970).

(9) W. G. Young, *Chem. Rev.*, **56**, 753 (1956); M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Englewood Cliffs, N. J., 1954, p 1154.

(10) A. J. Uitée, *Recl. Trav. Chim. Pays-Bas*, **68**, 125 (1949).

(11) We wish to acknowledge the technical assistance of Mr. Neil B. Tweedy in maximizing the yield of this reaction.

(12) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 6974 (1970).

(13) The intervention of γ -hydrogen abstraction in the saturated compound probably accounts for the fact that it decarbonylates less efficiently than di-*tert*-butyl ketone.