cies (in cm.$^{-1}$): 690(s), 880(w), 1040(w), 1840(vs), 2010(w), 2220(w), 2280(vw), 2420(vw), 3620(m). It is believed that the 690 cm.$^{-1}$ and 880 cm.$^{-1}$ peaks correspond to ν_6 and ν_8, respectively, since the corresponding peaks for digermane[6] and disilane[11] are of similar intensity and frequency. It is believed that the very strong peak at 1840 cm.$^{-1}$ is an unresolved pair of peaks corresponding to ν_5 and ν_7. The corresponding close pairs of peaks for digermane and disilane are of similar intensity and frequency. The 3620 cm.$^{-1}$ peak probably corresponds to the combination $\nu_1 + \nu_5$. It is perplexing that we found no peak corresponding to $\nu_3 + \nu_{11}$, which should occur around 1600 cm.$^{-1}$.

No attempt was made to separate the stannane from the carbon dioxide and any hydrogen chloride which might have been present. However, each sample of stannane was decomposed by flaming its glass container; the evolved hydrogen was pumped off and measured, and the change in volume of the condensable gases was noted. The data from a typical experiment indicate that one volume of stannane gave 2.15 volumes of hydrogen, as opposed to the theoretical value of 2.00 volumes of hydrogen. The evolved hydrogen was taken as a measure of the stannane.

Unsuccessful Experiments.—We found no bismuth compounds soluble in alkaline solution, so we were unable to use our method for the preparation of bismuthine. When a solution of hydroborate and plumbite was added to acid, we were unable to detect any trace of plumbane. Similarly, when a solution of hydroborate and silicate (water glass) was added to acid, no trace of silane was detected. Only very small amounts of phosphine were obtained from the addition of solutions of hydroborate and either hypophosphite or phosphite to acid.[12]

(11) G. W. Bethke and M. K. Wilson, J. Chem. Phys., **26**, 1107 (1957).

Discussion

It is particularly interesting that neither the silicate, the hypophosphite, nor the phosphite ion is appreciably reduced by hydroborate. It seems likely that, in each of these species, the central atom is too well protected by its four surrounding atoms to permit approach of a hydride ion. If germanium(IV), tin(II), arsenic(III) and antimony (III) have coördination numbers of four (as do Si(IV), P(I) and P(III)), then the greater size of the central atoms in these cases would explain their greater accessibility to hydride ions. Recent work has shown that sulfite (or sulfurous acid) is readily reduced to hydrogen sulfide by hydroborate.[13] Here the sulfur atom has a coördination number of only three and is accessible to hydride ions. The sulfate ion, with four coördinated oxygen atoms, is inert to hydroborate. The nitrous acid molecule, with only two oxygen atoms, is readily reduced to ammonium ion by aqueous hydroborate.[14] However, the three oxygen atoms of the nitrate ion are apparently enough to protect the nitrogen atom from attack by hydroborate, inasmuch as nitrate is inert to hydroborate in acid solution.[14]

The inability to detect any plumbane in the reduction of lead(II) by hydroborate may be explained by the extreme instability of plumbane. Since lead metal formed in the reaction flask, it is apparent that reduction took place; but any plumbane which may have formed underwent immediate decomposition to the elements.

Acknowledgments.—It is a pleasure to acknowledge helpful discussions with Professors R. E. Connick, R. E. Powell and G. C. Pimentel. This work was supported in part by the Atomic Energy Commission.

(12) Unpublished observations of J. D. Macomber, 1959.
(13) Unpublished observations of Floris Y. Tsang, 1959.
(14) M. E. Kramer, Ph.D. Thesis, Saint Louis University, 1954.

The Formation of Bitropyl in the Radiolysis of Carbon-14 Labeled Cycloheptatriene[1]

By Gottfried Juppe[2] and Alfred P. Wolf

Received June 24, 1960

The irradiation of carbon-14 labeled cycloheptatriene in a nuclear reactor or in a beam of 1.95 Mev. electrons from a Van de Graaff generator leads to the formation of labeled bitropyl among other products. Ozonization of bitropyl leads to dicyclopropyltetracarboxylic acid. Permanganate oxidation of bitropyl leads to benzoic acid. The extent of labeling in these degradation products suggests a symmetrical intermediate as a precursor of the dimer.

Introduction

Radicals, ions and molecule ions have been suggested as precursors for the numerous products one obtains on radiolysis of organic compounds.[3] The primary processes occurring in radiation chem-

(3) Cf. A. Charlesby and A. J. Swallow, Ann. Rev. Phys. Chem., **10**, 89 (1959).

istry are usually not product determining. The many secondary reactions which can occur as a result of the primary processes bear a formal analogy to carbanion, carbonium ion and radical reactions.[4]

One of the commonly observed products in radiation chemistry is a dimer containing two hydrogens less than the starting material. Bicyclohexyl from cyclohexane[5] and biphenyl from ben-

(4) Cf. A. Henglein, Ang. Chem., **71**, 15 (1959).
(5) H. A. Dewhurst, J. Phys. Chem., **63**, 813 (1959).

TABLE I

RESULTS OF THE PERMANGANATE OXIDATION OF THE DIELS–ALDER ADDUCT OF CYCLOHEPTATRIENE-C^{14}

	Specific act. $(m\mu c./mg.C.)$	Total activity
Cycloheptatriene	13.46	94.2 (spec. act. $\times$ 7)
Diene adduct (dimethyl-ester)	7.19	93.5 (spec. act. $\times$ 13)
Diene adduct dicarboxylic acid	8.44	92.8 (spec. act. $\times$ 11)
Cyclopropanedicarboxylic acid anhydride	18.62	93.1 (spec. act. $\times$ 5)

TABLE II

IRRADIATION OF CYCLOHEPTATRIENE-C^{14}

Irradiation	Van de Graaff 1.95 mev. electrons	Reactor Thermal flux $\sim1.5 \times 10^{13} n/cm.^2/sec.$ γ dose rate $\sim10^7 r/hr.$ Cd ratio ~48
Time (min.)	380	5060
Energy absorbed (ev./molecule)	11.4 ($\sim1.2 \times 10^9$ rads)	$\sim17^a$ ($\sim1.8 \times 10^9$ rads)
Decomposition	23%	$\sim34\%^a$
G value bitropyl formation	0.07^b	

^{a} These figures are estimates based on relations between irradiation time, energy absorbed and per cent. decomposition observed in calibration runs. ^{b} The sample was not degassed.

zene[6] are examples of this type of product. Reaction of an excited species with a solvent molecule[6] (1) and radical combination (2) are the mechanisms usually suggested as being responsible for these dimers. The appearance of "molecular"

$$RH^* + RH \longrightarrow RR + H_2 \qquad (1)$$

$$R\cdot + R\cdot \longrightarrow RR \qquad (2)$$
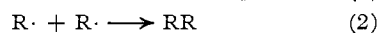
hydrogen (i.e., hydrogen not sensitive to radical traps) during radiolysis of these compounds has been used as support for the first (1) mechanism.

It seemed to us that a distinction between these two mechanisms in a particular case might be made by using a carbon-14 labeled precursor in which a redistribution of the label would result if the radical (resonance stabilized) intermediate were operative. Carbon-14 labeled cycloheptatriene was chosen for this purpose.

Results

Carbon-14 labeled cycloheptatriene was prepared by the photolytic reaction between benzene and diazomethane-C_1^{14}. The method of synthesis would support the contention that most if not all of the carbon-14 is located in the methylene group. Investigation of the properties of the Diels–Alder
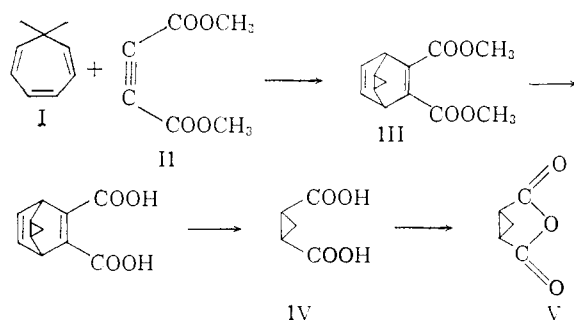
adduct (III) of cycloheptatriene (I) and acetylene dicarboxylic acid ester (II)[7] and its degradation products substantiate the fact that there is little or no activity in the four and five position of cycloheptatriene. The permanganate oxidation of the adduct leads to cyclopropane-1,2-dicarboxylic acid IV. This converted to the anhydride IV, contained all the initial activity, cf. Table I.

Data on the irradiation are given in Table II. Bitropyl (VI) was isolated by a carrier technique. Bicyclopropyltetracarboxylic acid (VII) was obtained by the peroxide cleavage of the ozonide of ditropyl. It can be seen from Table III that the

VI   VII
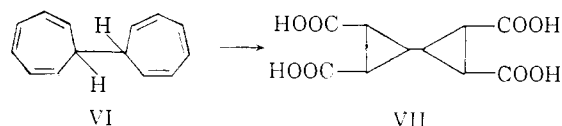
activity in the acid (VII) indicates random labeling in VI. It does not seem reasonable to suggest that this randomization occurred during the oxidation since this would necessitate a labile carbon-1-carbon-1' bond.

TABLE III

DEGRADATION OF BITROPYL-C^{14}

	Specific act. $(m\mu c./mgC.)$	Total activity
Bitropyl	1.48	20.7 (spec. act. $\times$ 14)
Bicyclopropyltetracarboxylic acid	1.50	15.0 (spec. act. $\times$ 10)

The degradation of benzoic acid, which can be readily obtained by the permanganate oxidation of bitropyl, leads to a result which is consistent with the previous result but perhaps somewhat less compelling. The oxidation must involve scission of the 1–1' bond but does not necessarily involve a tropylium ion intermediate (which would imply randomization before rearrangement) because of the nature of the oxidizing agent. It can be seen from Table IV that the carboxyl group of benzoic acid contains $1/7$th of the total activity and the benzene ring $6/7$ths of the total activity, again consistent with the contention of random labeling in bitropyl.[8]

(7) G. Juppe, B. Suryanarayana and A. P. Wolf on the thermal decomposition of the Diels–Alder Adduct, to be published.

(8) One needs to assume that the carbon–carbon single bond in ditropyl is not oxidized to give a symmetrical intermediate. The specificity of the bromotropone rearrangements (cf. W. von E. Doering and D. B. Denney, THIS JOURNAL, 77, 4619 (1955)) would support the view that once the methylene carbon has been oxidized, formation of a symmetrical intermediate in basic permanganate is unlikely.

(6) S. Gordon, A. R. Van Dyken and T. Doumani, J. Phys. Chem., 62, 20 (1958).

TABLE IV

DEGRADATION OF BITROPYL-C[14]

|	Specific act. (mμc./mg.C)	Total activity
Bitropyl	1.48	20.72 (spec. act. $\times$ 14)
Benzoic acid	1.50	10.50 (spec. act. $\times$ 7)
Carbon dioxide	1.50	1.50 (spec. act. $\times$ 1)
Acetanilide[a]	1.47	8.80 (spec. act. $\times$ 6)

10.30

[a] Corrected for inactive carbon.

Discussion

The degradative results which indicate that randomly labeled bitropyl is produced from "specifically" labeled cycloheptatriene[9] support the notion that a symmetrical precursor is involved in bitropyl formation. It is difficult to see how "molecular" formation [cf. eq. 1] could be involved. This would necessitate a transition state in which the methylenes have lost their identity and the hydrogen from these carbons assume a position which allows H_2 formation. It is equally difficult to see how the primary process, i.e. the formation of a positively charged radical ion, could be responsible for the randomization, cf. formulas VIII.
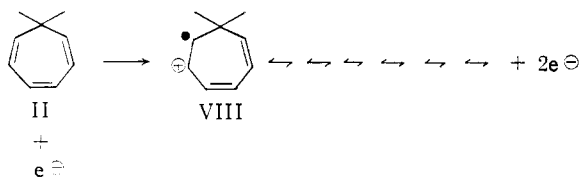
Radical recombination [cf. eq. 2] seems to be the most satisfactory explanation of the results. At least three secondary processes must be considered as resulting in the formation of a cycloheptatrienyl radical.
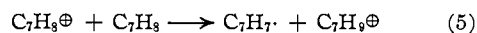
1. Electron capture by the primary radical ion to give an excited cycloheptatriene which then decomposes to the radical plus hydrogen[10]

$$C_7H_8{}^+ + e^- \longrightarrow C_7H_8{}^* \longrightarrow C_7H_7\cdot + H\cdot \quad (3)$$
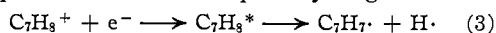
2. Hydrogen abstraction from a solvent molecule by a radical ion[11]

$$C_7H_8{}^\oplus + C_7H_8 \longrightarrow C_7H_9{}^\oplus + C_7H_7\cdot \quad (4)$$

3. Proton transfer from a radical ion to a solvent molecule[12]

$$C_7H_8{}^\oplus + C_7H_8 \longrightarrow C_7H_7\cdot + C_7H_9{}^\oplus \quad (5)$$

It is difficult to choose between these reactions. Common to all of them is the formation of a tropyl radical which can subsequently dimerize.

The appreciable resonance energy of the cycloheptatrienyl radical needs to be emphasized at this point.[13] The question of bond strength is usually

of lesser importance since the amount of energy available in the radiolysis is in considerable excess of this bond strength. The resonance stabilization of the radical increases its lifetime by decreasing its reactivity to a sufficient extent to allow dimerization to take place before the solvent is attacked. The formation of bitropyl from the zinc dust reduction of tropylium bromide in a one electron transfer reaction[14] indicates that an equilibrium between bitropyl and cycloheptatrienyl radical is not to be expected. The electron spin resonance spectrum of ditropyl is in accord with this supposition. No free radicals could be detected.

In summary, our results are consistent with the mechanism indicated by equations 2 and 3-5.

Experimental[15]

Cycloheptatriene-C[14].—The method of Doering and Knox[16] was used in preparing the cycloheptatriene-C[14].[17] The stock solution had an activity of 1.5 mμc./mg.C. This material was diluted with inactive material obtained from the Shell Chemical Corporation.[18] Before dilution, the major fraction of the toluene was removed from the inactive cycloheptatriene by repeated vapor phase chromatographic purification on a 1/2″ firebrick column using Dow Corning 710 silicone oil as the liquid phase. The inactive cycloheptatriene used in the reactor irradiation had all detectable (VPC) traces of toluene removed from it.

Irradiations.—The Van de Graaff irradiations were carried out in a vessel the design of which was described by Saldick and Allen.[19] Cycloheptatriene-C[14] [19.436 g., spec. activ. 37.7 mμc./mg C.] was kept under argon at all times. The irradiation vessel was air cooled. The irradiation data are given in Table II.

The reactor irradiation was carried out in the Brookhaven National Laboratory air cooled, graphite moderated reactor. Cycloheptatriene [0.847 g., spec. act. 44.98 mμc./mg.C.] was sealed in vacuo in quartz. The sample temperature was about 40° during the irradiation. The irradiation data are given in Table II. Ten days were allowed for the activity induced in the quartz to decay before the sample was processed.

Bitropyl-C[14].—Inactive bitropyl was prepared by the method of Doering and Knox,[15] m.p. 57–58°.

Active bitropyl from the Van de Graaff irradiated sample (spec. activ. 37.7 mμc./mg.C.) was isolated by first adding 4.0 g. of inactive bitropyl to the 10.86 g. of sample. Distillation of this mixture resulted in recovery of 3.8 g. of crude bitropyl. The bitropyl was brought to radiochemical purity by numerous recrystallizations from methanol, m.p. 57–58°; spec. activ. 1.463, 1.495 mμc./mg.C.

Active bitropyl from the reactor irradiation was isolated in an analogous fashion; an 0.84 g. reactor irradiated sample, spec. activ. 44.98 mμc./mg.C., was treated with 4.8 g. of inactive bitropyl. Radiochemically pure bitropyl, m.p. 57–58°, had a specific activity of 0.956 mμc./mg.C.

Bicyclopropyltetracarboxylic Acid.[20]—Bitropyl [2.0 g.; spec. activ. 1.495, 1.463 mμc./mg.C.] was ozonized in 65

(9) The activity in the 1-position in cycloheptatriene was not appreciably randomized (if at all) when cycloheptatriene was given doses equal to or greater than those used in this study. The method of degradation of radiolyzed cycloheptatriene allowed us to set an upper limit of ~10% randomization by assuming the amount of randomization to be reflected in the precision measure of our results. The question of partial hydrogen migrations (not resulting in complete randomization) was not resolved in those experiments. The results are the subject of a paper in preparation.

(10) Cf. A. H. Samuel and J. L. Magee, J. Chem. Phys., 21, 1080 (1953).

(11) Cf. D. P. Stevenson and D. O. Schissler, ibid., 23, 1353 (1955).

(12) D. P. Stevenson, J. Phys. Chem., 61, 1453 (1957).

(13) (a) E. Hueckel, "Grundzuege der Theorie Ungesaetigter und Aromatische Verbindungen," Verlag Chemie, Berlin, 1938, pp. 71–85.

(b) J. L. Franklin and F. H. Field, THIS JOURNAL, 75, 2819 (1953).

(c) J. D. Roberts, A. Streitwieser and C. M. Regan, ibid., 74, 4579 (1952).

(14) W. von E. Doering and L. H. Knox, ibid., 79, 352 (1957).

(15) Radioassays were performed by D. R. Christman and C. Paul of this Laboratory. The method of D. R. Christman, N. E. Day, P. R. Hansell and R. C. Anderson, Anal. Chem., 27, 1935 (1955), was used. The root mean square error encompassing all errors inherent in the analysis is not greater than 5%.

(16) W. von E. Doering and L. H. Knox, THIS JOURNAL, 72, 2305 (1950).

(17) This material was prepared by Dr. B. Suryanarayana during his stay as a research associate at B.N.L.

(18) Some inactive cycloheptatriene was prepared from bicycloheptadiene (also obtained from the Shell Chemical Corp.). The authors wish to thank Dr. E. J. Smutny of the Shell Development Corporation for his help in this regard.

(19) T. Saldick and A. O. Allen, J. Chem. Phys., 22, 438 (1954).

(20) R. Huisgen and G. Juppe prepared this compound for the first time; cf. G. Juppe, Dissertation, Univ. of Munich, June, 1958, Munich, Germany.

ml. of glacial acetic acid for 15 hr. An ice bath was used for cooling. The reaction mixture was allowed to stand at room temperature overnight after having been treated with 30 cc. of 10% H_2O_2. The mixture was concentrated on a steam-bath. The concentrate was treated with 20 cc. of 8% H_2O_2, six times, being again concentrated after each addition. A yield of 36 mg. of the tetracarboxylic acid was brought to radiochemical purity by recrystallization from an ether–petroleum ether mixture, m.p. > 350°, spec. activ. 1.50 mμc./mg.C.

Anal. Calcd. for $C_{10}H_{10}O_8$ 258.2: C, 46.51; H, 3.91. Found: C, 46.24: H, 4.42. Calcd. acid equiv.: 64.5. Found: 65.2.

Benzoic Acid.—Finely powdered potassium permanganate was added to a boiling solution of 1 g. of bitropyl (spec. act. 1.49; 1.463 mμc./mg.C.) in 10 ml. of acetone until the violet color of permanganate persisted. The acetone was removed *in vacuo.* The excess permanganate and the manganese dioxide was reduced with SO_2. Benzoic acid was isolated by continuous extraction with *n*-pentane. The acid was brought to radiochemical purity by recrystallization from water and from petroleum ether, spec. act. 1.50 mμc./mg.C.

Degradation.—A degradation of benzoic acid by the Schmidt reaction[21] gave carbon dioxide, spec. act. 1.50 mμc./mg.C. Acetanilide obtained from the aniline sulfate had a spec. act. of 1.10 mμc./mg.C. (not corrected for inactive carbon).

Diene Adduct of Cycloheptatriene.—The Diels–Alder adduct of cycloheptatriene-C_1[14] and acetylene dicarboxylic acid methyl ester was prepared by the method of Alder and Jacobs.[22] Cycloheptatriene, spec. act. 13.51, 13.41 mμc./mg.C., gave a 65% yield of the dimethylester adduct; spec. act. 7.19 mμc./mg.C. Saponification of the ester followed by treatment with HCl gave a dicarboxylic acid; spec. act. 8.44 mμc./mg.C.

Cyclopropanedicarboxylic Acid Anhydride.—This acid was made from the adduct acid by the method of Alder and Jacobs.[22]

Cyclopropanedicarboxylic acid anhydride was obtained in 4.2% yield, spec. act., 18.63 mμc./mg.C.

(21) *Cf.* R. C. Anderson and A. P. Wolf, BNL 3222, a modification of the method of E. F. Phares, *Arch. Biochem. Biophys.*, **33**, 173 (1951).

(22) V. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953).

Complex Ions of Chromium. IX. Mechanism of Racemization and Isomerization, Reactions of Chelated Chromium(III) Ions[1]

BY RANDALL E. HAMM, REINER KOLLRACK, GARTH L. WELCH AND RALPH H. PERKINS

The resolution of *cis*-potassium dioxalatodiaquochromate(III) is reported. Studies of the rates of racemization give an activation energy ($\Delta H\ddagger$) of 13.4 kcal./mole. Theoretical calculations indicate that a likely mechanism for this reaction and also for the *trans–cis* isomerization is one involving dissociation of a water molecule to give an intermediate which is most like a trigonal bipyramid. Similar calculations on trisoxalatochromate(III) are in agreement with the recent experimental measurements on this compound.

In a previous paper[2] from this Laboratory the kinetics of the *trans–cis* isomerization of potassium dioxalatodiaquochromate(III) were reported. A mechanism was suggested which involved the breaking of one bond to an oxalate and subsequent rearrangement to give the *cis* isomer. This suggested mechanism now appears less likely than one which starts with the dissociation of a water molecule.

A thorough search of the literature has shown no report of the successful resolution of *cis*-dioxalatodiaquochromate(III). This resolution has been found to be possible using the proper experimental conditions. Because of this the kinetics of the racemization of this optically active compound have been studied.

The mechanisms for the isomerization and for the racemization reactions should be identical. Theoretical calculations on the simple possible mechanisms were undertaken, along with similar calculations on the racemization of tris-oxalatochromate(III).

Experimental

Reagents.—The *trans* and *cis*-potassium dioxalatodiaquochromate were prepared by the method of Werner[3] using reagent grade oxalic acid and potassium dichromate. The *cis* compound was resolved by dissolving a weighed quantity of potassium dioxalato diaquochromate(III) in a minimum

quantity of warm water and adding to it a warm saturated solution of strychnine sulfate of sufficient volume to have 3 moles of strychnine per mole of chromium. After mixing the solution was cooled rapidly in an ice bath. A crystalline precipitate was formed which had an almost metallic luster with a slight reddish tinge. It was compact and easily filterable. After air drying this precipitate was readily soluble in water. Solutions of this precipitate gave a higher optical activity than the amorphous precipitates which were obtained on slower crystallization from the solution.

The crystalline diastereoisomer was analyzed for chromium and for oxalate by methods previously used,[2] with application of a modification following the method of Johnson and Mead[4] to avoid the interference of strychnine. Approximately 5 ml. of concentrated ammonium hydroxide was added to 50 ml. of the aqueous solution containing the weighed sample of the diastereoisomer, the solution was placed in a separatory funnel, an equal volume of chloroform was added and the mixture was shaken. The aqueous phase was separated and heated to remove dissolved chloroform, and the analysis for chromium and oxalate were then performed. An alternate method in which the precipitated strychnine was removed by filtration gave comparable results. Analyses of the diastereoisomer gave the following results. Found: 3.89% Cr, 18.57% C_2O_4. Calcd. for ($C_{21}H_{22}N_2$-O_2)₃·H[Cr(C_2O_4)₂(H_2O)₂], 3.89% Cr, 18.23% C_2O_4.

Polarimeter.—The polarimeter used was a Rudolph Model 80 High Precision Polarimeter, equipped with a Rudolph Model 95 Spectroscopic Monochrometer.

Polarimetric Rate Determinations.—For determination of the rates of racemization, a weighed sample (65–75 mg.) of the diastereoisomer was metathesized with a measured volume of thermostated 0.10 *M* potassium iodide solution, the ratio of strychnine to iodide being 1:1. The potassium salt of the complex went into solution, and the strychnine iodide remained as a white precipitate. This solution was

(1) Presented at the Northwest Regional Meeting of the American Chemical Society, Richland, Washington, June 16–17, 1960.

(2) R. E. Hamm, THIS JOURNAL, **75**, 609 (1953).

(3) A. Werner, *Ann.*, **406**, 216 (1914).

(4) C. H. Johnson and A. Mead, *Trans. Faraday Soc.*, **29**, 626 (1933).