

THE REACTIONS OF TRANS-2,3-DIMETHYLCYCLOPROPYL METHYLENE
PRODUCED PHOTOLYTICALLY IN THE GAS PHASE*

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A previous communication (1) has reported the synthesis and photolysis of cyclopropyldiazomethane. The intention of that work was to study the decomposition of the intermediate carbene (analogous to the presumed carbene produced in the reaction of hot carbon atoms with cyclopropane (2,3) and the presumed carbene produced in the carbon atom reactions described by Engel and Skell (4)) and attempt to correlate product distribution with mechanism and method of carbene production. Major products of decomposition are acetylene and ethylene, which arise from homolytic bond scission of the ring in the carbene. It is clear that more light could be shed on this whole process if the cyclopropane ring were substituted in such a way as to allow a "nascent" substituted ethylene a stereochemical choice in going to product.

To this end, trans-2,3-dimethylcyclopropyldiazomethane was prepared in a six step synthesis starting with trans-2,3-dimethylcyclopropyl chloride obtained from a ring forming reaction with butyl lithium and methylene chloride using the method of Closs and Closs (5). The chloride was converted to the carboxylic acid; the acid converted to the acid chloride; the acid chloride converted to the amide; and the amide reduced to the amine. The amine was diazotized to the diazo compound by the method of Adamson and Kenner (6). The purification of the diazo compound (exclusively the trans-dimethyl compound at this point), a beautiful orange yellow colored liquid, was accomplished by a bulb to bulb distillation in a high vacuum system by conventional high vacuum





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techniques. All intermediate compounds had correct analyses and spectral properties. A well defined I.R. spectrum was obtained showing an intense diazo band at 2075 cm^{-1} . The compound has an appreciable vapor pressure, is reasonably stable in the gas phase at room temperature (decomposition rate $\sim 6\%/hr$), and can be stored for longer periods at -195° . Photolyses of the gaseous diazo compound were carried out in a water cooled Pyrex vessel (440 ml) using a Hanovia medium pressure lamp (#654A36) positioned in a center well in the vessel. No diazo compound could be detected after 60 min. Products were separated and identified by emergence time using two different gas liquid chromatographic columns. All products were trapped, and identified by comparison with I.R. spectra of authentic materials. The products themselves are stable under the conditions of the photolysis. The results of our experiments are given in Table 1.

Table 1

Products from the gas phase photolysis of trans-2,3-dimethylcyclopropyldiazomethane

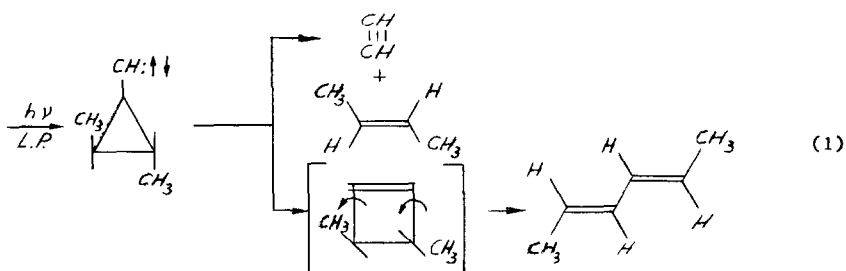
Gas Pressure	HC=CH				
11 torr	41%	43%	< 2%	20%	< 4%
23 torr	40%	41%	< 2%	25%	6%
21 torr + 739 torr N ₂	21%	10%	9%	8-15% ^a	7-13% ^a

^aSpread of yields in two runs.

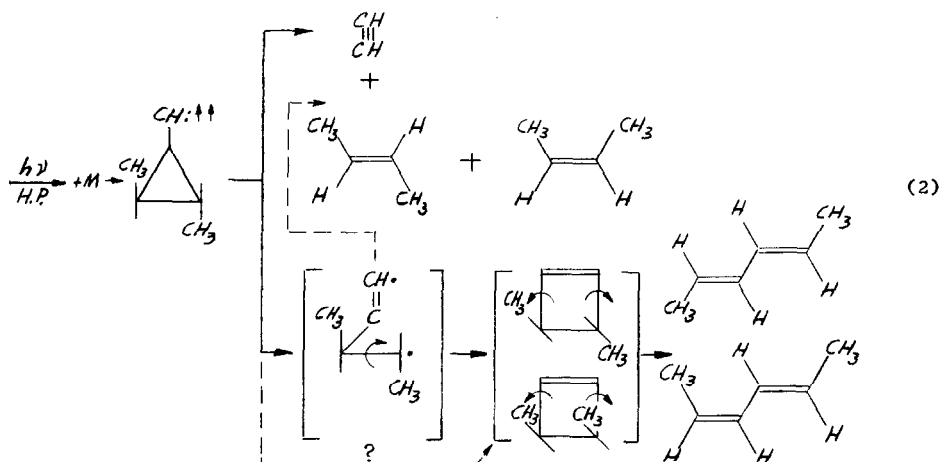
The data show that essentially complete stereospecificity obtains in the product butene (trans) when photolysis is carried out on the neat material at low pressure. It is reasonable to assume that most of the carbene is produced in the singlet state and this suggests that the pathway for decomposition of the carbene is indeed spin controlled. Strong support for this is adduced from the appearance of a third major product, trans,trans-2,4-hexadiene. Considered now in terms of the Orbital Symmetry rules (7) one would state that the singlet carbene rearranges in a concerted fashion to the trans-3,4-dimethylcyclobutene* which is produced in its electronic ground state but highly vibrationally excited. The cyclobutene then undergoes a typical thermal conrotatory ring opening.

* This intermediate product has not been identified as such but it should be noted that a compound as yet unidentified has been isolated in high yield (run at 23 torr, 30% yld) and may well be the "cyclobutene". This compound was not searched for in other runs.

The photolysis was also run near atmospheric pressure by raising the total pressure in the system to 760 torr with added nitrogen. As is conventional in gas phase carbene work the pressure was raised to allow collisional deactivation of the presumed excited electronic state to its ground state. The results support and extend the postulate of an excited singlet state being converted in part to a lower lying triplet. It is first noteworthy that deexcitation reduced the over-all ring scission yield.* The stereochemical course is now no longer unique, roughly equal amounts of the *cis* and *trans*-2-butene being produced. Thus the presumption of a ground state triplet is reflected in the fact that the ring scission proceeds in a manner allowing rotation about the C-C bond between methyl groups. Finally the product 2,4-hexadiene appears not only in the *trans-trans* form but also in the *cis-trans* form. This product formation is consistent with the hypothesis that those carbenes which are triplets rearrange to a postulated intermediate excited dimethylcyclobutene (both *cis* and *trans* forms), which then undergo a disrotatory ring opening to give the observed hexadienes. These postulates are summarized in schemes 1 and 2.



*The implication of this especially with regard to the spin state of the carbene will be the subject of a future communication to be published jointly with R. Hoffmann.



It must be made clear, however, that there are alternate explanations to the details of these reactions. We believe the results in this paper support the gross features delineated in the schemes.

This system, we believe, forms a particularly interesting one for relating spin state, "concertedness" of reaction, stereochemistry and conservation of orbital symmetry. Continuing work is directed towards determining proportion of spin state in the carbenes formed at each pressure, identification of unknown products and investigation of the products from the two possible cis-2,3-dimethylcyclopropyl-diazomethanes.

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