

transition metal. It is easy to imagine that the technique could have great value in probing the environment about cobalt in many other cobalt(III) compounds, including vitamin B₁₂, methylcobalamin, coenzyme B₁₂, and others. Similarly, compounds of several other transition elements might be studied. Unfortunately, the techniques usually employed by chemists in the past have lacked the requisite sensitivity to permit observation of nqr spectra for many nuclei of interest.

The most promising approaches for the future seem to lie in the use of double resonance techniques,^{45,46} capable of providing enormously increased sensitivity in observing quadrupolar transitions, and permitting observation of transitions of very low frequency, such as in ²H nqr spectra, where the transitions are observed in the 100–160-kHz re-

(45) S. R. Hartmann and E. L. Hahn, *Phys. Rev.*, **128**, 2042 (1962).

(46) R. E. Slusher and E. L. Hahn, *Phys. Rev.*, **166**, 332 (1968).

gion.⁴⁷ A most spectacular demonstration of the high sensitivity inherent in one of the techniques is the observation of ¹⁷O nqr in natural abundance (0.037%) in several quinones, by means of an adiabatic demagnetization in the lab frame, level-crossing, double-resonance experiment.⁴⁸ Extension of these techniques to observation of the quadrupole resonance spectra of transition elements in diamagnetic compounds seems entirely feasible.

Our research efforts in nqr have been supported by The Advanced Research Project Agency through contract SD-131 with the Materials Research Laboratory, and by the National Science Foundation through Contract GH 33634 and through Grants GP 6396X and GP 30256X. I am indebted to many of my former students for their collaborative efforts, but most especially to Cheryl Pribula and Robert LaRossa.

(47) J. L. Ragle and K. L. Sherk, *J. Chem. Phys.*, **50**, 3553 (1969).

(48) Y.-N. Hsieh, J. C. Koo, and E. L. Hahn, *Chem. Phys. Lett.*, **13**, 563 (1972).

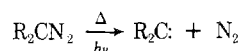
Gas-Phase Carbene Reactions¹

Maitland Jones, Jr.

Department of Chemistry, Princeton University, Princeton, New Jersey 08540

Received July 29, 1974

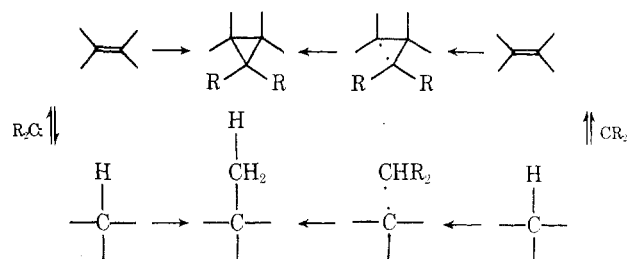
The thermal or photochemical decomposition of diazo compounds is the most common method of generating species containing divalent carbon (carbenes).^{2,3} As spin is conserved in the decomposition and as nitrogen is far more stable as a singlet than a triplet, the carbene is usually born in a singlet state.



Methods have been developed for producing the triplet states, which are often the ground-state species.^{2,3}

Singlet carbenes are voracious electrophiles, reacting with weak Lewis bases such as π bonds and even σ bonds to give products. The triplets are far less reactive, but also combine with multiple and single bonds to give the same overall products as the singlets (although by quite different mechanisms).

Maitland Jones, Jr., was born in New York City in 1937, and raised in the small town of Bedford, N. Y. He turned to chemistry only after the discovery of the curve ball by his contemporaries made it clear that he would never be a major league center fielder, and the intransigence of his parents removed him from the tennis circuit. He worked as a child at the Hickrill Chemical Research Foundation in Katonah, N. Y., where he acquired what experimental skill he possesses from Lawrence Knox and Gunther Laber and first came under the influence of William von Eggers Doering. He went on to Yale, where he worked for Professor Doering both as an undergraduate and graduate student. He came to Princeton in 1964 after a happy year of postdoctoral study with Professor J. A. Berson at Wisconsin, and is now Professor of Chemistry and Master of Stevenson Hall, an undergraduate college. He maintains a measure of sanity by escaping each year with his wife, Susan Hockaday, and their three children to Orangedale, Nova Scotia, in the peace and quiet of which this Account was written.



In the chemistry that follows in this Account, many intramolecular additions and insertions will appear.

Our general reason for studying carbene reactions in the gas phase, after so much effort had been applied already to studies of carbene reactions in solution,^{2,3} was to examine the intramolecular reactions of carbenes. Carbenes seem to fall into two classes: one in which intramolecular reactions are virtually inevitable and another in which they are most difficult to observe. It simply depends on the ease of intramolecular reaction. If a multiple bond, carbon-hydrogen bond, or even a carbon-carbon bond is within range, and intramolecular reaction would not generate a very high energy species, then intermolec-

(1) The work described herein was supported most generously by the National Science Foundation through Grants GP-12759 and GP-30797X, and by the Donors of the Petroleum Research Fund, administered by the American Chemical Society.

(2) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

(3) "Carbenes," M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, N. Y., 1973.

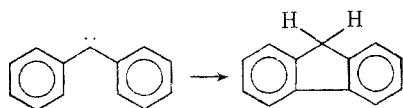
ular processes do not compete favorably with intramolecular reactions. On the other hand, if the intramolecular process is difficult for steric or electronic reasons, reaction with the external environment dominates the chemistry.

As it was exactly carbenes in the second class that we wished to observe, some means had to be found to "remove" the local environment. The easiest way to do this, it seemed, was to generate the carbene in the gas phase where collisions with other molecules were sure to be infrequent, and where intramolecular reaction might be coerced.

The techniques used for these gas-phase reactions are simple, even crude. Stable, volatile diazo compounds are either distilled at low pressure through a hot tube or carried through with a stream of inert gas. If the diazo compound is unstable, the corresponding tosylhydrazone salt is flash pyrolyzed by slowly dropping the finely powdered material onto a hot surface connected, *via* a trap, to a vacuum pump. Although we have not examined every case, those comparisons we have made between tosylhydrazone salt and diazo compound decompositions have never revealed significant differences in product composition.

Reactions in the gas phase had not been completely neglected previously. Indeed, the gas-phase chemistry of methylene itself has received seemingly endless scrutiny.^{2,3} However, methylene is one of the few carbenes unable to achieve normal tetravalency at carbon through intramolecular reaction and can (happily) be considered outside the scope of this Account. A scattering of other reactions appears in the literature, and interesting reactions are often mentioned.

An example from the older German literature is due to Staudinger and Endle,⁴ who found that diphenylcarbene, produced by the pyrolysis of diphenylketene, led to fluorene. A similar observation was later made by Franzen and Joschek.⁵ No satisfactory mechanism was advanced until recently,^{6,7} and we shall return to this reaction shortly.



The chemistry of carbenes ($R_2C:$) in the gas phase depends quite obviously on the structure of the R group, and a variety of reactions has been discovered. Here we will arrange the material not historically, but rather conceptually, proceeding from the least to most useful reactions. Four topics will be considered: fragmentation reactions, degenerate rearrangements, synthesis of paracyclophanes, and generation of bridgehead olefins.

Spin will not be discussed explicitly in discussions of mechanism. It is possible to construct plausible mechanisms using either singlets or triplets and we have done no experiments which allow a choice to be made.

(4) H. Staudinger and R. Endle, *Ber.*, 46, 1437 (1913).

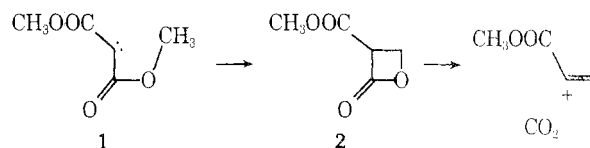
(5) V. Franzen and H.-I. Joschek, *Justus Liebigs Ann. Chem.*, 633, 7 (1960).

(6) C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, 53, 1459 (1970).

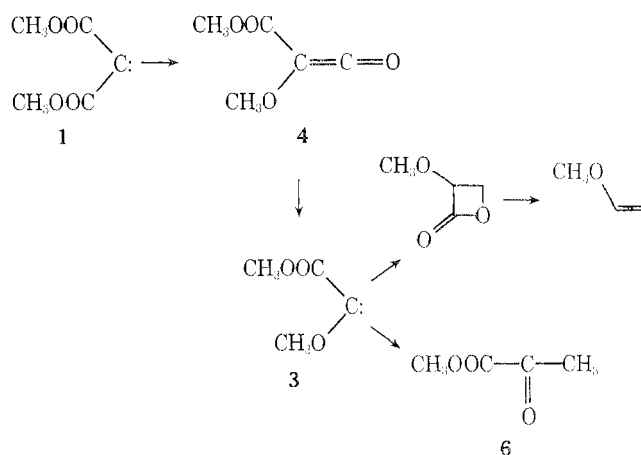
(7) J. A. Myers, R. C. Joines, and W. M. Jones, *J. Amer. Chem. Soc.*, 92, 4740 (1970).

Fragmentation Reactions

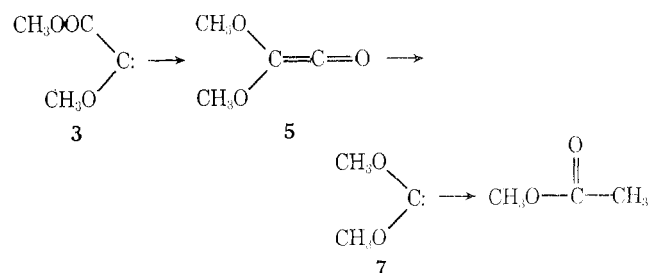
Some carbenes simply fly to pieces when generated in the gas phase. An example is bis(carbomethoxy)carbene (1), produced in a flow system by the pyrolysis of methyl diazomalonate.⁸ The isolable products are three esters and an ether, all of which involve loss of material from the carbene, and which appear as a function of the pyrolysis temperature. At relatively low temperature methyl acrylate is by far the major product. Apparently the easiest reaction of 1 is insertion into the lone available carbon-hydrogen bond to give the β -lactone 2. Lactone 2 does not survive 280° but loses CO_2 to give the observed acrylate. As



the temperature is increased, two new compounds, methyl vinyl ether and methyl acetate, grow at the expense of the acrylate. Both of these products involve further losses of carbon oxides and are, it seems, derived from (carbomethoxy)methoxycarbene, 3.



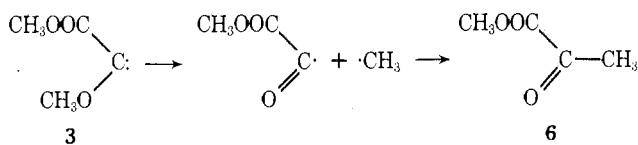
The formation of 3 most likely involves Wolff rearrangement of 1 to ketene 4 which loses carbon monoxide to give 3. Carbene 3 gives methyl vinyl ether by a repetition of the carbon-hydrogen insertion-loss of CO_2 route previously noted. Methyl acetate is a known⁹ product of dimethoxycarbene (7), which is itself evidently the result of Wolff rearrangement-loss of CO from 3, *via* 5.



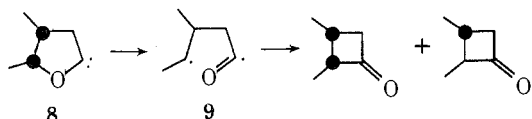
The last product, methyl pyruvate (6) can also be formed from 3, in a process similar to the production of methyl acetate from 7. The reaction is a formal

(8) D. C. Richardson, M. E. Hendrick, and M. Jones, Jr., *J. Amer. Chem. Soc.*, 93, 3790 (1971).

(9) D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Amer. Chem. Soc.*, 88, 582 (1966).

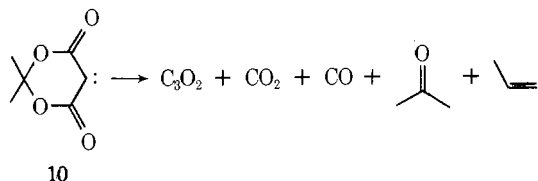


carbon-oxygen insertion reaction, but we doubt if a true insertion is really involved. The key experiment is that of Foster and Agosta,¹⁰ who found that carbene 8 gave a mixture of *cis*- and *trans*-cyclobutanones. They logically postulated 9 as the intermedi-



ate permitting scrambling of stereochemistry. We suspect that a similar mechanism applies in the formations of acetate and pyruvate. It is easy to devise test experiments, but in the absence of such we can only surmise.

The cyclic relative of 1, "Meldrum's carbene" (10) also fragments, even in solution.^{11,12} The known products are carbon monoxide, carbon dioxide, carbon suboxide, acetone, propylene, and an unknown larger compound. Propylene is probably formed by

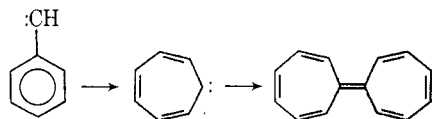


deoxygenation of acetone by any of a number of possible intermediate carbenes.¹³ More interesting is the formation of the compound of unknown structure which shows an infrared spectrum featuring a band at 1830 cm^{-1} .

It is certainly fair to ask what possible utility the chemistry described above can have. We confess to seeing none for the diazo ester pyrolyses, but can suggest that one may be found in the pyrolysis of related cyclic diazo ketones which, if properly designed, may lead to π systems difficult to produce in other ways.

Degenerate Rearrangements

In 1969 W. M. Jones and his collaborators, R. C. Joines and A. B. Turner, reported the formation of dimers of cycloheptatrienylidene on generation of phenylcarbenes in the gas phase.¹⁴ Our interest in



(10) A. M. Foster and W. C. Agosta, *J. Amer. Chem. Soc.*, **95**, 608 (1973).

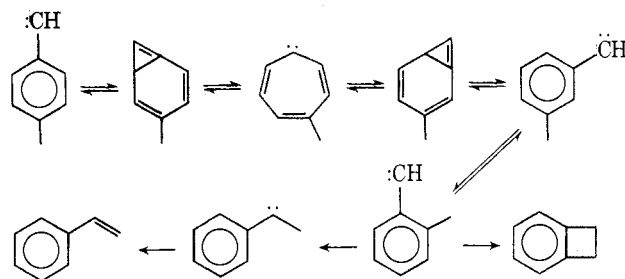
(11) P. M. Howley, A.B. Thesis, Princeton University, 1970; P. B. Shevlin and S. Kammula, unpublished results from Auburn University.

(12) For the chemistry of triplet 10, see: M. Jones, Jr., W. Ando, M. E. Hendrick, A. Kulczycki, Jr., P. M. Howley, K. F. Hummel, and D. S. Malament, *J. Amer. Chem. Soc.*, **94**, 7469 (1972).

(13) For an example see H. Nozaki, H. Takaya, and R. Noyori, *Tetrahedron*, **22**, 3393 (1966).

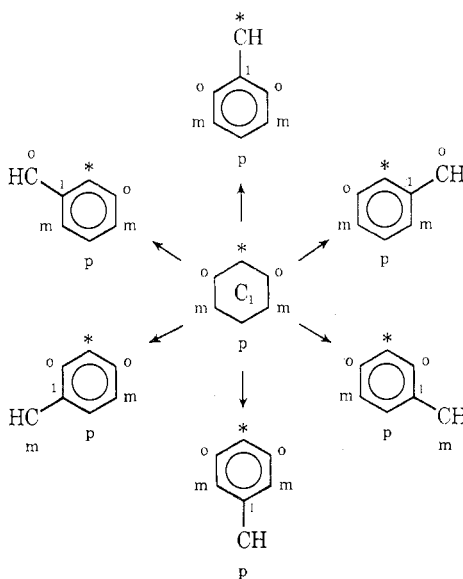
(14) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969). For the latest results on this subject from this group, see R. A. LaBar and W. M. Jones, *J. Amer. Chem. Soc.*, **96**, 3645 (1974), and R. L. Tyner, W. M. Jones, Jr., and J. R. Sabin, *ibid.*, **96**, 3765 (1974).

the chemistry of phenylcarbenes led us to search for the reverse reaction, and the following experiment was devised in collaboration with W. J. Baron of Princeton and Peter Gaspar of Washington University.¹⁵ If phenylcarbene were in equilibrium with cycloheptatrienylidene, then the tolylcarbenes should interconvert as shown below. The mechanism chosen seems the most reasonable to us, but variations can be devised which do not alter the overall conclusions. Addition of the carbene to the adjacent π system leads to the bicyclic cyclopropene shown. Reorganization of electrons gives the monocyclic cycloheptatrienylidene. In the presence of the label, reversal of this two-step process can lead either directly back to *p*-tolylcarbene or to *m*-tolylcarbene. Repetition of the entire process gives the final products, *o*-tolylcarbene and phenylmethylcarbene:



o-Tolylcarbene and phenylmethylcarbene, unlike their meta and para relatives, have easy and direct routes to stable products (benzocyclobutene and styrene) through carbon-hydrogen insertions.

Before discussing the utility of this reaction, we point out a simple device for generating the six (and only six) interrelated phenylcarbenes. This graphic process is completely equivalent to the mechanism above. The unique hydrogenless carbon, C_1 , is placed at the center of a hexagon, the vertices of which are labeled in order with the original divalent carbon (*) and the ortho, meta, and para carbons.

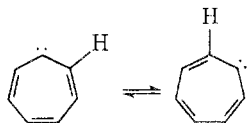


Any of the available phenylcarbenes can be generated simply by mentally displacing the appropriate vertex with C_1 . Also, the available cycloheptatrienyl-

(15) W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *J. Amer. Chem. Soc.*, **92**, 4739 (1970).

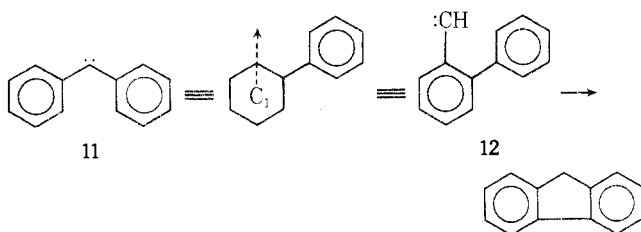
idenes can be produced by displacing not a vertex, but an edge of the hexagon.

The situation would have been far more complicated if 1,2-hydrogen shifts were occurring in the cycloheptatrienylenes. Such a reaction gets C_1 "into

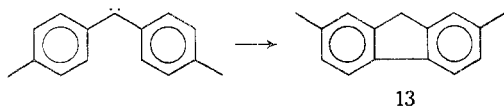


the game," and it is easy to show that, if such a reaction is permitted, the entire system becomes degenerate, with all carbons, on time average, connected with all others. However, labeling experiments both in our laboratories¹⁶ and much more completely by Hedaya and Kent,¹⁷ have shown that the vital hydrogen shift is unimportant, at least at temperatures below 700°. However, at 770° the shift is apparently occurring before ring contraction to fulveneallene.¹⁸ At this point it appears that the hydrogen shift cannot compete with the carbene interconversion, but that both these processes are faster than ring contraction.¹⁸

To illustrate the utility of this reaction, let us take the case of diphenylcarbene (11). Displacement of a vertex adjacent to the phenyl substituent in the appropriately constructed graph yields carbene 12, which by simple carbon-hydrogen insertion can give the mysterious fluorene first observed by Stauding-

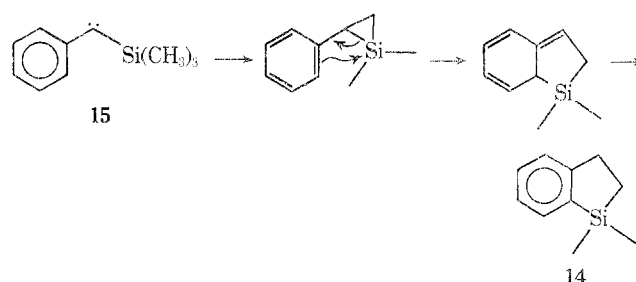


er.⁴ Thus a mechanism can be constructed in seconds for a reaction unsuccessfully interpreted for several decades. Happily this mechanism turns out to be the correct one, as labeling studies have shown 13 to be the fluorene produced from di-*p*-tolylcarbene.^{7,8}

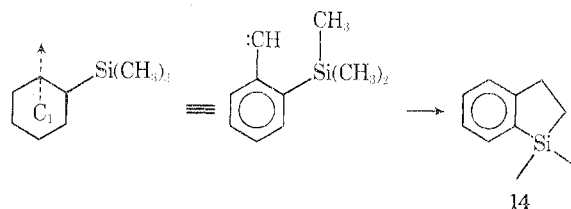


New reactions explicable (although not always so explained!) in these terms continue to appear. Thus both we¹⁹ and others²⁰ have noticed formation in the gas phase of indan 14 from (trimethylsilyl)phenylcarbene (15). This reaction has been rationalized²⁰ in terms of an intermediate silacyclopropane.

We felt that the formation of 14 was more likely to involve carbene-carbene rearrangements of the type just discussed. In this mechanism, the trimethylsilyl group is merely a substituent, with the final step



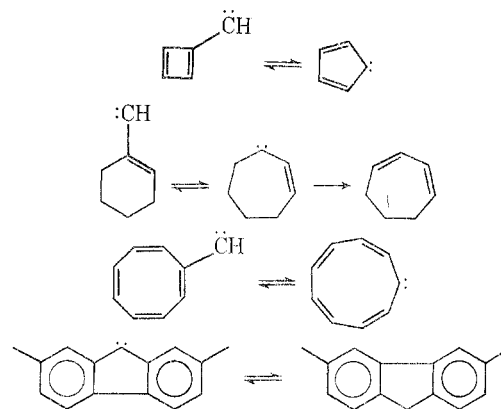
being insertion of the rearranged phenylcarbene into one of the methyl groups.



A ¹³C labeling experiment, carried out in collaboration with T. J. Barton and John A. Kilgour of Iowa State University, showed that this was indeed the route followed, and that silacyclopropanes are not involved.²¹

In principle, the gas-phase formation of benzocyclobutene and styrene can serve as a diagnostic for the presence of phenylcarbenes, and at least one such use has been reported.²²

Many relatives of this reaction are available for study. The pyridylcarbene-phenylnitrene interconversion has already seen much intensive work,²³ and the chemistry of the vinylcarbene-cyclopropene pair is being unraveled.^{24,25} Several other possibilities for further work exist and a few unexamined, or at least unreported, examples follow below. It is worth warning that our preliminary attempts to observe the first of these have resulted in several violent explosions.



Synthesis of Paracyclophanes

In the midst of an examination of the conventional chemistry of 4,4-dimethylcyclohexadienylenide (16), it occurred to us to look for the xylenes as products.

(16) W. J. Baron, unpublished results, Ph.D. Thesis, Princeton University, 1972.

(17) E. Hedaya and M. E. Kent, *J. Amer. Chem. Soc.*, **93**, 3283 (1971).

(18) W. D. Crow and M. N. Paddon-Row, *J. Amer. Chem. Soc.*, **94**, 4746 (1972).

(19) A. J. Rothschild, unpublished results.

(20) W. Ando, A. Sekiguchi, T. Hagiwara, and T. Migita, *J. Chem. Soc., Chem. Commun.*, 372 (1974).

(21) T. J. Barton, J. A. Kilgour, R. R. Gallucci, A. J. Rothschild, J. Slutsky, A. D. Wolf, and M. Jones, Jr., submitted for publication.

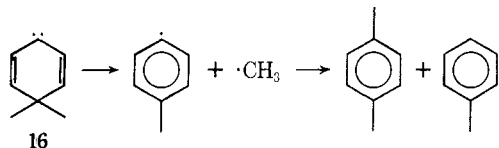
(22) W. J. Baron and M. R. DeCamp, *Tetrahedron Lett.*, 4225 (1973).

(23) C. Wentrup, C. Thetaz, and R. Gleiter, *Helv. Chim. Acta*, **55**, 2633 (1972).

(24) E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergman, *J. Amer. Chem. Soc.*, **95**, 5680 (1973).

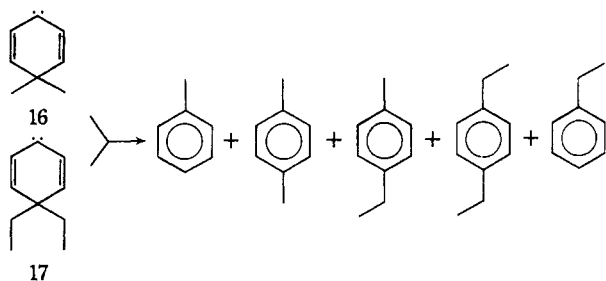
(25) J. A. Pincock, R. Morchat, and D. R. Arnold, *J. Amer. Chem. Soc.*, **95**, 7536 (1973).

None was found,²⁶ but the idea persisted and later, when we began to work on gas-phase reactions, the intramolecular reactions of **16** were reinvestigated. In contrast to what had been observed in solution, generation of **16** in the gas phase led to 16% xylene along with even greater amounts (27%) of toluene. Strikingly, the xylene is exclusively the para isomer.²⁷ One might have expected otherwise, as "rea-



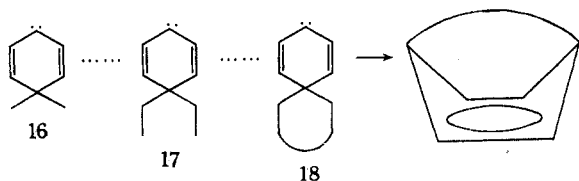
sonable" mechanisms can be written for the formations of the other isomers and there is at least one report in the literature of reaction in a steroidal system that would lead one to expect other isomers.²⁸ Nevertheless, only *p*-xylene is formed. This provides both a mechanistic problem and a synthetic opportunity.

Several intramolecular mechanisms come to mind, but none economically explains the formation of toluene. An intramolecular process in which **16** cleaves to a pair of radicals does explain the products, but was, as far as we knew, unprecedented. A crossover experiment of the classical type served to differentiate this latter possibility from the set of intramolecular reactions. Carbene **16** and its diethyl relative **17** were cogenerated and the products examined for the cross-product *p*-ethyltoluene, which should be found as well as *p*-xylene and *p*-diethylbenzene. In



surprisingly close to a statistical 1:2:1 ratio, the three dialkylbenzenes are found (1:1.6:0.75). Thus the intermolecular process prevails and, as would be expected, the products of dimerization of the aryl radicals can also be found.

But what of the advertised synthetic utility? Surely even if the work just described is mechanistically interesting, it is not synthetically useful. However, a trivial extension of the pair **16/17** leads to **18**, a mol-



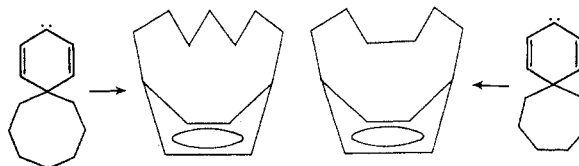
ecule that promised to be most useful. If the reaction path followed by **16** and **17** were still pursued, then

(26) M. Jones, Jr., A. M. Harrison, and K. R. Rettig, *J. Amer. Chem. Soc.*, **91**, 7462 (1969).

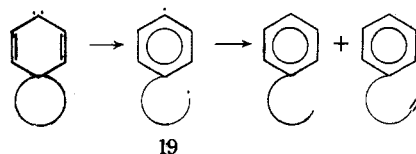
(27) T. E. Berdick, R. H. Levin, A. D. Wolf, and M. Jones, Jr., *J. Amer. Chem. Soc.*, **95**, 5087 (1973).

(28) H. Dannenberg and H. J. Gross, *Tetrahedron*, **21**, 1611 (1965).

18 must lead to a 1,4-bridged benzene or paracyclophane. At the time we began our work the smallest known paracyclophane was the [8] isomer and no new [*m*]paracyclophane had been reported for about a decade.^{29,30} During the course of our work this state of affairs was changed by the construction of [7]paracyclophane-3-carboxylic acid by Allinger and Walter,³¹ but our method remains, we think, a most simple means of fashioning easily available starting materials into the relatively inaccessible small [*m*]paracyclophanes. In actual practice, both [7]- and [6]paracyclophane can be produced easily by the gas-phase decomposition of the appropriate carbene.^{32,33}



We cannot be certain that the mechanism of this reaction follows that of the acyclic molecules, but it seems a reasonable presumption in the absence of the required labeling experiment. The products expected of the diradical **19**, alkyl- and alkenylbenzenes, are found in the reaction mixture.



The beauty of this synthesis lies in its simplicity, even inevitability, once the formation of *p*-xylene from **16** is known. Its drawback is that all of the strain in the product is introduced at once and one would expect that eventually **19** would find closure to a cyclophane too difficult and no bridged products formed. Indeed we may be at such a point, as to date all our efforts directed at [5]paracyclophane have met with failure. Nor have we been able to isolate the related Dewar benzene. Besides C₅-substituted benzenes the only product so far found in any appreciable quantity is styrene! Prospects for the future seem bright, however, as a host of para- and metacyclophanes should be available through this route. If the [5] isomer continues to evade isolation, it should be possible to build up supplies of a functionalized [6]paracyclophane and then ring contract using conventional methods, thus introducing the strain in increments.

Synthesis of Bridgehead Olefins

The past several years have seen a proliferation of methods for achieving what was once thought to be impossible. The number of routes to bridgehead olefins or "anti-Bredt" compounds is now quite large.³⁴

(29) D. J. Cram, C. S. Montgomery, and G. R. Knox, *J. Amer. Chem. Soc.*, **88**, 515 (1966).

(30) For a review see D. J. Cram and J. M. Cram, *Accounts Chem. Res.*, **4**, 204 (1971).

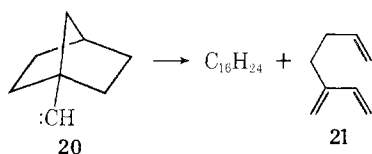
(31) N. L. Allinger and T. J. Walter, *J. Amer. Chem. Soc.*, **94**, 9267 (1972).

(32) A. D. Wolf, V. V. Kane, R. H. Levin, and M. Jones, Jr., *J. Amer. Chem. Soc.*, **95**, 1680 (1973).

(33) V. V. Kane, A. D. Wolf, and M. Jones, Jr., *J. Amer. Chem. Soc.*, **96**, 2643 (1974).

Nevertheless, it seemed to us that none of the known methods combined efficiency with generality. Further, a few of the methods seemed suspect in that organometallic reagents capable of producing the products attributed to the bridgehead olefins were probably involved. Having a synthesis at hand that seemed to us both extremely simple and probably quite general, we proceeded in spite of the spate of other methods.

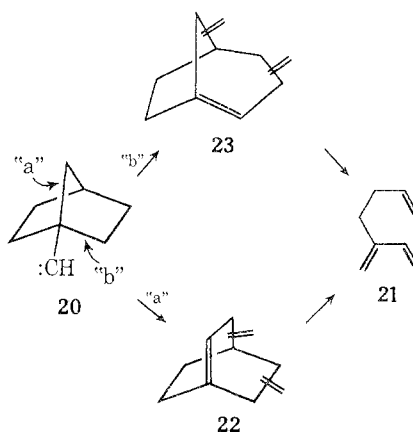
Our procedure involved the ring expansion of compounds containing a divalent carbon attached to the bridgehead of a small, bicyclic system. The idea was evidently not new with us, as it had been tried in solution some years previously by Wilt and coworkers.³⁵ It was apparent to these authors that even under "aprotic" conditions carbonium ions were involved and that the carbene was unusually unreactive. Generation in the gas phase of course removes any possibility of protonation, and it seemed to us inevitable that the carbene would ring-expand. We first examined the carbene initially investigated by Wilt, *et al.*, 1-norbornylcarbene (20). There are several products of the flash pyrolysis of the lithium salt of 1-norbornylcarboxaldehyde tosylhydrazone. Gas chromatography serves to separate a group of several dimers from the lone monomeric compound, triene 21.³⁶



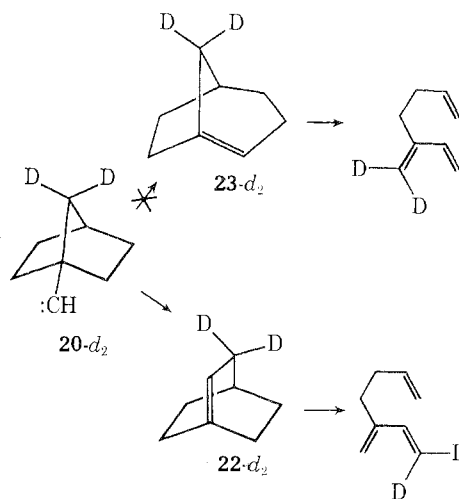
We can say little at this point about the structures of the dimers. Precise mass spectroscopy establishes the composition as $C_{16}H_{24}$, and the nmr spectra reveal no hydrogens attached to double bonds. Thus the dimers are not (a) Diels-Alder products from 21, (b) products of addition of 20 to 21, or (c) products of the dimerization of 20. They are entirely consistent with cyclobutanes formed from the dimerization of an intermediate bridgehead olefin.

Although 21 seems at first an unlikely product of 20, we can see at least two routes available for its formation. Both involve reverse Diels-Alder reactions of initially produced bridgehead olefins. There are two ring expansions possible in the unsymmetrical carbene 20. These give 22 and 23, each of which contains the bridgehead double bond in a six-membered ring. Carbene 20 is generated at high temperature (*ca.* 330°) and, moreover, the ring expansion is exothermic. The gas phase provides relatively poor opportunities for deactivation of energetic 22 and 23, and it is scarcely surprising, in retrospect, to find decomposition to 21. In accord with this scheme the ratio of dimers to monomer is temperature dependent. The higher the temperature, the more monomer. The lower the temperature, the more time available for 22 and/or 23 to dimerize, and the more $C_{16}H_{24}$ products appear.

The problem of which ring expansion (bond a or

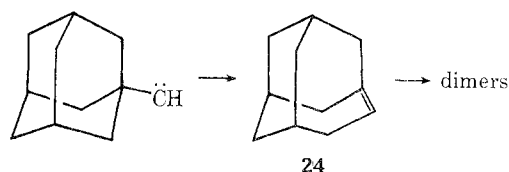


bond b) is taking place can be solved by an uncomplicated labeling experiment. Carbene 20- d_2 is generated and the labeling pattern in 21 must be different, depending upon the mode of ring expansion. Our original communication³⁶ gives the details of the analysis of the nmr spectra from which it could be deduced that the dominant mode of ring expansion involves bond a.



It seems most likely that 22 is the less stable of the two possibilities,³⁴ and naturally the question arises as to why it is formed in preference to 23. This example of kinetic control resembles that found in the related carbonium ions.³⁷ Indeed the two processes are most alike, as each begins with the interaction of an empty p orbital with an adjacent carbon-carbon bond containing a pair of electrons. Apparently in the initial stages of the reaction migration of bond a provides more release of strain than does movement of bond b, and both the carbonium ion and carbene take this route.

It seems to us that this method is likely to be extremely general. So far we can provide only one other example, in work done in collaboration with Paul



(34) G. Köbrich, *Angew. Chem.*, 85, 494 (1973); *Angew. Chem., Int. Ed. Engl.*, 12, 464 (1973); G. L. Buchanan, *Chem. Soc. Rev.*, 3, 41 (1974).

(35) J. W. Wilt, C. A. Schneider, H. F. Dabek, Jr., J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, 31, 1543 (1966).

(36) A. D. Wolf and M. Jones, Jr., *J. Amer. Chem. Soc.*, 95, 8209 (1973).

(37) R. C. Fort, Jr., "Carbonium Ions," Vol. IV, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1973, p 1783.

Schleyer's group at Princeton.³⁸ In this case, 1-adamantylcarbene ring-expands to 3-homoadamantene (24). The structure of 24 was inferred from the formation of appropriate dimers.

Most of the experimental skill and much of the conceptual input for the work just described were provided by an exceptionally skilled group of young coworkers. Drs. William Baron, Mark DeCamp, Michael Hendrick, and Ronald Levin all did portions of

(38) M. Farcasiu, D. Farcasiu, R. T. Conlin, M. Jones, Jr., and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8207 (1973).

this work as part of their Ph.D. Theses at Princeton. Dave Richardson's A.B. Thesis concerned the gas-phase pyrolysis of diazomalonic ester and Tom Berdick successfully worked out the formation of xylenes from 16. Dr. V. V. Kane was instrumental in making the synthetic efforts feasible, and Dr. Anthony Wolf carried out the paracyclophane and bridgehead olefin isolations and labeling experiments with great skill.

It has been a pleasure to collaborate with Professors Philip Shevlin of Auburn University, Peter Gaspar of Washington University, and Paul Schleyer at Princeton. Over the years conversations with Professor Gaspar, who is ever critical and insightful, have been especially stimulating and encouraging.

Some Chemistry of Alkanediazotates

Robert A. Moss

Wright and Rieman Laboratories, School of Chemistry, Rutgers University, The State University of New Jersey, New Brunswick, New Jersey 08903

Received April 24, 1974

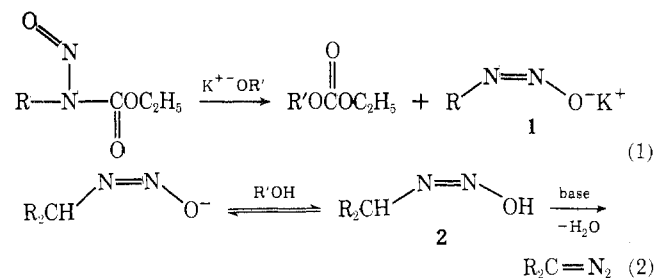
The structure and chemistry of arenediazotates, $\text{ArN}=\text{NO}^-$, have long been of interest, and, from 1894 to 1912, were the subject of heated controversy between A. Hantzsch and E. Bamberger.^{1a} They can be formed by the action of hydroxide ions on arenediazonium ions.

The importance of the latter in azo coupling reactions was an early driving force for the study of the diazotates. Today, there is intense interest in the rates and equilibria of the reactions of arenediazonium ions with nucleophiles,^{1b} and the related chemistry of the arenediazotates is still being developed.

Alkyldiazonium ions are much less stable than their aryl counterparts, are seldom isolated, and rarely participate in azo coupling reactions. Accordingly, the chemistry of alkanediazotates, $\text{RN}=\text{NO}^-$, is not accessible *via* the diazonium ions. Although alkanediazotates have been known for a long time, the development of their chemistry has been somewhat haphazard.

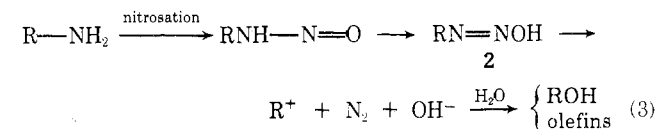
We therefore initiated a broad study of alkanediazotates, and have found that their chemistry has important mechanistic and synthetic features. This Account will explore those aspects. We also make brief note of the past and present context of alkanediazotate chemistry.

A Brief History of Alkanediazotates. Alkanediazotates, 1, may be generated by the basic cleavage of *N*-alkyl-*N*-nitrosourethanes (eq 1). In alcoholic KOH, 1, when possessing an α proton, can afford a diazoalkane (eq 2). The intermediacy of 1 in Pech-



mann's diazomethane synthesis² was established by Hantzsch,³ who cleaved *N*-methyl-*N*-nitrosourethane with ethereal KOC_2H_5 , isolating solid potassium methanediazotate (1, $\text{R} = \text{CH}_3$), which gave diazomethane upon addition of base and wet ether. Similar behavior was observed for 1, $\text{R} = \text{C}_6\text{H}_5\text{CH}_2$.

The conjugate acid of 1, diazotic acid (2), is a key intermediate in the nitrosative deamination of primary carbinamines⁴ (eq 3). The centrality of 2 in



diazoalkane synthesis (eq 2) and in deaminative reactions was implicit in observations that 1 ($\text{R} = \text{C}_6\text{H}_5\text{CH}_2$) gave rise to benzyl alcohol, benzyl methyl ether, and phenyldiazomethane in aqueous metha-

(1) (a) Historical and chemical considerations appear in H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N.Y., 1961; (b) H. Zollinger, *Accounts Chem. Res.*, **6**, 335 (1973).

(2) H. v. Pechmann, *Chem. Ber.*, **27**, 1888 (1894); **28**, 855 (1895).

(3) A. Hantzsch and M. Lehmann, *Chem. Ber.*, **35**, 897 (1902). The $\text{CH}_3\text{N}=\text{NOK}$ was probably contaminated with potassium ethyl carbonate. Pure material can be prepared from CH_3NH_2 , NOCl , and CH_3OK : E. Müller, H. Haiss, and W. Rundel, *Chem. Ber.*, **93**, 1541 (1960).

(4) Reviews include: (a) R. A. Moss, *Chem. Eng. News*, **49** (48), 28 (1971); (b) J. T. Keating and P. S. Skellern in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N.Y., 1970, p 573 ff; (c) L. Friedman in ref 4b, p 655 ff; (d) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N.Y., 1968, pp 440-483.

Robert A. Moss was born in Brooklyn, N. Y. He received a B.S. degree from Brooklyn College, and M.S. and Ph.D. degrees from the University of Chicago, where he studied with Professor G. L. Closs. After a post-doctoral year at Columbia with Professor Ronald Breslow, he joined the School of Chemistry at Rutgers University (1964), where he is now Professor of Chemistry. Dr. Moss has been National Institutes of Health Special Postdoctoral Fellow and Visiting Scientist at M.I.T., and a Fellow of the A. P. Sloan Foundation. Besides diazotate and deamination chemistry, he is interested in carbenes, the synthesis of azoxyalkanes, and micellar organic chemistry.