2-Oxo-1,3-alkadiyl Diradicals. Dehalogenation of α,α′-Dihalo Ketones with Potassium Vapor[1,2]

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Abstract: 2-Oxo-1,3-alkadiyl diradicals were prepared by the gas-phase reaction of α,α′-dihalo ketones with potassium vapor. The diradicals cyclize to cyclopropanones, which decarbonylate under the reaction conditions to give the olefin residue. The preparation of 2,2-dimethoxy-1,3-propadiyl diradical by the reaction of the corresponding dichloride and potassium vapor results in the isolation of dimethyl ketal of cyclopropanone.

The 2-oxo-1,3-alkadiyl diradicals (or the corresponding zwitterions) have been proposed as intermediates in the Favorsky rearrangement[3] and in the photolysis of 1,3-cyclobutanediones.[4] The products obtained from the photolysis of tetrasubstituted 1,3-cyclobutanediones consist of the tetrasubstituted olefin and carbon monoxide, suggesting that the initial diradical cyclizes to the cyclopropanone, and the latter decarbonylates.[4a,b] Photolysis of tetramethyl-1,3-cyclobutanedione in furan resulted in the trapping of the cyclopropanone or the 2-oxo-1,3-diradical as a furan adduct,[4c,d] and photolysis in the presence of oxygen indicates that the intermediate of this reaction acts as a biradical toward oxygen.[4b,e] Tetramethylcyclopropanone in a pentane solution reacts with furan or oxygen, but is stable in the absence of these reactants.[4f]

The reactions of 1,3-dihaloalkanes with alkali metal vapor lead to 1,3-alkadiyl diradicals which cyclize to cyclopropanes in over-all yields up to 85%.[5] We report here the reaction of α,α′-dihalo ketones with alkali metal vapor under similar conditions as a method of investigating the intermediate 2-oxo-1,3-alkadiyl diradicals. The reaction of 1,3-dichloropropanone with sodium vapor was studied in the past, but the only information obtained was that the reaction occurs with a weak luminescence.[6] However, relevant information was derived from the reaction of chloroacetone with sodium vapor. The collision yield is 0.1–0.2, indicating that less than ten collisions are necessary per reaction event.[7] The isolation of biacetonyl as a product of the reaction proved the intermediacy of acetonyl radicals.[8]

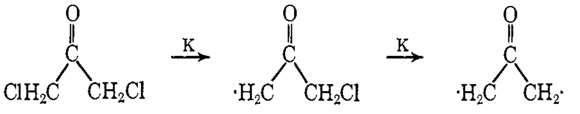
2-Oxo-1,3-propadiyl and 2,2-Dimethoxy-1,3-propadiyl

2-Oxo-1,3-propadiyl diradical (**3**) was generated by the reaction of potassium vapor[9] with 1,3-dichloropropanone (**1**). The results of this reaction are presented in Table I. The mole ratios of the components are also equal to the mole per cent of the total product. The amount of carbon monoxide recovered from the reaction would be decreased by the secondary reaction of carbon monoxide with potassium.[10]

Table I. Major Products Obtained from the Reaction of 1,3-Dichloropropanone with K

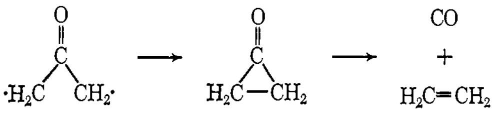
	Reaction		
	1[a]	2	3
	Temp, °C		
	295–303	272–281	257–265
Products	Mole ratios		
Carbon monoxide		12.4	10.8
Methane		19.1	35.2
Ethane	3.3	15.2	6.6
Ethene	88.1	50.4	44.0
Propene	1.2	1.3	1.9
	92.6	98.4	98.5
Yield of ethene, %	33.3	16.2	11.9

[a] Methane and carbon monoxide were not collected.



1 2 3

The high yield of ethene and the presence of carbon monoxide can be explained by the cyclization of the 1,3-diradical **3** to cyclopropanone (**4**), followed by a thermal decarbonylation of cyclopropanone to ethene (*vide infra* for a discussion of the energetics).



3 4 5

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(1) From the Ph.D. Thesis of R. Doerr.

(2) This work was supported by the National Science Foundation.

(3) (a) A. S. Kende, *Org. Reactions*, **11**, 261 (1960); (b) J. G. Aston and J. D. Newkirk, *J. Am. Chem. Soc.*, **73**, 3900 (1951); (c) J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954); (d) H. O. House and W. F. Gilmore, *J. Am. Chem. Soc.*, **83**, 3980 (1961); (e) H. O. House and W. F. Gilmore, *ibid.*, **83**, 3972 (1961); (f) A. W. Fort, *ibid.*, **84**, 2620 (1962); (g) *ibid.*, **84**, 4979 (1962); (h) *ibid.*, **84**, 2625 (1962); (i) R. C. Cookson and M. J. Nye, *J. Chem. Soc.*, 2009 (1965); (j) R. C. Cookson and M. J. Nye, *Proc. Chem. Soc.*, 129 (1963); (k) W. B. Hammond and N. J. Turro, *J. Am. Chem. Soc.*, **88**, 2880 (1966).

(4) (a) N. J. Turro, G. W. Byers, and P. A. Leermakers, *ibid.*, **86**, 955 (1964); (b) N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *ibid.*, **87**, 2613 (1965); (c) H. G. Richey, J. M. Richey, and D. C. Clagett, *ibid.*, **86**, 3906 (1964); (d) R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.*, 144 (1964); (e) P. A. Leermakers, G. F. Vesley, and N. J. Turro, *J. Am. Chem. Soc.*, **86**, 4213 (1964); (f) N. J. Turro, W. B. Hammond, and P. A. Leermakers, *ibid.*, **87**, 2775 (1965).

(5) P. S. Skell and E. J. Goldstein, unpublished work; E. J. Goldstein, Ph.D. Thesis, The Pennsylvania State University, 1964.

(6) C. E. H. Bawn and W. J. Dunning, *Trans. Faraday Soc.*, **35**, 185 (1939).

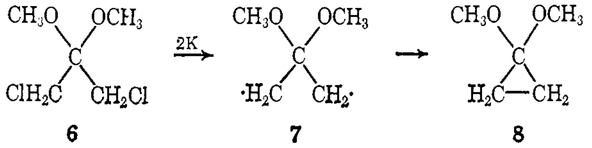
(7) E. Warhurst, *Quart. Rev.* (London), **5**, 44 (1951).

(8) J. N. Haresnape, Thesis, University of Manchester, quoted by C. E. H. Bawn, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **39**, 36 (1942).

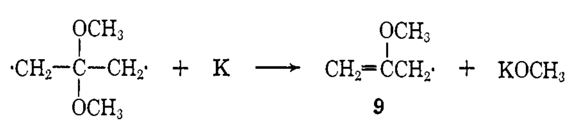
(9) The predominant reacting species in the previously described sodium–potassium alloy spray apparatus would be monatomic potassium: P. S. Skell, E. J. Goldstein, R. J. Petersen, and G. L. Tingey, *Ber.*, **100**, 1442 (1967).

(10) F. Ephraim, "Inorganic Chemistry," 6th ed, Oliver & Boyd, Ltd., London, 1954, p 827.

Employing the same reaction conditions, the dimethyl ketal of 1,3-dichloropropanone (**6**) is converted in 11% yield to 1,1-dimethoxycyclopropane (**8**), a ketal of cyclopropanone. The products (and their mole ratio) obtained from the reaction of 1,3-dichloro-2,2-dimethoxypropane with potassium vapor at 246–262° are: 1,1-dimethoxycyclopropane (24.7), 2-methoxypropene (11.9), allene (3.3), propene (34.1), propane (1.4), ethene (0.5), ethane (0.7), and methane (16.6). Under the reaction conditions allene is converted primarily to nonvolatile material, and, in low yields, to propene and propane. Thus, allene formation is a substantial reaction. Stoichiometrically the formation of allene involves the elimination of two methoxy radicals from the 1,3-diradical **7**. The decomposition of **7** to the methoxy radicals and allene is unlikely. The first methoxy elimination would lead to **9** in an approximately thermoneutral step (~ −60 kcal for double bond formation, ~ −20 kcal for allylic stabilization, and ~ +80 kcal for carbon–oxygen bond cleavage). With these same values the second step is 40 kcal endothermic. It is more probable that the formation of allene is due to reaction of the 1,3-diradical **7** with potassium atoms resulting in the elimination of potassium methoxide from the reaction complex.[11] Acquisition of a hydrogen atom by the monoradical **9** would give 2-methoxypropene.



6 **7** **8**



$$\cdot CH_2-\overset{OCH_3}{\underset{OCH_3}{C}}-CH_2\cdot + K \longrightarrow CH_2{=}\overset{OCH_3}{C}CH_2\cdot + KOCH_3$$

7 **9**

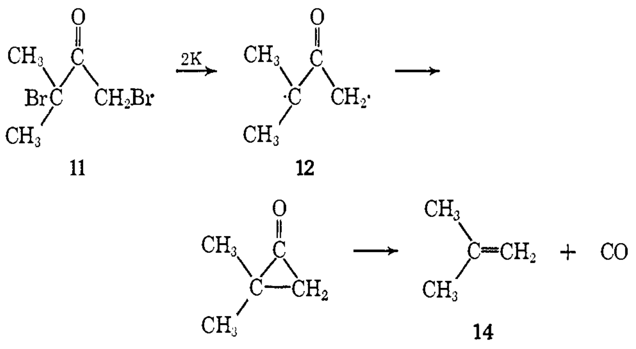
$$\mathbf{9} + K \longrightarrow CH_2{=}C{=}CH_2\cdot + KOCH_3$$

10

1,1-Dimethoxycyclopropane was identified on the basis of the following evidence: the infrared spectrum resembled closely that of the corresponding diethoxy compound;[12] the mass spectrum had a parent peak at *m/e* 102; the nmr spectrum consisted of two singlets at 0.76 and 3.29 ppm (δ scale) in a respective ratio of 2:3. 2-Methoxypropene was identified by comparison of its infrared spectrum and its vpc retention time with that of an authentic sample.

2-Oxo-3-methyl-1,3-butadiyl

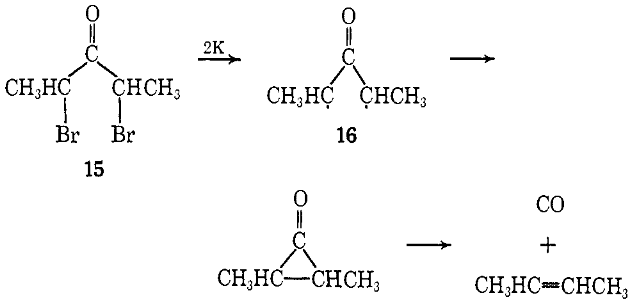
The major products from the reaction of 1,3-dibromo-3-methyl-2-butanone (**11**) with potassium vapor at 217–232° are (mole ratios): carbon monoxide (6.4), methane (24.7), propene (4.9), and 2-methylpropene (62.0). The yield of 2-methylpropene is 22.9%. The results suggest the cyclization of the 2-oxo-3-methyl-1,3-butadiyl diradical (**12**) to 2,2-dimethylcyclopropanone (**13**), and subsequent decarbonylation to 2-methylpropene (**14**). The reaction was also conducted at 115–125°, but 2-methylpropene was obtained in a yield of only 1%. The concentration of potassium vapor is insufficient for complete dehalogenation at this temperature.



11 **12** **13** **14**

3-Oxo-2,4-pentadiyl

The 3-oxo-2,4-pentadiyl diradical (**16**), formed by the reaction of a mixture of *meso*- and *dl*-2,4-dibromo-3-pentanone (**15**) with potassium vapor, cyclizes to 2,3-dimethylcyclopropanone (**17**). Elimination of carbon monoxide from the cyclopropanone **17** results in the isolation of *cis*- and *trans*-2-butene (**18**) in yields of 11.5 and 15.1%, respectively. The mole ratios of the major products obtained from this reaction at 224–257° are: *cis*-2-butene (11.7), *trans*-2-butene (15.4), ethene (1.8), ethane (13.3), methane (47.5), and carbon monoxide (7.4). The reaction was also carried out (180–190°) using one of the pure isomers (the *meso* or the *dl*). The same products were produced as were obtained from the mixture of isomers; the yields of *cis*- and *trans*-2-butene were 0.33 and 0.34%, respectively. The isolation of both 2-butenes indicates the absence of stereochemical control in the steps leading to ring closure.



15 **16** **17** **18**

3-Oxo-2,4-dimethyl-2,4-pentadiyl

2,4-Dibromo-2,4-dimethyl-3-pentanone (**19**) reacts with potassium vapor at 277–297° to give 2,3-dimethyl-2-butene (**22**), the same product observed in the photolysis of tetramethyl-1,3-cyclobutanedione.[4b] This indicates that the 3-oxo-2,4-dimethyl-2,4-pentadiyl diradical (**20**) cyclizes to tetramethylcyclopropanone (**21**). The mole ratios of the products of this reaction are: 2,3-dimethyl-2-butene (18.8), 2,3-dimethyl-1-butene (1.9), 2-methylpropene (1.6), propene (4.6), propane

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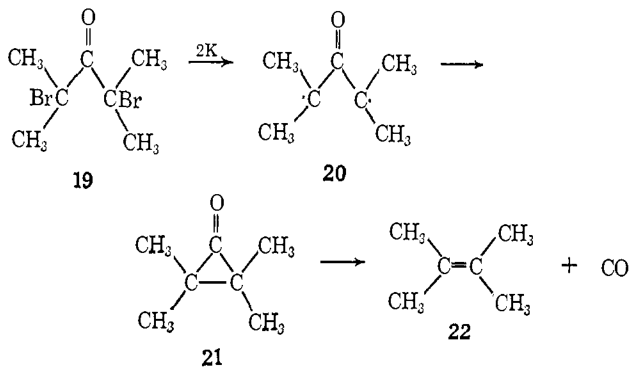
[11] The elimination of a methoxy radical could also take place from the 3-chloro-2,2-dimethoxypropyl radical.

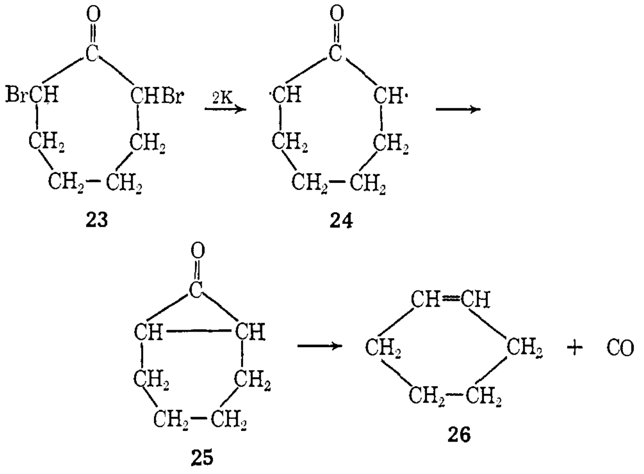
[12] S. M. McElvain and P. L. Weyna, *J. Am. Chem. Soc.*, **81**, 2579 (1959).



(3.1), ethane (1.2), and methane (69.4). The yield of C_6 olefin is 11.6%.

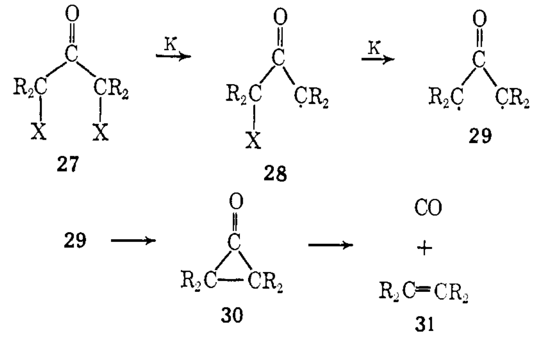
2-Oxo-1,3-cycloheptadiyl

The isolation of carbon monoxide and cyclohexene (**26**) from the reaction of 2,7-dibromocycloheptanone (**23**) with potassium vapor suggests that the resulting 2-oxo-1,3-cycloheptadiyl diradical (**24**) closes to give bicyclo[4.1.0]heptan-7-one (**25**). The products of this reaction effected at 255–265° are cyclohexene (47.1), benzene (12.1), propane (2.1), propene (1.2), ethane (3.2), ethene (0.2), methane (11.0), and carbon monoxide (22.3). The combined yields of cyclohexene and benzene are 22.0%. Benzene is probably formed by the dehydrogenation of cyclohexene by potassium. The conversion of 1,4-dimethylenecyclohexane to *p*-xylene under similar conditions has been reported.[13]



Conclusions

The 2-oxo-1,3-alkadiyl diradicals (**29**), formed by the reaction of α,α'-dihalo ketones **27** with potassium vapor, cyclize to the cyclopropanones **30**. The resulting cyclopropanones eliminate carbon monoxide to give the olefins **31** as the major products.



The steps leading to the cyclopropanone are exothermic, producing a cyclopropanone "hot" by 40–50 kcal. The exothermicity is not readily calculated, but can be estimated as follows. The halo radical **28** would be collisionally quenched by helium atoms, so that its energy is that of the delocalized (~7 kcal/mole[14a]) ground state. The conversion of **28** to **29** is exothermic, and a substantial part of this exothermicity could be left in **29** since the additional stabilization energy of **29** could not be generated until there had been extensive C–X stretching and KX formation. Thus **29** would be "hot," being stabilized only by the original delocalization energy of **28**. If ring closure (47–57 kcal/mole[14b]) to **30** is fast compared to collisional deactivation by helium, **30** would be hot by approximately 40–50 kcal. The decompositions of cyclopropanones to carbon monoxide and olefins (**30** → **31**) are exothermic by about 56 kcal/mole, and could easily have an energy of activation less than 40–50 kcal/mole. If this were the case, the primary product from the ring closure, the "hot" cyclopropanone, would have an energy in excess of that needed for the elimination of carbon monoxide, and thus would not be likely to survive long enough for collisional deactivation. This possibility coupled with the demonstrable high reactivity of ketones with NaK (*vide infra*), and the high temperature of the reaction zone precluded the isolation of cyclopropanones in this system.

The behavior of the 2-oxo-1,3-propadiyl diradicals should be contrasted to that of their carbon analog, trimethylenemethane (2-methylene-1,3-propadiyl), which was generated under similar conditions.[13] While cyclization to cyclopropanone is the predominant reaction of 2-oxo-1,3-propadiyl, dimerization to 1,4-dimethylenecyclohexane is a predominant reaction of trimethylenemethane. The difference in the behavior of the two species is attributed to a difference in electronic states. From spin considerations a singlet species should cyclize to the three-membered ring and a triplet species should not, giving it a longer lifetime and thus favoring dimerization. On this basis alone the 2-oxo-1,3-propadiyl diradicals generated in this system can be assigned to singlet states and trimethylenemethane to triplet. Molecular orbital calculations[3c,15] predict a triplet ground state for trimethylenemethane and a singlet ground state for 2-oxo-1,3-propadiyl.

The formation of cyclopropanones by the cyclization of the 2-oxo-1,3-alkadiyl diradicals indicates that it reacts from the singlet state. However the law of conservation of spin angular momentum predicts that the reaction between the intermediate halo radical (such as **2**) and a potassium atom should give a 3:1 ratio of triplet to singlet 2-oxo-1,3-propadiyl if the E_{act} for **28** → **29** is the same, without regard for multiplicity. The triplet state could decay to the singlet state by collision with a potassium atom, or could react to give other products. Since the yield of olefin **31** is usually about 25%, it is intriguing to speculate that the singlet is con-

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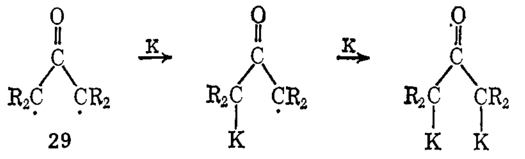
[13] R. G. Doerr and P. S. Skell, *J. Am. Chem. Soc.*, **89**, 3062 (1967).

[14] (a) P. Nangia and S. W. Benson, *ibid.*, **84**, 3411 (1962); (b) J. P. Chesick, *ibid.*, **85**, 2720 (1963).

[15] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapters 2, 5.

verted to cyclopropanones, and the triplet is converted to fragmentation or nonvolatile products, perhaps by reaction with potassium forming a potassium dienolate (**33**).



29 32 33

Reaction of Ketones with Potassium Vapor

Simple ketones do not survive the conditions of the reaction system. The reaction of acetone (0.046 mole) with potassium vapor at 278–298° resulted in complete conversion of the acetone, the only products isolated being methane (0.0308 mole) and 2-methylpropene (0.00104 mole). These products account for 48% of the hydrogen and 25% of the carbon of the acetone. Since the pyrolysis of acetone proceeds only slowly at 500°,[16] the products must be formed by reaction with potassium vapor.

Subjecting 2,4-dimethyl-3-pentanone to the reaction conditions at 248–258° led to the recovery of 2% of the starting ketone. The reaction products, obtained in 2.6% yield, consisted primarily of propane and propene. At 170–182°, 2-butanone is recovered in 43% yield. The products, which accounted for only 0.19% of the consumed 2-butanone, were predominantly ethane, ethene, and ethyne.

At higher temperatures ketones are completely converted while at lower temperatures a portion of ketone survives the reaction conditions. The conversion of the ketone to volatile products can be explained either by a thermolysis of an intermediate potassium ketyl or by a catalyzed pyrolysis of the ketone. The catalysis would probably involve the abstraction of hydrogen by potassium atoms, similar to that observed in the iodine-catalyzed pyrolysis of acetone.[17] The nonvolatile products which are predominant at lower temperatures are most likely formed from the potassium ketyl.

Experimental Section

1,3-Dibromo-3-methyl-2-butanone, bp 98–100° (18 mm), was prepared by the method of Favorsky and Wanscheidt, bp 99° (18 mm).[18] The compound was redistilled before use, bp 87° (10 mm), n^{25}D 1.5162. The nmr spectrum consisted of two singlets at 1.95 and 4.37 ppm (δ scale) in a respective ratio of 3:1.

Preparation of 2,4-Dibromo-3-pentanone. A mixture of 3-pentanone (53 ml, 43 g, 0.50 mole), glacial acetic acid (50 ml), and water (50 ml) was placed in a 300-ml flask fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel. Bromine (160 g, 1.00 mole) was added dropwise to the solution maintained at 25°. After the addition of bromine, the mixture was washed with water and dried over calcium chloride.

The liquid was then distilled on a 10-cm Vigreux column. A total of 102 g (84% yield) of product, bp 67–82° (10 mm), was obtained [bp 65–70 (8 mm)].[19] A center fraction, bp 75–78° (10 mm), gave an nmr spectrum which showed two doublets at 1.79 and 1.87 ppm and two quartets centered at 4.78 and 4.97 ppm, indicating that the fraction consisted of a mixture of *meso* and *dl* forms of the symmetrical dibromo ketone. The lower boiling isomer was separated by distillation through a 30-cm Vigreux column, bp 69–71° (10 mm). The nmr spectrum of this fraction showed that it was the isomer with the peaks at 1.79 and 4.97 ppm.

Preparation of 2,4-Dibromo-2,4-dimethyl-3-pentanone. Bromine (160 g, 1.00 mole) was added dropwise to 2,4-dimethyl-3-pentanone (58 g, 0.50 mole) contained in a 250-ml, three-necked flask, fitted with a stirrer, reflux condenser, and dropping funnel. At 0°, bromine color was discharged rapidly until half of the bromine was added. Phosphorus tribromide (1 ml) was added as a catalyst, and the reaction mixture was heated overnight on a steam bath. Helium was swept through the solution to displace hydrogen bromide; the solution was dried over calcium chloride and distilled through a 30-cm Vigreux column to give 2,4-dibromo-2,4-dimethyl-3-pentanone, 85.6 g (62% yield); bp 87–89° (10 mm) [bp 84–85° (9 mm)[20]], n^{25}D 1.5026. The nmr spectrum consisted of a singlet at 2.14 ppm.

Preparation of 2,7-Dibromocycloheptanone. Bromine (80 g, 0.50 mole) was added dropwise to a 25° mixture of cycloheptanone (28 g, 0.25 mole), acetic acid (25 ml), and water (25 ml). After 2 hr, dilution with water separated a semisolid. The crude product (57 g, 85% yield) was recrystallized from methanol and from pentane to give white crystals (31.0 g, 46% yield), mp 65–66° (mp 68–69° [21]).

1,3-Dichloro-2,2-dimethoxycyclopropane, mp 82°, was prepared by the method of Pryanishnikov and Leontowitsch,[22] who reported a melting point of 81.5°.

Reaction with Alkali Metal Vapor. The reactant was added slowly to the heated vaporization coil of the previously described apparatus,[9] while helium (300 mm) was passed through the coil at a flow of 1.0 l./min (STP). The helium stream, containing 5–25 mm partial pressure of the reactant, was passed through a fine spray of heated sodium–potassium alloy (78 wt % potassium) which kept the helium saturated with alkali metal vapor.

The products of the reaction were collected in two −196° traps packed with glass wool and a −196° trap packed with silica gel. The fractions were analyzed by vapor phase chromatography and the individual components identified by comparison of their infrared spectra and vpc retention times with those of the known compounds. Corrections were made for thermal conductivity differences of the components.

Preparation of 2-Methoxypropene. Iodine (57 g, 0.23 mole) was added over a period of 0.5 hr to a stirred mixture of propene (10 g, 0.42 mole), HgO (37.2 g, 0.152 mole), and methanol (100 ml) at −78°. The mixture was allowed to warm to room temperature while stirring. It was filtered, and the filtrate was poured into 300 ml of water. The lower layer was separated, added to a flask containing KOH (15 g, 0.27 mole) in methanol (50 ml), and refluxed for 3 hr. Distillation of the reaction mixture separated 2-methoxypropene, 5.5 g (34% yield), bp 34–36° (bp 33.5° [23]).

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(23) H. P. Crocker and R. H. Hall, *J. Chem. Soc.*, 2052 (1955).