port this concept.[14] However, the decrease in dipole moment in going from THF or THT to the totally unsaturated molecules is not great (1.03 and 1.37 D, respectively),[8] and would be expected to decrease to some extent simply by the introduction of a π system in the carbon portion of the ring. Thus the resonance forms in Figure 3 (which neglect any thiophene canonical forms arising from sulfur d-orbital participation) do not control the molecular dipole direction of these molecules.

(14) R. J. Abraham, R. C. Sheppard, W. A. Thomas, and S. Turner, *Chem. Commun.*, 43 (1965); J. A. Elvidge, *ibid.*, 160 (1965); D. W. Davies, *ibid.*, 258 (1965); H. A. P. DeJong and H. Wynberg, *Tetrahedron*, **21**, 515 (1965).

Acknowledgment. We wish to thank the Public Health Service, National Institutes of Health (GM-16689), for generous support of this work.

Alkyl Shifts in Thermolyses. V.[1] Thermal Epimerization of the 1,4-Dimethylspiropentanes[2]

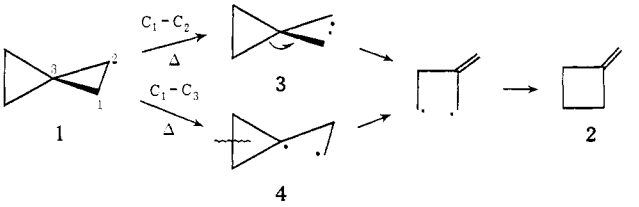
Joseph J. Gajewski*[3] and Leo T. Burka

Contribution No. 2133 from the Indiana University, Bloomington, Indiana 47401. *Received March 21, 1972*

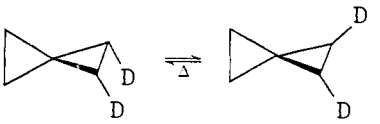
Abstract: In order to ascertain which of the two different types of bonds in spiropentane is reversibly cleaved prior to the thermally induced structural rearrangement to methylenecyclobutane, the proximal, medial, and distal 1,4-dimethylspiropentanes were pyrolyzed in the vapor phase. Geometric isomerization (epimerization) occurred substantially faster than structural isomerization. However, initially, the proximal and distal isomers gave only the medial isomer indicating that reversible cleavage of only the C_1–C_2 (peripheral) bonds occurred. The kinetics of epimerization of the distal compound revealed that the epimerization was first order and that k (sec^{-1}) = $10^{14.7}$ exp(−50000/1.987T).

The migration of groups to vicinal cationic centers is well known,[4,5a] but examples of the analogous migration to radical[5b] or anionic[5c] sites are rare, especially when the migrating group is a hydrogen or a saturated carbon. The best characterized reaction involving such a migration to a radical site is the cyclopropane to propene rearrangement which is actually a biradical case.[6] The work of Schlag, Rabinovitch, and Wiberg has shown that the rearrangement is preceded by reversible ring opening followed by migration of a hydrogen atom to give propene.[6b,c] It appears, however, that in all the well-characterized cyclopropane pyrolyses alkyl group migration is not an important process.[7]

The rearrangement of spiropentane (**1**) to methylenecyclobutane (**2**) which was first studied by Flowers and Frey[8] and by Burkhardt[9] could be envisioned as a vicinal shift of a methylene group in the second ring after fission of the C_1–C_2 (peripheral) bond in the first. There is an alternate pathway in which the C_1–C_2 (radial) bond breaks first followed by bond breaking in the other ring to give product.

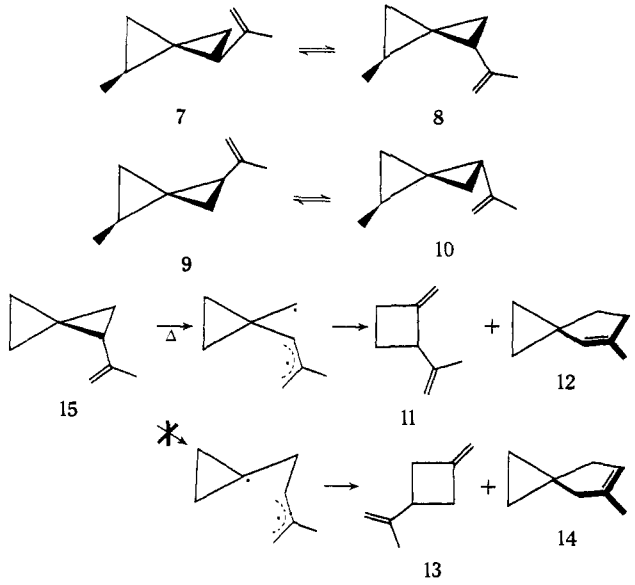


An investigation by Gilbert[10] has shown that *cis*- and *trans*-1,2-dideuteriospiropentanes (**5** and **6**) undergo geometric isomerization about ten times faster than structural isomerization. Thus, there must be some species present on the reaction pathway which allows for cis–trans isomerization; diradical **3** or **4** could be invoked to account for this observation.

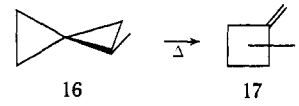


Gajewski[11] pyrolyzed the four 4-methylisopropenylspiropentanes **7**, **8**, **9**, and **10** and found that each of the compounds equilibrated relatively rapidly with its C_1 epimer, but interconversion of all four occurred slowly. These results indicate that there was predominant peripheral bond fission since, in principle, radial bond cleavage would allow the interconversion of all four compounds. Further evidence for initial peripheral bond cleavage was the observation of products **11** and **12** from the pyrolysis of isopropenylspiropentane (**15**) and the absence of compounds **13** and **14**. Compounds **11** and **12** can arise only by peripheral fission followed by rearrangement.

(1) For part IV see J. J. Gajewski and L. T. Burka, *J. Amer. Chem. Soc.*, **94**, 2554 (1972).
(2) Taken from the thesis of L. T. B., submitted in partial fulfillment of the requirements for the Ph.D. degree, Indiana University, Jan 1972.
(3) Fellow of the Alfred P. Sloan Foundation.
(4) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967.
(5) (a) "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963; (b) C. Walling, *ibid.*, Chapter 7; (c) H. E. Zimmerman, *ibid.*, Chapter 6.
(6) (a) T. S. Chambers and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **56**, 399 (1934); (b) E. W. Schlag and B. S. Rabinovitch, *ibid.*, **82**, 5996 (1960); (c) E. W. Schlag, B. S. Rabinovitch, and K. Wiberg, *J. Chem. Phys.*, **28**, 506 (1958).
(7) See, for example, the compilation by S. W. Benson and H. E. O'Neal, *J. Phys. Chem.*, **72**, 1866 (1968).
(8) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 5550 (1961).
(9) P. J. Burkhardt, *Diss. Abstr.*, **23**, 1524 (1962).
(10) J. C. Gilbert, *Tetrahedron*, **25**, 1459 (1969).
(11) J. J. Gajewski, *J. Amer. Chem. Soc.*, **92**, 3688 (1970).

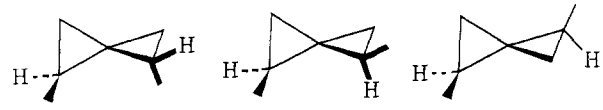


More recently Flowers has investigated the pyrolysis of methylspiropentane (**16**) to the methyl-substituted methylenecyclobutanes (**17**)[12] and made the suggestion,



based on Benson's group additivity of thermodynamic properties of biradicals,[7] that the radial bond (C_1–C_3) was weaker than the peripheral (C_1–C_2) bond by about 2 kcal/mol. However, Flowers' experiment does not indicate which bond is breaking nor if reversible fission precedes structural isomerization.

We wish to report our studies of the reversible bond fission that precedes the spiropentane structural rearrangement in a simple dialkyl-substituted spiropentane system. Thus, the kinetics of interconversion of proximal, medial, and distal 1,4-dimethylspiropentane (**18**, **19**, and **20**, respectively[13]) were determined.



Results

Pyrolyses were carried out in both a well-conditioned static system and in a flow apparatus. At 304° in the static reactor and at 385° in the flow system with pyrolysis times giving about 10% reaction, interconversion of **18** to **19**, **20** to **19**, and **19** to a mixture of **18** and **20** was observed.

At 385° in the flow system, **19** gave a mixture of **18** and **20** in the ratio of about 2.4:1 after 7% conversion with **20** being the major product. At 304° in the static reactor, the ratio was 2.1:1 after 6% reaction. No rearrangement to methylenecyclobutane products was observed in either pyrolysis.

Epimerization rate constants for **18**, **19**, and **20** in the first 0–37% of the reaction over the temperature range 259–319° are given in Table II.

(12) M. C. Flowers and A. R. Gibbons, *J. Chem. Soc. B*, 612 (1971).
(13) J. J. Gajewski and L. T. Burka, *J. Org. Chem.*, **35**, 2190 (1970).

Table I. Product Distribution from Short Term Pyrolyses of 1,4-Dimethylspiropentanes[a]

Compd	% conversion	% 18[b]	% 19[b]	% 20[b]
18	8.9		≥95	≤5[c]
19	4.1	25		75
19	6.9	30		70
19	11.6	35		65
20	8.5	≤5[c]	≥95	

[a] At 385° in a flow system. [b] Per cent of epimerized material. [c] Limits of detection of instrument.

Table II. Epimerization Rate Constants of 1,4-Dimethylspiropentanes

Compd	Temp, °C	Obsd rate constant disappearance, sec^{-1}	Highest % conversion
18	385.0[a]	1.82×10^{-2}	
18	303.8[b]	6.72×10^{-5}	21.9
19	385.0[a]	1.37×10^{-2}	
19	303.8[b]	4.90×10^{-5}	15.5
20	385.0[a]	1.72×10^{-2}	
20	318.7[b]	1.57×10^{-4} (1.89×10^{-4})[c]	36.7
20	303.9[b]	5.64×10^{-4} (6.05×10^{-4})[c]	18.6
20	283.4[b]	1.25×10^{-5} (1.30×10^{-5})[c]	9.7
20	258.8[b]	1.47×10^{-6} (1.53×10^{-6})[c]	11.7

[a] Flow system. [b] Static reactor, rate constants are average values for three or more reaction times. [c] Values in parentheses are corrected for back-reaction; see text.

Since *medial*-1,4-dimethylspiropentane (**19**) is in equilibrium with **20**, the observed rate of epimerization of **20** appears to slow as the reaction proceeds. After correction for this, the rate constant becomes $k(sec^{-1}) = 10^{14.7} \exp(-50{,}000 \pm 1000/1.987T)$.[14a] This correction was made as follows: for two compounds, A and B, in equilibrium

$$A \underset{k'}{\overset{k}{\rightleftharpoons}} B \qquad (1)$$

the expression

$$\ln \frac{kA_0}{(k + k')A - k'A_0} = (k + k')t \qquad (2)$$

applies.[14b] A_0 is the initial concentration of A, which is in this case unity. The approximate ratio of the rate constants, k and k', is known at 304°; *medial*-1,4-dimethylspiropentane (**19**) epimerizes to **20** at a rate 0.55 times the rate **20** epimerizes to **19** ($2.3/3.1 \times 4.68 \times 10^{-5}$ or 3.18×10^{-5} sec^{-1} *vs.* 5.64×10^{-5} sec^{-1}). Substituting $k' = 0.55k$ into eq 2, gives

$$\ln \frac{1}{1.55A - 0.55} = 1.55kt$$

This expression was used to determine the corrected rates of reaction for epimerization of **20** to **19**, and the Arrhenius parameters were determined from these rate constants.

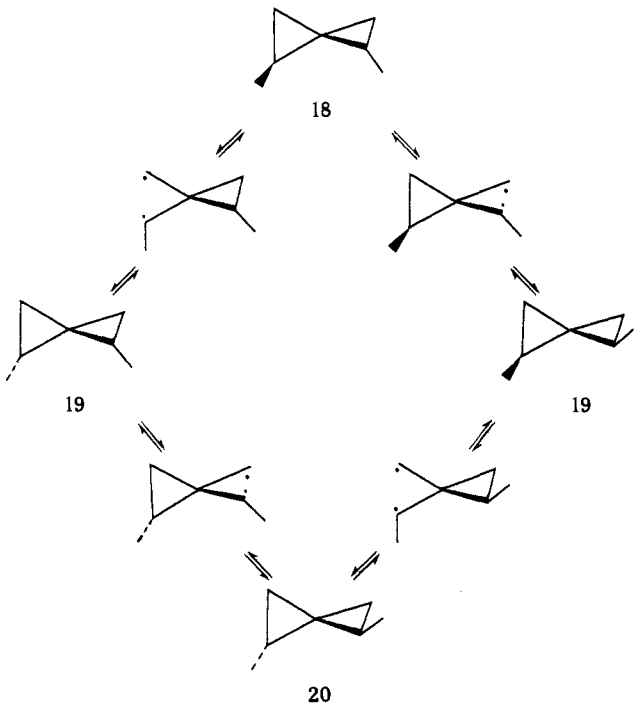
Discussion

In an earlier study,[11] the epimerization of 4-methylisopropenylspiropentane was explained by initial peripheral bond fission; the present study substantiates

(14) (a) The standard deviation from a least-squares line is reported; (b) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1965. Here we assume that **18** is formed irreversibly from **19**.

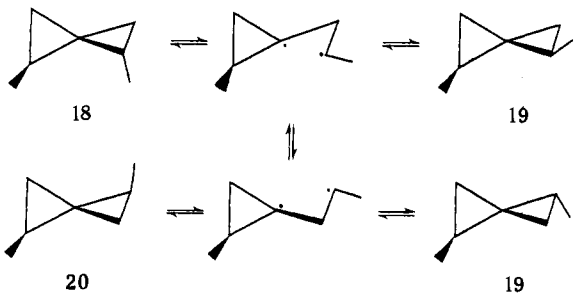
this finding in a less perturbed system. The fact that **18** and **20** give only **19** at short reaction times can be explained by the initial rupture of a peripheral bond. As can be seen in Scheme I, *medial*-1,4-dimethylspiropentane (**19**) can epimerize to **18** or **20** depending upon which bond breaks, but **18** and **20** give only **19** from fission and reclosure of either peripheral bond.

Scheme I



If the initial step was the breaking of the radial bond, one should observe formation of all three epimers in the first few per cent of reaction as shown in Scheme II.

Scheme II



This, of course, depends upon the rate of inversion of the cyclopropyl radical being competitive with the rate of reclosure to spiropentane since the radial bond-breaking with slow inversion at the cyclopropyl radical site would give the same epimerization results as peripheral bond-breaking. However, cyclopropyl radical inversion is fast on the esr time scale at liquid nitrogen temperatures indicating a barrier of less than 2 kcal/mol,[15] and a calculation by O'Neal and Benson[7] predicts about 9 kcal/mol activation energy for reclosure of a trimethylene biradical. On this basis, formation of spiropentane from a biradical might be expected to be slower than cyclopropyl radical inversion. However, the extended Hückel calculations of Hoffmann[16] on the trimethylene biradical predict that ring closure to cyclopropane should have a very small activation energy (about 1 kcal/mol). Similar results were obtained by Salem with the *ab initio* quantum chemical approach.[17]

Thus, it would appear that an unequivocal decision based on model systems and calculations as to whether initial radial or peripheral cleavage is occurring in the spiropentane rearrangement cannot be made. However, there does seem to be strong circumstantial evidence for initial peripheral bond fission. In the isopropenylspiropentane pyrolyses[11] the products obtained can arise only by peripheral bond fission, and the epimerization in that system as well as the 1,4-dimethyl system can be explained by the same process. It would appear that, in the absence of compelling evidence to the contrary, peripheral bond cleavage is the initial step in the spiropentane rearrangement since it best explains all the experimental results in relatively unperturbed systems.

Finally, it should be mentioned that there is inconsistency between the activation parameters for structural and geometric isomerizations for spiropentane as compared with those for cyclopropane. For cyclopropane $k_s = 10^{15.2} \exp(-65{,}400/RT)$ and $k_g = 10^{16.4} \exp(-65{,}100/RT)$,[6b] whereas for spiropentane $k_s = 10^{15.2} \exp(-55{,}500/RT)$[12] and $k_g = 10^{14.5} \exp(-51{,}500/RT)$.[10] Flowers' rate constant for structural rearrangement of methylspiropentane is $10^{14.85} \exp(-53{,}800/RT)$ which is expected relative to k_s in the parent case, and the rate constant for epimerization of *distal*-1,4-dimethylspiropentane (**20**) is $10^{14.7} \exp(50{,}000/RT)$ which is also reasonable in relation to k_g for spiropentane itself. Thus, all of the kinetic data appear correct but the preexponential term for geometric isomerization in cyclopropane is $10^{1.2}$ *greater* than that for structural isomerization while in spiropentane the preexponential term for geometric isomerization is $10^{0.15-0.7}$ *smaller* than that for structural isomerization. Moreover, the activation energy for geometric isomerization of cyclopropane is only 0.3 kcal/mol less than that for structural isomerization, but the activation energy for geometric isomerization of spiropentane is 4 kcal/mol less than that for structural isomerization. Yet the k_g/k_s ratio in both cases is about 10. In terms of free energies of activation the two systems appear related, but the relative contributions of enthalpies and entropies of activation are quite different despite similar symmetry characteristics.

Experimental Section

The static pyrolyses were carried out in a well-conditioned 200-m glass bulb attached to a standard vacuum line set-up and immersed in a molten potassium nitrate–sodium nitrite bath. Temperature control was by a Bayley Controller Model 76-8 in connection with a 125-W knife heater. A Variac and a 450-W knife heater were used for gross temperature control. Stirring was supplied by a "Lightening stirrer." Temperature readout was provided by two matched copper–constantan thermocouples. The temperature gradient in the vicinity of the bulb ranged from 0.7 at 319° to 0.2 at 259°. The temperature remained constant to 0.1° in readings taken at any single point over a 24-hr period. The reported temperature of pyrolysis represents the average of ten readings taken in various places in the vicinity of the bulb. Dead volume errors were reduced

(15) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(16) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(17) L. Salem, *Bull. Soc. Chim. Fr.*, 3161 (1970); Y. Jean and L. Salem, *Chem. Commun.*, 382 (1971); L. Salem and C. Rowland, *Angew. Chem.*., submitted for publication; J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *J. Amer. Chem. Soc.*, **94**, 279 (1972).

by placing a glass rod in the capillary tubing leading to the bulb and heating the tubing with heating tape to a temperature near that of the bath.

The sample was vaporized into the bulb as a mixture with *n*-heptane; this operation required less than 30 sec. Timing was started as soon as the stopcock leading to the bulb was opened. Samples were removed by allowing the material in the bulb to expand into a 10-ml volume; the stopcock was allowed to remain open for 12 sec. The material was then condensed with liquid nitrogen and analyzed by a capillary glpc. The shortest reaction time examined was 16 min.

The flow system employed was a Chemical Data Systems Model 1100 Pyrochrom used in conjunction with capillary glpc.

Analysis in both cases was by a Varian Associates Series 1220-2 chromatograph using a 200 ft × 0.01 in. i.d. didecyl phthalate column operated at room temperature and 15 psi helium pressure. Integration of the signal was by a Vidar Model 6210 digital integrator.

The 1,4-dimethylspiropentanes were prepared as described earlier[13] and purified immediately prior to use by preparative glpc using a 12 ft × 0.25 in. di-*n*-butyl tetrachlorophthalate column operated at 70° and 100 ml/min helium flow. Distal **20** and medial **2** were homogeneous by capillary glpc. Proximal **18** contained a 3% impurity which was neither of the two other isomers.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Alkyl Shifts in Thermolyses. VI.[1] Synthesis and Characterization of the 2,4- and 4,5-Dimethyl-1-carbethoxyspiropentanes and the 2-Methyl-3-ethylidene-1-carbethoxycylopropanes[2]

Joseph J. Gajewski[3]* and Leo T. Burka

Contribution No. 2134 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received March 21, 1972*

Abstract: In order to examine the complete stereochemistry of a spiropentane to methylenecyclobutane thermal rearrangement, three stereoisomeric 4,5-dimethyl-1-carbethoxyspiropentanes were prepared by copper-catalyzed addition of ethyl diazoacetate to *cis*- and *trans*-2,3-dimethylmethylenecyclopropane. Only one isomer was found in the former case while two, in a 3:1 ratio, were produced from the latter. The structures were assigned primarily on the basis of anticipated steric effects in the additions. Seven of the eight possible 2,4-dimethyl-1-carbethoxyspiropentanes were prepared by Gaspar–Roth cyclopropanation of the four 2-methyl-3-ethylidene-1-carbethoxycyclopropanes whose structures were partly assigned by pmr spectroscopy. Chemical degradation of the 2,4-dimethyl-1-carbethoxyspiropentanes to the various 1,4-dimethylspiropentanes established the relationships between the methyls of these esters and their precursors.

The spiropentane to methylenecyclobutane thermal rearrangement[4] appears to be closely related to the cyclopropane to propylene thermal isomerization,[1] a reaction which has received considerable experimental[5] and theoretical[6] attention. Since both interconversions could be envisioned as proceeding *via* either a concerted conservation of orbital symmetry controlled pathway[7a] or a two-step pathway involving biradicals,[7b] a complete stereochemical study of the former reaction appeared to be essential. In order to determine the stereochemical outcome at the migration origin, terminus, and migrating carbon, it was necessary to prepare and to assign the stereostructures of a number of 4,5-dimethyl- and 2,4-dimethyl-1-carbethoxyspiropentanes whose pyrolytic behavior is described in the next paper of this series. In addition to the impetus provided by the thermal rearrangements of the spiropentane system, the further possibility of examining the stereochemistry of multiple cyclopropylcarbinyl cation, anion, and radical rearrangements of spiropentylcarbinyl derivatives motivated this endeavor.

Results and Discussion

Synthesis of the 4,5-Dimethyl-1-carbethoxyspiropentanes. Slow addition of ethyl diazoacetate to *cis*-2,3-dimethylmethylenecyclopropane (**1**)[8] in octane containing cupric sulfate and copper bronze at reflux gave mostly one spiropentane ester, **3**, as evidenced by vpc and pmr. Since the product of attack from the least hindered side of the olefin usually predominates in these additions,[9] the *cis*-4,5-dimethyl-*anti*-1-carbethoxyspiropentane structure was assigned to **3**. Inspection of molecular models reveals the large degree to which the side of the π bond syn to the cis, vicinal methyls is shielded from attack by reagents, so the fact that *cis*-4,5-dimethyl-*syn*-1-carbethoxyspiropentane (**4**) was not formed to any appreciable extent is not unreasonable.

Under the same reaction conditions, *trans*-2,3-di-

(1) For part V see J. J. Gajewski and L. T. Burka, *J. Amer. Chem Soc.*, **94**, 8857 (1972).
(2) Taken from the thesis of L. T. B. submitted in partial fulfillment of the Ph.D. requirements, Indiana University, Jan 1972.
(3) Fellow of the Alfred P. Sloan Foundation, 1971–1973.
(4) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 5550 (1961); P. J. Burkhardt, *Diss. Abstr.*, **23**, 1524 (1962).
(5) For a review see W. L. Carter and R. G. Bergman, *J. Amer. Chem. Soc.*, **90**, 7343 (1968).
(6) R. Hoffmann, *ibid.*, **90**, 1475 (1968); L. Salem, *Bull. Soc. Chem. Fr.*, 3101 (1970); Y. Jean and L. Salem, *Chem. Commun.*, 382 (1971); L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).
(7) (a) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); (b) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).
(8) J. J. Gajewski, *J. Amer. Chem. Soc.*, **93**, 4450 (1971).
(9) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.