# Trimethylenemethane[1]

**Philip S. Skell and Robert G. Doerr**

*Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802.* *Received April 10, 1967*

**Abstract:** Trimethylenemethane (II) was prepared by the reaction of 2-halomethyl-3-halopropene (I) with potassium vapor. The products of this reaction consisted of 1,4-dimethylenecyclohexane (III), *p*-xylene, 2-methylpropene (IV), methylenecyclopropane, and the normal butenes. These results suggest the intermediacy of trimethylenemethane existing in the triplet state. 1,4-Dimethylenecyclohexane is formed by the dimerization of two triplet molecules with opposite spins, and 2-methylpropene is formed by the abstraction of two hydrogen atoms. The three butenes are produced, at least in part, by a secondary reaction of potassium vapor with methylenecyclopropane. In contrast, the saturated 1,3-diradical VI, formed in the reaction of 1,3-diiodo-2-methylpropane (V) with potassium vapor, gives methylcyclopropane and 2-methylpropene. 1,4-Dimethylcyclohexane or other products due to dimerization were not detected. Trimethylenemethane does not react with ethene, but does react with other triplet molecules. The generation of triplet methylene in the presence of trimethylenemethane leads to methylenecyclobutane and 2-methyl-1-butene.

Trimethylenemethane (II) has been the subject of considerable theoretical discussion. Molecular orbital calculations[2] predict that trimethylenemethane will have a triplet ground state and a delocalization energy of $1.46\beta$ ($\sim$34 kcal) relative to the classical structure of one double bond and two localized electrons. The complete configuration interaction treatment of trimethylenemethane also predicts a triplet ground state.[3] The sum of the bond orders at the central carbon is 4.732. This is the maximum value for the sum of the bond orders at a carbon atom,[4] and is used as a reference for the calculation of free valence indices.[5] This molecule has been used as a model for the calculation of negative spin densities in triplet molecules[6] and for the calculation of the energy involved in the formation of a diradical isomer of cyclopropanone.[7]

Trimethylenemethane has recently been prepared by matrix photolysis of 4-methylene-1-pyrazoline at $-185°$ [8a] and of 3-methylenecyclobutanone at $-196°$.[8b] The esr spectrum confirmed that trimethylenemethane was a symmetrical ground-state triplet.[8] Pyrolysis of 4-methylene-1-pyrazoline resulted in its conversion to methylenecyclopropane.[9] Deuterium labeling showed that the original methylene group in the pyrazoline was at least partially equilibrated with the methylene groups in the cyclopropane ring. The results were explained by the formation of a symmetrical intermediate in which dideuteriomethylene groups were slower to rotate into position for ring closure than were diprotiomethylene groups. A similar equilibration was observed in the formation of alkylidenecyclopropanes from the photolysis of 4-alkylidene-1-pyrazolines.[10] The extent of equilibration was greatly increased when the photolysis was photosensitized with benzophenone or triphenylene.[10b] The authors suggested that the photosensitized photolysis led to the triplet state of the trimethylenemethane derivative and direct photolysis involved the singlet state.

Derivatives of trimethylenemethane have been postulated as intermediates in the rearrangement of substituted methylenecyclopropanes.[11] On the basis of stereochemical evidence, Ullman[11c] concluded that the rearrangement of the dimethyl ester of Feist's acid proceeded through both a symmetrical intermediate and a "valence tautomerization" involving simultaneous cleavage and re-formation of the cyclopropyl ring bonds.

Trimethylenemethaneiron tricarbonyl, an organometallic complex of this intermediate, was prepared.[12]

The reaction of alkali metal vapor with organic halogen compounds is a method for generating mono- and diradical species. This reaction has been studied extensively from a kinetic viewpoint.[13] For example, the reaction between sodium atoms and methyl iodide, methyl bromide, or methyl chloride occurs with 1, 50, and 10,000 respective collisions. Passage of the organic species formed by the reaction of methyl bromide and sodium vapor into a vessel of iodine vapor produces methyl iodide.[14] The same species removes mirrors of antimony and tellurium, in the latter case forming dimethyl ditelluride.[15] Product analysis also supports the formation of methyl and ethyl radicals,[16–18] the vinyl radical,[19,20] and halomethyl radicals.[21–24] Sim-

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(1) (a) This work was communicated previously: R. G. Doerr and P. S. Skell, *J. Am. Chem. Soc.*, **89**, 3062 (1967). (b) Abstracted from the Ph.D. Thesis of R. Doerr. (c) This work was supported by the National Science Foundation.

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(11) (a) J. K. Crandall and D. R. Paulson, *J. Am. Chem. Soc.*, **88**, 4302 (1966); (b) J. P. Chesick, *ibid.*, **85**, 2720 (1963); (c) E. F. Ullman, *ibid.*, **82**, 505 (1960).

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(17) C. E. H. Bawn and C. F. H. Tipper, *Discussions Faraday Soc.*, **2**, 104 (1947).

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(19) A. W. Tickner and D. J. LeRoy, *ibid.*, **19**, 1247 (1951).

ilarly, the reaction of dihaloalkanes with alkali metal vapor produces organic diradicals.[25–30] For example, 1,3-dihalopropane gives the 1,3-diradical which cyclizes to cyclopropane or rearranges to propene.[25–26]

### Trimethylenemethane

Trimethylenemethane was prepared by the reaction of potassium vapor[31] with 2-iodomethyl-3-iodopropene. The products from this reaction carried out at different temperatures are given in Table I.

**Table I.** Reaction of 2-Iodomethyl-3-iodopropene with NaK

| | Reaction | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4[a] |
| | Temp, °C | | | |
| | 228-235 | 232-236 | 247-267 | 226-232 |
| Products | Mole % yield | | | |
| 2-Methylpropene | 14.0 | 13.3 | 13.0 | 13.5 |
| 1-Butene | 2.2 | 2.7 | 2.2 | 4.3 |
| *trans*-2-Butene | 8.1 | 5.8 | 4.4 | 5.8 |
| *cis*-2-Butene | 5.3 | 4.7 | 3.5 | 3.7 |
| Methylenecyclopropane | 0 | 0 | 0.8 | 0 |
| 1,4-Dimethylenecyclohexane | 1.3 | 11.0 | 11.3 | 14.0 |
| *p*-Xylene | 33.5 | 22.3 | 16.0 | 14.0 |
| Total | 64.3 | 59.8 | 51.2 | 55.8 |

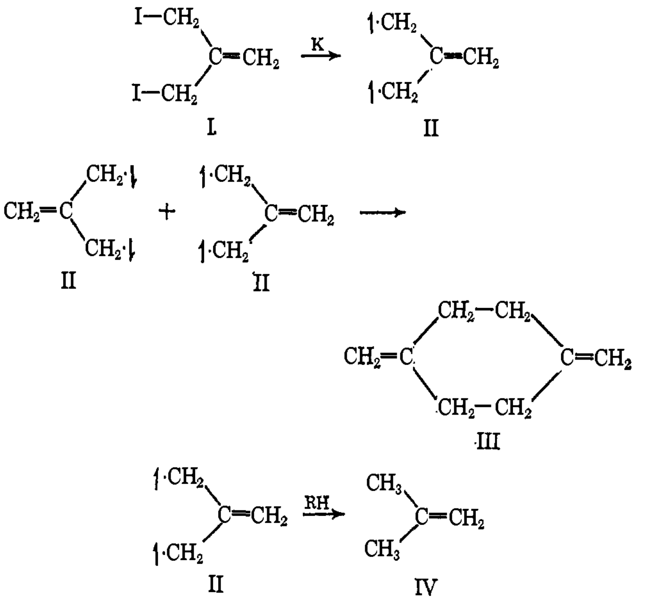
[a] Conducted in the presence of a 20-fold excess of ethene.

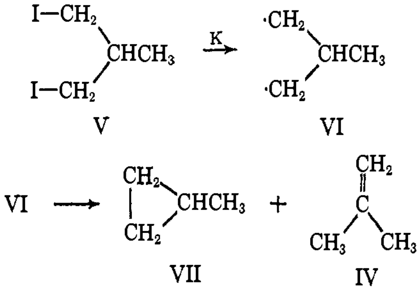
The formation of 1,4-dimethylenecyclohexane and 2-methylpropene suggests the intermediacy of trimethylenemethane existing in the triplet state. 1,4-Dimethylenecyclohexane would be formed by the dimerization of two triplet molecules of trimethylenemethane with opposite spins, and 2-methylpropene by the abstraction of two hydrogen atoms from neighboring hydrocarbon or potassium hydride.

The formation of *p*-xylene is due to a secondary reaction of 1,4-dimethylenecyclohexane. The sum of the yields of the two compounds remains constant at similar temperatures (*i.e.*, 34.7% in reaction 1 and 33.3% in reaction 2), while the ratio of the two is variable. The dehydrogenation of cyclohexene to benzene under similar conditions has been reported.[30]

To determine whether any of the above products could arise from a thermal reaction of 2-iodomethyl-3-iodopropene, a sample of the diiodide was decomposed at 210°. The pyrolysis produced only iodine and a black polymeric material.

The reactions of trimethylenemethane (II) and 2-methyl-1,3-propadiyl (VI), the diradical formed from the saturated diiodide V, are different. Reaction of 1,3-diiodo-2-methylpropane (V) with potassium vapor at 227–228° results in the formation of methylcyclopropane (VII), 2-methylpropene (IV), 2-methylpropane, and 1-butene in yields of 76.7, 3.3, 0.2, and 0.3%, respectively. 1,4-Dimethylcyclohexane or other products due to dimerization were not detected. Extensive studies of 1,2-, 1,3-, 1,4-, and 1,5-diradicals testify to the insignificance of dimerization in the reactions of saturated diradicals generated from dihalides in this system.[26,28] Dimerization products were not formed by pyrolysis of 1-pyrazolines.[32]





While reaction of potassium vapor with 1,3-diiodo-2-methylpropane would give both the singlet and triplet 1,3-diradicals, the formation of methylcyclopropane and 2-methylpropene would take place only from the singlet. Ring closure of the triplet to triplet cyclopropane (conservation of spin multiplicity) and hydrogen migration in the triplet 1,3-diradical to form triplet 2-methylpropene are endothermic processes, the latter by about 14 kcal/mole.[29] The triplet 1,3-diradical can easily be converted to the singlet state (or to singlet cyclopropane or 2-methylpropene) by collision with a doublet potassium atom.

The unusual behavior of trimethylenemethane compared to other 1,3-diradicals can be explained by the large delocalization energy of the triplet ground state which makes it the favored state under either thermodynamic or kinetic control. Cyclization of triplet trimethylenemethane to triplet methylenecyclopropane is endothermic by about 25–50 kcal/mole. If cycliza-

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(23) J. W. Hodgens and R. L. Haines, *Can. J. Chem.*, **30**, 473 (1952).

(24) H. B. Palmer and W. J. Miller, *J. Chem. Phys.*, **38**, 278 (1963).

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(27) P. S. Skell and R. J. Petersen, *J. Am. Chem. Soc.*, **86**, 2530 (1964).

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(29) G. L. Tingey, Ph.D. Thesis, The Pennsylvania State University, 1963.

(30) R. G. Doerr and P. S. Skell, *J. Am. Chem. Soc.*, **89**, 4684 (1967).

(31) The predominant reacting species in the previously described sodium–potassium alloy (NaK) spray apparatus would be monatomic potassium: P. S. Skell, E. J. Goldstein, R. J. Petersen, and G. L. Tingey, *Chem. Ber.*, **100**, 1442 (1967).

(32) R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **88**, 3963 (1966).

tion of triplet trimethylenemethane to singlet methylenecyclopropane (~20 kcal exothermic) were not strongly spin forbidden, trimethylenemethane would not survive in solid matrices at −185°.[8] Thus since no favorable unimolecular path is available, trimethylenemethane accumulates until its concentration becomes high enough for bimolecular coupling to become a dominant reaction. Hydrogenation to 2-methylpropene is also favored by the long life of the trimethylenemethane triplet. The analogous reactions are minor with the saturated 1,3-diradicals.

Trimethylenemethane was generated in the presence of a 20-fold excess of ethene to determine whether this intermediate would react with olefins. The results of the reactions are presented in column 4 of Table I. A comparison of these results to those obtained from the reaction of 2-iodomethyl-3-iodopropene in the absence of ethene show that trimethylenemethane does not react with ethene and that the presence of ethene has little effect on the distribution of products obtained from trimethylenemethane.

Two reactions in which the precursor of trimethylenemethane was changed from a diiodide to a dichloride were carried out. The results of the reactions of 2-chloromethyl-3-chloropropene with potassium vapor are recorded in Table II.

**Table II.** Reaction of 2-Chloromethyl-3-chloropropene with NaK

| | Reaction | |
|---|---|---|
| | 1 | 2 |
| | Temp, °C | |
| | 237–243 | 270 |
| Products | Mole % yield | |
| Methane | 0.5 | 1.5 |
| Ethane | 0.8 | 3.4 |
| Ethene | 0.9 | 1.4 |
| 2-Methylpropene | 9.7 | 12.4 |
| 1-Butene | 5.2 | 5.7 |
| *trans*-2-Butene | 4.7 | 8.0 |
| *cis*-2-Butene | 5.7 | 5.9 |
| Methylenecyclopropane | 5.2 | 0 |
| Benzene | 0.5 | 0 |
| 1,4-Dimethylenecyclohexane | 5.9 | 2.1 |
| *p*-Xylene | 3.0 | 4.7 |
| Total | 41.1 | 43.1 |

The same products are observed as appeared in the reaction of the diiodide, but the yields of 2-methylpropene and especially the dimerization products have been reduced. The differences in the reactions of the diiodide and the dichloride can be explained by the greater reactivity of alkyl iodides.

Methyl iodide has been reported to require an average of only one collision with a sodium atom for reaction.[13] Since the diiodide in question is an allyl iodide, it would be expected to be equally reactive. Allyl chloride has a reactivity about 0.005 times that of methyl iodide, and saturated primary alkyl chlorides are ~$10^{-4}$ times as reactive as methyl iodide.[13] It would then be expected that after one halogen had been removed from 2-halomethyl-3-halopropene, the remaining chloro radical would have a lifetime at least 200 times that of the corresponding iodo radical. Thus the buildup of trimethylenemethane concentration required for dimerization would not be as great as with the diiodide, and reactions with first-order involvement of trimethylenemethane are preferred.

The sum of the yields of the normal butenes and methylenecyclopropane remains reasonably constant. This fact suggests that the formation of the butenes may be due to a secondary reaction of methylenecyclopropane. To test this hypothesis, a sample of methylenecyclopropane was subjected to the reaction conditions. Only 7% of the methylenecyclopropane was recovered and a mixture of the normal butenes was produced in good yield.

The apparent formation of singlet methylenecyclopropane from a triplet intermediate deserves some comment. The law of conservation of spin angular momentum predicts that the encounters between the intermediate iodo radical and potassium atoms should lead to triplet combinations three times as frequently as singlet. The elimination of potassium iodide from either of these collision complexes is probably high since alkyl iodides react at nearly every collision. Thus a 3:1 ratio of triplet to singlet trimethylenemethane is predicted. Singlet trimethylenemethane could either form methylenecyclopropane or decay to the triplet state. Conversion of triplet trimethylenemethane to singlet is improbable on energetic grounds, but three out of four collisions with potassium atoms could lead directly, by an energetically favorable route, to singlet methylenecyclopropane and potassium atoms with inverted spin designations.

## Reaction of Triplet Methylene and Allene

An attempt was made to produce trimethylenemethane by the reaction of dibromomethane with potassium vapor in the presence of allene. It has been reported that dibromomethane reacts with potassium to give triplet methylene.[29] Triplet methylene could add to the center carbon of allene, as do methyl radicals,[33] to give a triplet intermediate which upon rotation about the carbon–carbon single bond would give planar trimethylenemethane.

The experiment was conducted at 205–230° using 0.051 mole of dibromomethane and 0.35 mole of allene. The products obtained from the reaction of triplet methylene and allene consisted of 1-butene (8.4% yield) and methylenecyclopropane (11.3% yield). Products expected for the intermediacy of trimethylenemethane were not detected. At 270–280° the products (and their yields) were butane (0.6%), 1-butene (2.4%), *cis*-2-butene (1.3%), *trans*-2-butene (1.2%), and 2-methylpropene (0.6%). Again the dimerization products of trimethylenemethane were absent.

The failure to produce trimethylenemethane can be explained in two ways. The first is the sensitivity of allene to the reaction conditions. Allene is efficiently converted to nonvolatile products and, in low yield, to a mixture of propane and propene. The second is the possibility that triplet methylene does not add to the center carbon of allene but, like the trifluoromethyl radical,[34] adds to the terminal carbon.

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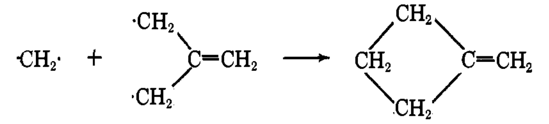
## Reaction of Triplet Methylene and Trimethylenemethane

Since trimethylenemethane appears to be a triplet species that dimerizes, addition of another triplet intermediate should be the most effective means of trapping trimethylenemethane. Diiodomethane should yield triplet methylene as does dibromomethane. Simultaneous reaction of 2-iodomethyl-3-iodopropene and a fivefold excess of diiodomethane with potassium vapor was effected at 235–240°. The results are given in Table III. In addition to the usual products from trimethylenemethane, a number of $C_5$ olefins were obtained, indicating a reaction of trimethylenemethane with methylene.

**Table III.** Reaction of 2-Iodomethyl-3-iodopropene with Excess Diiodomethane and NaK

| Products | Mole % yield |
|---|---|
| 2-Methylpropane | 0.3 |
| 2-Methylpropene | 10.4 |
| Butane | 1.2 |
| 1-Butene | 7.2 |
| *trans*-2-Butene | 8.6 |
| *cis*-2-Butene | 6.2 |
| 1,3-Butadiene | 0.1 |
| 2-Methyl-1-butene | 1.5 |
| 2-Methyl-2-butene | 1.3 |
| 3-Methyl-1-butene | 0.1 |
| Methylenecyclobutane | 1.4 |
| 1-Methylcyclobutene | 0.6 |
| Pentane | 0.1 |
| 1-Pentene | 0.1 |
| *trans*-2-Pentene | 0.2 |
| Benzene | 0.5 |
| 1,4-Dimethylenecyclohexane | 6.3 |
| *p*-Xylene | 10.4 |
| Unidentified liquids (largest component is 1.4%) | 6.8 |
| Total | 63.3 |

The products can be rationalized by the formation of a vibrationally excited methylenecyclobutane (~100 kcal exothermic) which is partially quenched, the remainder isomerizing to 1-methylcyclobutene and the open-chain dienes, 2-methyl-1,3-butadiene and 1,3-pentadiene. Under the reaction conditions the conjugated dienes are expected to be hydrogenated to the $C_5$ olefins. At 180° 1,3-butadiene is converted in 47% yield as a mixture of butane and the butenes, the remainder being nonvolatile material.[28]



Trimethylenemethane is effectively trapped with triplet cyclobutadienes.[1a,b] The details of these reactions will be presented later.

## Experimental Section

**Preparation of 2-Chloromethyl-3-chloropropene.** 2-Methyl-3-chloropropene (272 g, 3.00 moles) was chlorinated[35] until the refractive index ($n^{25}\text{D}$) was 1.4775. The mixture was washed with water and dried over anhydrous $Na_2SO_4$. Analysis by vpc (Carbowax, 74°) showed that the mixture consisted of 2-chloromethyl-1-chloropropene (30 and 9%, probably *cis* and *trans*), 2-chloromethyl-3-chloropropene (31%), and 2-methyl-1,2,3-trichloropropane (30%).

The mixture was distilled on a spinning-band column, following the progress of the distillation by vpc. A 10-g sample of 2-chloromethyl-3-chloropropene was obtained, bp 60° (50 mm) [58° (50 mm)[35a]], which was greater than 99% pure. The nmr spectrum consisted of two singlets at 4.19 and 5.32 ppm (δ scale) in a ratio of 2:1. The nmr of a 2-chloromethyl-1-chloropropene fraction, bp 54–55° (50 mm) [lit.[35a] bp 54° (50 mm)], showed a fine doublet at 1.90 ppm, a singlet at 4.21 ppm, and a multiplet at 5.97 ppm in a ratio of 3:2:1. The nmr spectrum of 2-methyl-1,2,3-trichloropropane, bp 80° (50 mm) [bp 74° (45 mm)[35b]], consisted of two singlets at 1.73 and 3.89 ppm in a ratio of 3:4.

**Preparation of 2-Iodomethyl-3-iodopropene.** A mixture (24 g, 0.19 mole) consisting of 25% 2-chloromethyl-3-chloropropene and 75% 2-chloromethyl-1-chloropropene was added to KI (63 g, 0.38 mole) in 400 ml of acetone. A precipitate formed immediately. The mixture was refluxed 8 hr. It was filtered and concentrated to 100 ml by distillation. The concentrate was poured into 300 ml of water and extracted with 100 ml of pentane. The pentane solution was washed with $Na_2S_2O_3$ solution and water and dried over anhydrous $Na_2SO_4$.

The pentane was removed by distillation and the product was distilled (5 mm) through a 10-cm Vigreux column. Two products were obtained: 2-iodomethyl-1-chloropropene (22.5 g, 0.104 mole, 73%; bp 49–52°) and 2-iodomethyl-3-iodopropene (9.6 g, 0.031 mole, 65%; bp 83–85°).

2-Iodomethyl-3-iodopropene crystallized on cooling. The solid was washed with $Na_2S_2O_3$ and recrystallized from hexane at reduced temperature to give white plates, mp 32–33°.

**Reaction of 2-Iodomethyl-3-iodopropene with NaK.** 2-Iodomethyl-3-iodopropene (2.8 g, 0.0091 mole) was placed in the vaporization coil of the NaK apparatus.[31] The atmosphere inside the apparatus was maintained at 200-mm helium pressure. Helium flowed through the vaporization coil (2.0 l./min, STP), carrying the diiodide through a preheater into the reaction zone. Simultaneously, a fine spray of NaK (88 wt % K) saturated the helium in the reaction zone with potassium vapor. The helium stream containing the products was passed successively through two traps packed with glass wool and a trap packed with silica gel, all at −196°. The temperature of the vaporization coil was 60°, and the temperature of the reaction zone varied between 232 and 236° during the 18-min reaction.

Analysis of the material in the −196° silica gel trap by infrared spectroscopy and vpc (molecular sieve, 25°) showed that only air had been trapped. The products in the two −196° traps packed with glass wool were distilled through a −78° trap into a −196° trap on the vacuum line.

A liquid remained in the −78° trap which weighed 0.16 g. Analysis by vpc (Carbowax 1000, 100°; and dipropylene glycol dibenzoate, 115°) showed that the liquid consisted of two components. The components were collected individually and identified as 1,4-dimethylenecyclohexane, 33.2%, and *p*-xylene, 66.8%, on the basis of the following evidence. The mass spectrum of *p*-xylene has a parent peak at *m/e* 106, corresponding to $C_8H_{10}$. The nmr spectrum consisted of two singlets at 2.27 and 6.93 ppm in a ratio of 3:2. The infrared spectrum was identical with that of the known compound. The mass spectrum of 1,4-dimethylenecyclohexane had a parent peak at *m/e* 108, corresponding to $C_8H_{12}$. The nmr showed two singlets at 2.20 and 4.64 ppm in a ratio of 2:1. The infrared spectrum was identical with that given in the literature.[36] 1,4-Bis(bromomethyl)-1,4-dibromocyclohexane, mp 132–134° (134–135° [36]), a known derivative of 1,4-dimethylenecyclohexane, was obtained by reaction with bromine in ether at −20°.

The gas in the −196° trap on the vacuum line (0.00247 mole) was analyzed by vpc (2,5-hexanedione, 0°). The products were identified by comparison of their infrared spectra and vpc retention times with those of the known compounds. The infrared spectrum of methylenecyclopropane was identical with that in the literature.[21] Relative response corrections were made for differences in thermal conductivity.

The complete results of this reaction are given in column two of Table I. The results of two similar reactions at different temperatures are given in columns one and three of Table I. The reactions using 2-chloromethyl-3-chloropropene were conducted in a

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(35) (a) B. C. Anderson, *J. Org. Chem.*, **27**, 2720 (1962); (b) J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **75**, 3344 (1953).

(36) F. Lautenschlaeger and G. F. Wright, *Can. J. Chem.*, **41**, 1972 (1963).

similar manner, except that the dichloride was added dropwise into the vaporization coil.

**Pyrolysis of 2-Iodomethyl-3-iodopropene.** 2-Iodomethyl-3-iodopropene (2 g) was placed in a 25-ml distilling flask, and the flask was heated to 210°. Nothing volatile were observed. Iodine and a black polymeric material remained in the flask.

**Reaction of 2-Iodomethyl-3-iodopropene with NaK in the Presence of Ethene.** The reaction was carried out as above (3.1 g, 0.010 mole of 2-iodomethyl-3-iodopropene) except that ethene (0.20 mole) was added to the helium stream over the duration of the 18-min reaction period. Analysis of products was the same as above.

**Preparation of 1,3-Diiodo-2-methylpropane.** Attempts to prepare this compound by the Finkelstein exchange from 1-bromo-3-chloro-2-methylpropane under the usual conditions of refluxing acetone or 2-butanone resulted in replacement of the bromine alone. 1-Iodo-3-chloro-2-methylpropane, bp 45–47° (5 mm), was obtained in 74% yield. The mass spectrum had a parent peak at *m/e* 218. The nmr spectrum consisted of doublets at 1.12, 3.30, and 3.54 ppm, and a multiplet at 1.83 ppm in a ratio of 3:2:2:1.

The diiodide was obtained in 20% yield by carrying out the exchange reaction in a 100° acetone solution for 68 hr, employing a high-pressure bomb. The pure diiodide was isolated by distillation, bp 56–57° (1 mm). The nmr spectrum showed two doublets at 1.16 and 3.27 ppm, and a multiplet at 1.60 ppm in a ratio of 3:4:1.

**Reaction of 1,3-Diiodo-2-methylpropane.** The diiodide (2.47 g, 0.00797 mole) was vaporized from the 95° coil over a period of 12 min and was carried into the 227–228° reaction zone. The products were distilled through a −78° trap into a −196° trap on a vacuum line. Nothing was collected in the −78° trap. The gas in the −196° trap (0.00640 mole, 80.3% yield) was analyzed by vpc.

**Simultaneous Reaction of Allene and Dibromomethane with NaK.** Dibromomethane (8.8 g, 0.051 mole) was added dropwise to the vaporization coil of the NaK apparatus, and allene (0.34 mole) was added simultaneously to the helium carrier stream. The temperature of the vaporization coil was 74° and that of the reaction zone varied between 200 and 230°. The reaction time was 25 min.

The product was distilled through a −78° trap into a −196° trap on the vacuum line. The product in the −78° trap (0.1 g) consisted of six unidentified liquids with retention times less than those of 1,4-dimethylenecyclohexane and *p*-xylene. The gas in the −196° trap (0.125 mole) consisted of (mole ratios) propane (5), propene (55), allene (33), 1-butene (3), and methylenecyclopropane (4). From a reaction at 270–280° none of the allene was recovered.

**Reaction of 2-Iodomethyl-3-iodopropene with Excess Diiodomethane and NaK.** 2-Iodomethyl-3-iodopropene (2.7 g, 0.0087 mole) and diiodomethane (12.2 g, 0.046 mole) were mixed and added dropwise to the vaporization coil of the NaK apparatus. The temperature of the vaporization coil was 100° and that of the reaction zone varied between 235 and 240°. The reaction was conducted over a period of 20 min.

The product was distilled through a −78° trap into a −196° trap on the vacuum line. A liquid, weighing 0.12 g, remained in the −78° trap. Analysis by vpc (Carbowax, 63°; and dipropylene glycol dibenzoate, 118°) showed that the liquid consisted of (mole ratios) benzene (2), 1,4-dimethylenecyclohexane (20), *p*-xylene (33), and 17 unidentified components (45). The gas (0.00945 mole) was analyzed by vpc (dipropylene glycol dibenzoate, 25°; and 2,5-hexanedione, 0°). The products probably derived only from $CH_2I_2$ consisted (mole ratio) of ethane (9.8), ethene (80.0), propane (1.9), propene (6.7), and cyclopropane (1.7), the remainder of the gases being derived from trimethylenemethane (see Table III

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# Reaction of Triphenylmethyl with Diazomethane

**Donald B. Denney and Neil F. Newman**

*Contribution from the School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903.* *Received February 25, 1967*

**Abstract:** The reaction of triphenylmethyl with diazomethane has been studied under several sets of conditions. The major products are 1,1,1,3,3,3-hexaphenylpropane, triphenylmethane, triphenylethylene, and 1,1,2-triphenylethane. The yields of products are strongly dependent on the concentration of reactants with the hexaphenylpropane being formed in greatest amount under more concentrated conditions. The results of these experiments are most easily explained by a mechanism which involves formation of a 2,2,2-triphenylethyl radical by reaction of a triphenylmethyl radical with diazomethane. This radical can then rearrange or react with triphenylmethyl to give 1,1,1,3,3,3-hexaphenylpropane. It has been found that this substance decomposes quantitatively at 250° to triphenylmethane and triphenylethylene.

Although diazomethane most commonly reacts by ionic or carbene pathways, it is also susceptible to attack by free radicals. The presence of radical intermediates in diazomethane reactions has been demonstrated by Urry and co-workers[1] who observed a high quantum yield in photoinitiated reactions of diazomethane with polyhalomethanes. They proposed that a radical chain reaction was involved.

More recently Müller and co-workers[2] have investigated the reaction of diazomethane with aryloxy radicals. The products are methylene acetals and these can be most easily explained by a free radical mechanism. These workers also reinvestigated the reaction of triphenylmethyl with diazomethane which was originally described by Schlenk.[3] Schlenk reported that 1,1,1,3,3,3-hexaphenylpropane (II) was formed as the product of this reaction.

$$\underset{\text{I}}{(C_6H_5)_3C\cdot} + CH_2N_2 \longrightarrow \underset{\text{II}}{(C_6H_5)_3CCH_2C(C_6H_5)_3} + N_2$$

The structural assignment was based on molecular weight and analytical data. Müller, *et al.*, isolated the same compound and reported its nmr spectrum which showed a single absorption at 4.13 ppm and aromatic protons at 6.86 ppm in the ratio of 1:15. This spectrum is certainly in agreement with the structural assignment except perhaps for the position of the $-CH_2-$ absorption which is downfield from the normal region where this is found. This downfield shift could be due to deshielding by the aromatic rings.

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[1] W. H. Urry, J. R. Eiszner, and J. W. Wilt, *J. Am. Chem. Soc.*, **79**, 918 (1957).

[2] E. Müller, A. Moosmayer, and A. Rieker, *Z. Naturforsch.*, **186**, 982 (1963).

[3] W. Schlenk and C. Bornhardt, *Ann.*, **394**, 183 (1912).