Hot-Atom Chemistry of $^{14}C^+$ in Benzene. Partial Degradations and Suggested Mechanisms

Helmut M. Pohlit, Tz-Hong Lin, and Richard M. Lemmon

Contribution from the Laboratory of Chemical Biodynamics, Lawrence Radiation Laboratory, University of California, Berkeley, California 94720.
Received January 2, 1969

Abstract: Seven ^{14}C-products (toluene, cycloheptatriene, phenylacetylene, "U-2," biphenyl, diphenylmethane, and phenylcycloheptatriene) from hot-atom reactions of ^{14}C ions of 5-keV kinetic energy in solid (−196°) benzene have been partially degraded. The results indicate the formation of the intermediate ^{14}C-carbenes, methylene, benzylidene, and cycloheptatrienylidene, and reactive ^{14}C-containing fragments, particularly a C_2 species. Cycloheptatrienylidene and cycloheptatriene apparently undergo extensive isomerization during, or immediately following, their formation. This isomerization is compared with other known modes of isomerization of cycloheptatriene and found to be best represented as 1,2-hydrogen shifts. It appears that, in the system under investigation, a mechanism different from the thermal has to be assumed.

In the preceding paper[1] we reported on the identity and yields of products from the irradiation of benzene at −196° by ^{14}C ions and atoms. The present paper proposes the mechanisms that we believe are involved in the formation of the observed products.

Dependence, or rather, nondependence of kind and yields of the products on state and energy of the irradiating carbon over the range (15–0.1 keV) tested[1] is very limited with respect to the information it provides on the identity and energy of the reactive intermediates. However, the identity of the final products is very often strongly suggestive of the mechanisms involved in their formation. An even more powerful means for elucidating the detailed mechanism is the knowledge of the location of the former hot ^{14}C atom within the product molecule. We have, therefore, partially degraded all of the major products (*i.e.*, those with yields larger than 1% with respect to the entering hot particle): toluene (T), cycloheptatriene (CHT), phenylacetylene (PhAc), biphenyl (Ph_2), diphenylmethane (Ph_2CH_2), phenylcycloheptatriene (PhCHT), and a compound, "U-2," whose identity has not been established yet, but whose two principal hydrogenation products, methylcyclohexane and toluene, are taken as proxies. From the results, we have drawn specific, though tentative, conclusions concerning the primary reaction products, their dynamics (isomerization), and their subsequent chemical fate.

Results

Figure 1 shows the label distributions that we have determined. The values listed (percentages of activity in each position) are averages of usually two or three independent activity determinations. The estimated errors reflect both the accuracy of the liquid scintillation counting method and the errors in the weight determination of the radioactive samples.[2] Values in parentheses have been obtained by difference.

Comparison with degradations by other authors is possible only for toluene because our other products have either not been reported or were not degraded. Wolf and coworkers report that 86% of the radioactivity is in the methyl carbon of toluene formed from the interaction of recoiling ^{14}C atoms with benzene.[3] The activity found in other positions are: 1, 8%; 2, 4%; 3, 2%; 4, 1%.[4] (The asterisk in Figure 1 denotes that although phenylcycloheptatriene isomerizes under the conditions of glpc, presumably due to [1,5]-hydrogen shifts,[5] the original irradiation product may well be the 7-phenylcycloheptatriene as indicated in the figure. However, we have shown that it does not isomerize to diphenylmethane under the same glpc conditions, so that the latter is indeed an original hot-atom product.)

Experimental Section

Irradiations. The irradiation techniques have been described in the preceding paper.[1] The kinetic energy in this irradiation was 5 keV; the length of irradiation was 3 hr; the total amount of incorporated activity was *ca.* 6 × 10^6 dpm (6 × 10^4 dpm per 1% product; see preceding paper).

Gas–Liquid Chromatographic Separation. Glpc separations of all compounds, with the exceptions (noted in the text) of the dimethyl acetylenedicarboxylate adduct of CHT and of dimethyl phthalate were carried out on columns of 20% Carbowax 20M on DMCS-treated Chromosorb W. The columns were: analytical, 10 ft × 0.25 in. o.d., 40 ml He/min; preparative, 12 ft × 0.75 in. o.d., 300 ml/min.

Isolation of Compounds from the Irradiation Mixtures. To 500 μl of the benzene solution of the products we added 5 μl each of T, CHT, PhAc, Ph_2, Ph_2CH_2, PhCHT, and phenylhexane (as "carrier" for U-2). Aliquots of this mixture were then separated into component compounds by analytical glpc (70° for 12 min, then 10°/min to 200°, and then held at that temperature). Individual compounds ("peaks") were trapped (−196°) as they emerged from the glpc column.

Degradation Procedures. (1) Toluene. In order to remove contaminating cycloheptatriene, the toluene was first hydrogenated (2 atm of H_2, PtO_2, 2 hr at room temperature). The resultant cycloheptane is easily separated from the toluene by glpc. The distribution of activity between the ring and the methyl group of the toluene is accomplished by chromic acid oxidation to benzoic acid, followed by a decarboxylation *via* the Schmidt reaction;[6] the resultant CO_2 and aniline were counted by liquid scintillation methods.[2]

(2) Cycloheptatriene. This compound was isolated under glpc conditions that did not cause isomerization (all parts of the glpc instrument were below 120°). Partial degradation was accomplished by thermal decomposition (after glpc purification) of a

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[1] H. M. Pohlit, T.-H. Lin, W. Erwin, and R. M. Lemmon, *J. Am. Chem. Soc.*, 91, 5421 (1969).

[2] T. H. Lin and H. M. Pohlit, *Anal. Biochem.*, 28, 150 (1969).

[3] A. P. Wolf, B. Gordon, and R. C. Anderson, *J. Am. Chem. Soc.*, 78, 2657 (1956).

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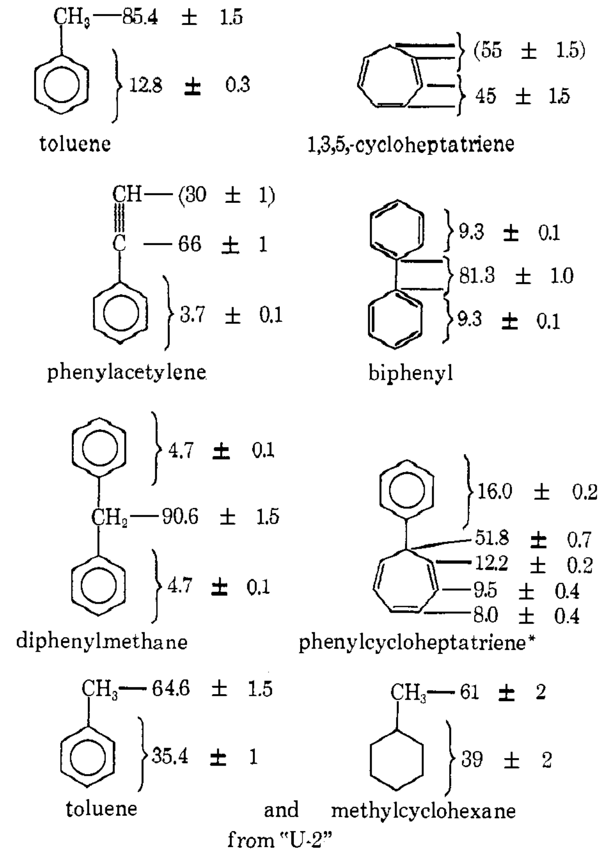
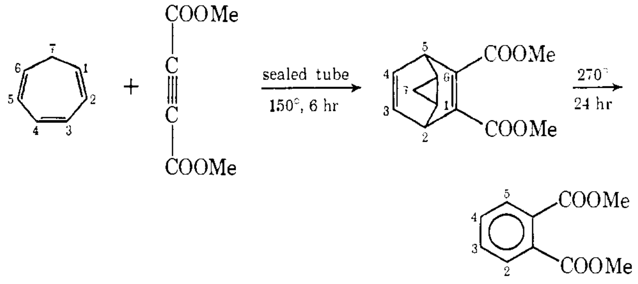


Figure 1. Distribution of ^{14}C in major products formed by the irradiation of solid benzene with $^{14}C^+$ ions (KE = 5 keV).

Diels–Alder adduct[7] (dimethyl acetylenedicarboxylate). The adduct was glpc purified on 10% SE 30 on DMCS-treated Chromosorb W.



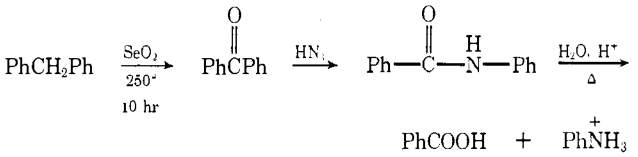
Counting the dimethyl phthalate (glpc purified under the same conditions as the Diels–Alder adduct) gives the activity in carbons 2, 3, 4, and 5 of the CHT. The summed activities of carbons 1, 6, and 7 were determined by difference.

The validity of the above degradation scheme was checked by synthesis of 1,3,5-cycloheptatriene-7-^{14}C, *via* $^{14}CH_2N_2$ and benzene over CuBr,[8] and subsequent degradation. [$^{14}CH_2N_2$ was obtained through hydrolysis of N-methyl-^{14}C-N-nitrosourea, which was synthesized from $^{14}CH_3NH_2 \cdot HCl$ (New England Nuclear Corp.) and urea in the standard procedure.[9]] After applying the above degradation to a glpc-purified sample of cycloheptatriene-^{14}C, the resultant dimethyl phthalate was found to contain 2.5 mole % of the starting specific activity. The implied label isomerization was presumably due to the synthesis mechanism. We assume this because the activity in dimethyl phthalate was increased only to 3% when a sample of the same batch of cycloheptatriene-^{14}C was kept at 150° for 6 hr (Diels–Alder addition reaction conditions) before degradation. The latter experiment indicates, in line with rate measurements,[10] that a label isomerization concurrent with the Diels–Alder addition cannot amount to more than 0.1–0.2% activity in dimethyl phthalate, assuming 90% completion (yields of over 80% are commonly obtained) in 6 hr and essentially first-order reaction because of the large excess (about fourfold) of the dienophile.

(3) **Phenylacetylene.** After isolation and purification by glpc, 150 μl of both ethylbenzene and benzene were added to the labeled phenylacetylene, and the mixture was hydrogenated (PtO_2, 2 atm of H_2, room temperature, 6 hr). The ethylbenzene was separated and purified by preparative glpc at 100°. Oxidation of this compound with chromic acid gave (after purification by sublimation) 30 mg of benzoic acid, which was degraded *via* the Schmidt reaction, giving the activity in the α carbon and the ring. The activity in the β carbon was determined by the difference between those of the ethylbenzene and the benzoic acid.

(4) **Biphenyl.** After repeated glpc purification at 200°, 100 mg of unlabeled biphenyl was added. The compound was then oxidized by chromic acid in acetic acid. From the activity of the resultant benzoic acid, the specific activity of the two C_1's of the biphenyl was calculated. A confirmation of this value was obtained through the Schmidt degradation of the benzoic acid.

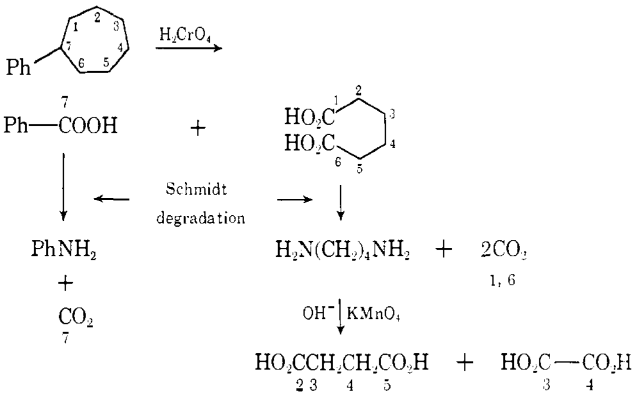
(5) **Diphenylmethane.** In order to remove all contamination which would yield benzoic acid upon oxidation of diphenylmethane, the latter was first oxidized to benzophenone, purified on preparative glpc, and degraded to benzoic acid and aniline according to



$$PhCH_2Ph \xrightarrow[250^\circ,\ 10\ hr]{SeO_2} PhC(=O)Ph \xrightarrow{HN_3} Ph{-}C(=O){-}NH{-}Ph \xrightarrow[\Delta]{H_2O,\ H^+} PhCOOH + Ph\overset{+}{N}H_3$$

The specific activity of the methylene carbon of the Ph_2CH_2 was obtained from that of the benzoic acid. The activity in the phenyl groups was revealed by that of the aniline.

(6) **Phenylcycloheptatriene.** The phenylcycloheptatriene sample was hydrogenated (2 atm of H_2, PtO_2, 25°) and the resultant phenylcycloheptane isolated and purified by preparative glpc. Phenylcycloheptane was oxidized to benzoic acid and adipic acid, which were further degraded according to



The activity in the phenyl group, and in C_7 of PhCHT, was determined from that of the aniline and CO_2, respectively, obtained from the Schmidt degradation of the benzoic acid. The activity of $C_{1,6}$ was obtained from the CO_2 that resulted from the Schmidt degradation of the adipic acid. The 1,4-butanediamine was oxidized to succinic acid and oxalic acid; the activity in the carboxyl groups of the former gave the activity in $C_{2,5}$ of the PhCHT, in the oxalic acid that of $C_{3,4}$.

The validity of the above degradation procedure was verified as follows, starting with cyclohexanone-1-^{14}C (purchased from New England Nuclear Corp.). This compound was converted to cycloheptanone-1-^{14}C by reaction with CH_2N_2, and then to phenylcycloheptane, as follows.

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(8) E. Müller and H. Fricke, *Ann.*, **661**, 38 (1963).

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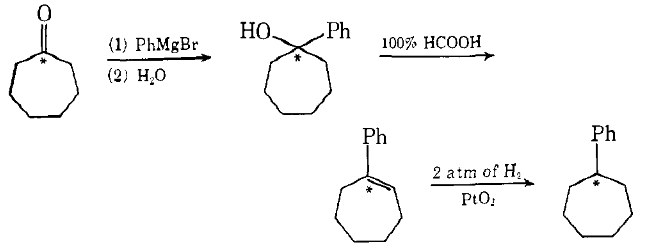

The phenylcycloheptane was then subjected to the degradation procedure described above. The activity found in the resultant adipic acid was 2.9% of that in the starting phenylcycloheptane-^{14}C. It is not known whether this minor scrambling occurred during the synthesis reactions or during the degradation of the phenylcycloheptane.

(7) U-2. To the glpc-purified U-2 were added 150-μl portions of both toluene and methylcyclohexane. The mixture was hydrogenated (2 atm of H_2, PtO_2, 25°, 1.5 hr), and the toluene and methylcyclohexane were separated by preparative glpc. The determinations of the methyl ring activity distribution in the toluene was made just as described above under Toluene. The same is true for the methylcyclohexane, which was first converted to toluene by vapor-phase dehydrogenation (30% Pd–C, 515°).

Discussion

Because of journal-space limitations, this section is necessarily limited. An expanded discussion is to be found in the Ph.D. theses of Helmut M. Pohlit and Tz-Hong Lin, University of California, Berkeley, 1969.

Toluene and Cycloheptatriene. It has long been postulated that fast carbon atoms abstract hydrogen atoms from organic molecules to form CH and, in subsequent similar steps, CH_2, etc., radicals,[3,11–14] even though the bond-energy differences involved may, as in this case, indicate endothermicity.[15] Toluene and cycloheptatriene were therefore assumed to be due to a bimolecular reaction between CH_2 and benzene, in analogy with the thermal and photochemistry of CH_2 radicals. Rather than invoking a new mechanistic scheme (involving, *e.g.*, something other than a CH_2 radical), we assume that the small deviation (13%) from expectation in toluene as well as the large (at least 45%) in cycloheptatriene are due to isomerization of the latter following or during its formation.

Suryanarayana and Wolf[16] suggested, among other mechanisms, that all of T is formed from an intermediate norcaradiene and CHT. This is in contrast to Lemmon and Strohmeier's[17] observation that there is less than 0.2% activity in the ring of toluene, prepared by the photolysis of $^{14}CH_2N_2$ in benzene, while under the same conditions the cycloheptatriene product exhibits a large degree of isomerization, apparently due to 1,2-hydrogen shifts.[18,19] In other words, isomerization of cycloheptatriene to toluene seems to be absent under the photolysis conditions.

More detailed mechanisms for the reactions of CH_2 were suggested by DeMore and Benson[20] and by Cvetanović;[21] that work suggests that our results may be interpreted as (see Figure 2) (a) in the C–H "insertion" reaction the ring carbon skeleton remains unaltered, and (b) in the C=C "insertion" there is formed the intermediate biradical I, which is assumed to isomerize as indicated and thus cause the deviations from labeling specificity (13% in T, more than 45% in CHT). It is clear that, if this biradical is the precursor to cycloheptatriene, the ring-enlarging followup reaction (and the reverse) must be much faster than the 1,2-hydrogen shift which produces toluene. This is supported by Berson and Willcott's observations[22] and DeMore and Benson's calculations.[20] If hydrogen shifts occur while in the seven-membered ring constitution (II or III), some activity will appear in the ring part of I, and thus eventually also in that of toluene. The reason why this should be observed in this system, while it is obviously not observed in photolysis, has to be seen in the much higher kinetic energy that CH_2 can attain in our system.[20]

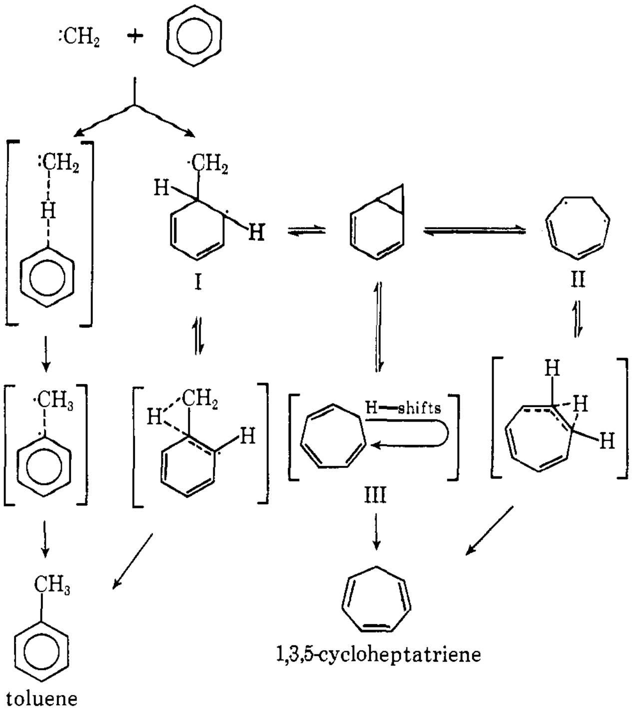

Figure 2. Detailed mechanisms for "insertion" reactions and isomerizations leading to toluene and cycloheptatriene.

An essential implication of this mechanism is that those hydrogen shifts which cause the label isomerization in cycloheptatriene have to be faster than the ring enlargement (or reverse) reaction. Much information is available on the isomerization of CHT by thermal activation.[10,23,24] However, in the latter process the assumption of equilibrium for all degrees of freedom is more nearly fulfilled than in our system. In fact, "migration" of energy from the forming bond into the other degrees of freedom of the same molecule competes with the rate of deactivation through collisions with other molecules ($\approx 10^{-11}$ sec). If, indeed, a thermal mode

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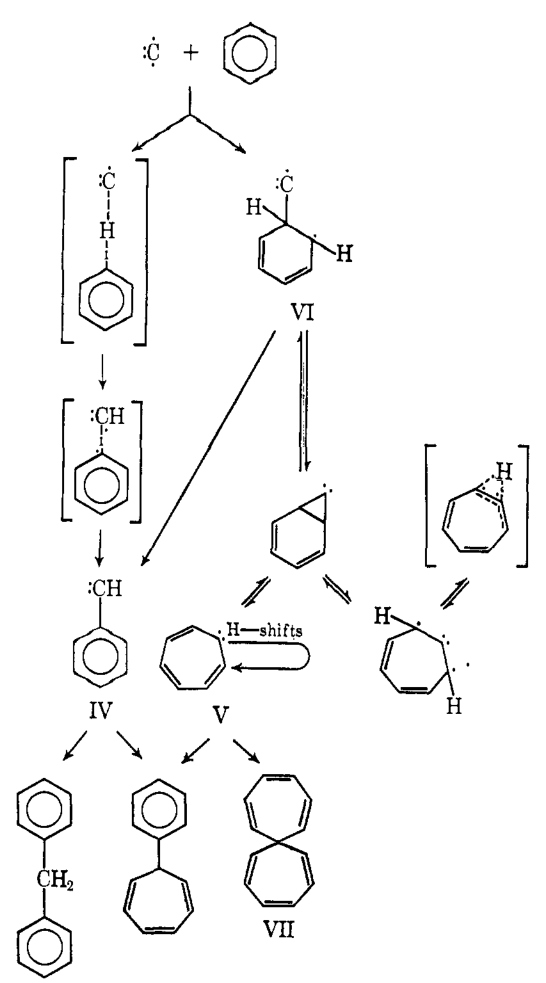

Figure 3. Routes to labeled diphenylmethane and phenylcycloheptatriene.

should account for the label isomerization in CHT and T ([1,5]-H-shift[10,25]), it would have to produce a labeling pattern in T that increases from carbon 1 to 4. In cycloheptatriene the 7, 3, 1, and 2 positions should be labeled in decreasing order. While detailed degradation data on cycloheptatriene are not yet available, our own preliminary, as well as Wolf's,[4] data on toluene indicate the opposite. Calculations on the basis of consecutive 1,2-hydrogen shifts, however, best fit the data.

Characteristically, 1,2-hydrogen shifts in cycloheptatriene have been observed (besides during photochemical synthesis) in nonthermal systems, *e.g.*, in photolysis of cycloheptatriene,[18,19] where toluene is also a product.[26] It is therefore reasonable to conclude that most of the isomerization is caused by a nonthermal process and that a "hot spot,"[27] if this implies equilibration of the degrees of freedom of the microcanonical subsystems, does not exist.

A difficulty arises from the fact that the considerable activity in positions 2 and 3 of cycloheptatriene, and the still considerable labeling of the *meta* and *para* positions of toluene, require repetition of these 1,2-hydrogen shifts. A way out would be to assume that in addition to the (in the Woodward–Hoffmann terminology[25]) sigmatropic rearrangement of order [1,7] there are also those of [1,3] and [1,5] taking place between formation and the next deactivating collision, or, more likely, that it takes more than one collision to deactivate the collision complex completely and that these successive collisions open up different rearrangements, possibly also one of order [1,5], that is, the predominant thermal isomerization.

Phenylcycloheptatriene and Diphenylmethane. These two isomeric compounds can best be regarded as products of two-step reactions. The first, in complete analogy to the "insertion" mechanisms for CH$_2$, leads to the carbenes benzylidene and cycloheptatrienylidene. The second is the familiar reactions of these carbenes with another benzene molecule (see Figure 3).[28–31] If no isomerization of the intermediates, IV and V, is assumed, the products should be specifically methylene-labeled diphenylmethane and 7-phenyl-1,3,5-cycloheptatriene-7-^{14}C. This is essentially the case for the first compound (91% activity in the methylene) but not for the second (only 52% in C-7). The decreasing activity in the cycloheptatriene ring for carbons 1, 2, and 3 of PhCHT demonstrates what we had to infer for cycloheptatriene in order to understand the labeling in toluene. Apparently, an entirely analogous situation exists as for the cycloheptatriene–toluene system: considerable isomerization in the seven-membered ring carbene, but only a little in the benzylidene, which we assume to be due to isomerization of cycloheptatrienylidene *via* intermediate VI. The large amount of activity in the phenyl ring of phenylcycloheptatriene is much more than would be compatible with a common precursor, benzylidene, for diphenylmethane and phenylcycloheptatriene. One way of rationalizing this is to assume that a benzylidene (IV) rearranged from cycloheptatrienylidene (V) has a different spin state than that from C—H bond insertion of C, and that the subsequent reaction with a C—H and C=C bond are strongly spin selective. Another rationale is the intermediate formation of the spiro[6.6]tridecahexaene (VII of Figure 3), subsequently rearranging to phenylcycloheptatriene. Our attempts to identify this compound among the products has led to an upper yield limit of 0.01% (compared to about 6% for phenylcycloheptatriene), making this route less appealing.

C$_7$H$_6$ intermediates of various conformations have been suggested for hot-atom reactions of carbon in benzene.[32] The structure of the intermediates postulated by us is inferred from (a) the nature of the final products, (b) the activity distribution in these products, and (c) the similarity with carbene chemistry. It is, of course, not excluded that these inferred intermediates are in themselves rearrangement products of "adducts" of quite different structures. Wolfgang and coworkers[33–35] have substantiated "adducts" between carbon and various substrate molecules, in particular, ethylene. In these systems, also, extensive isomerization of these

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intermediates was observed, as double-labeling experiments revealed.

Phenylacetylene. With more than 96% of the total activity in the acetylene part, there is strong support for a C_2H_x ($x = 0, 1$, or 2) precursor which reacts with a benzene molecule in a second step, rather than the decomposition, as part of a random fragmentation, of one particular, possibly $C_{13}H_{12}$, intermediate. Additional support comes from the high concentration of label in both the α and β carbon. The pickup of another carbon atom by a fast ^{14}C atom can, as classical mechanical calculations for inelastic two-body collisions show, occur at rather high energies, *via* a stripping mechanism, rendering the product C_2 fast and reactive. Some of these precursors may, however, originate from a "low-energy" mechanism as proposed by Rose, *et al.*, for acetylene.[32] On the other hand, acetylene may also be formed *via* the stripping mechanism. The double-labeling experiments on the acetylene formation[36,37] in various systems are not necessarily incompatible with such a stripping mechanism since the "stripped" carbon may very well carry along its hydrogen(s), because of their small mass.

Temporary incorporation of carbon into the ring with incomplete fragmentation could be the source, besides for phenylacetylene at lower energies, for various *n-alkylbenzenes*, of which we have identified all up to $n = 7$ in the hydrogenated sample. Their degradation is pending.

Benzene and Biphenyl. These compounds may be due to the same initial process, however, the decay mode being the exact reverse (benzene), or quasi-reverse, leading to a phenyl radical which reacts with another benzene molecule. The 80% activity in the 1 carbon is quite surprising because, if we are dealing with a phenyl radical in a "hot spot," we would expect little restriction to isomerization. This is another indication for the virtual absence of "thermalization" in such a hypothetical "hot spot."

U-2. The two hydrogenation products, toluene and methylcyclohexane, exhibit equal (within the error limits) methyl/ring activity ratios. Label incorporation into the phenyl ring is highest here of all phenyl-labeled products. However, the significance of this fact depends very much on the origin and identity of U-2.

Throughout the preceding discussions we attempted to explain the formation of each product with one type of mechanism only. This may, occasionally, permit different products (such as cycloheptatriene and toluene) depending on certain dynamic parameters, such as internal energy, of the transition state pertaining to the particular mechanism. We do not wish to imply by the foregoing discussion that there could not be two, or even more, completely different routes in some cases, particularly with respect to the two extremes of the energy scale. Alternatives are readily conceived. Support or exclusion of the suggested mechanisms may come from experiments now in progress, namely, determination of the energy dependence of the integral reaction probability, coupled with degradations of products from low-energy irradiations.

Acknowledgment. This research was sponsored, in part, by the U. S. Atomic Energy Commission.

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Photolysis of Matrix-Isolated 1,3,5-Cyclooctatriene and Bicyclo[4.2.0]octa-2,4-diene. Spectra of Their Transient Photolysis Products[1]

Pabitra Datta,[2] Theodore D. Goldfarb, and Robert S. Boikess

Contribution from Department of Chemistry,
State University of New York at Stony Brook, Stony Brook, New York 11790.
Received February 24, 1969

Abstract: Ultraviolet and infrared spectroscopy have been used to study the photochemistry of 1,3,5-cyclooctatriene (I) and bicyclo[4.2.0]octa-2,4-diene (IV) suspended in inert vapor matrices at 20°K. *cis,cis*-1,3,5,7-Octatetraene, benzene, and ethylene were found to be common primary photoproducts of the two parent valence isomers. Photolysis of I also yields another primary product. This product reverts to the starting material at room temperature and has a vibrational spectrum which supports its assignment as a strained cyclic stereoisomer of I. These results are discussed in conjunction with the results of previous flash photolysis and solution photochemical mechanisms involved.

The photochemistry of cyclic polyenes has attracted a great deal of recent interest. Numerous rearrangements and attempts at mechanistic interpretation have been reported and are summarized in a recent review.[3]

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(1) This research was supported by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, U. S. Air Force, Grant No. 837-67.

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