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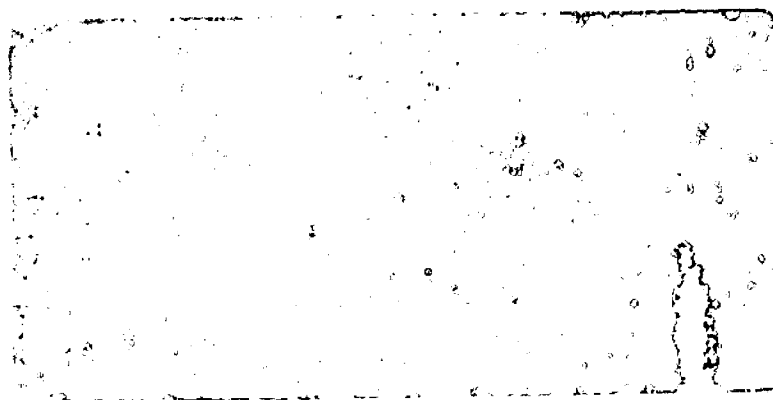
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Publication Date

1958-05-01

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Contract No. W-7405-eng-48

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IN TOLUENE FORMED FROM BENZENE
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ABSTRACT

Diazomethane-C¹⁴ was photolyzed (both by visible and by ultraviolet light) in benzene solution. The resultant labeled toluene was degraded in order to determine the distribution of radioactivity between the methyl group and the ring. No detectable activity was found in the ring; this result indicates the operation of a different mechanism from that observed in the production of labeled toluene by the interaction of benzene with recoiling C¹⁴ atoms. In addition, it was found that x-rays have, at most, only a negligible effect in promoting the decomposition of diazomethane in benzene solution.

THE DISTRIBUTION OF RADIOACTIVITY
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INTRODUCTION

A number of reports have appeared recently describing the irradiation of organic compounds with recoiling C¹⁴ atoms, derived from the N¹⁴(n, p)C¹⁴ reaction,³ or with C¹⁴ ions in a mass spectrometer.⁴ These reports have heightened interest and speculation concerning the kind of interaction that is taking place when the "hot" atom or ion is reduced in energy to the point (probably 25 to 50 ev) at which a chemical bond can form.

Wolf and coworkers have shown that when toluene is formed by the irradiation of benzene with recoiling C¹⁴ atoms, not all of the C¹⁴ activity is present in the methyl group.⁵ About 86% of the activity was found in this position and the remaining 14% in the ring. A similar result was obtained for o-xylene formed from the C¹⁴-atom irradiation of toluene.

Doering and Knox⁶ photolyzed diazomethane in the presence of benzene and formed toluene and cycloheptatriene. Wolf has concluded that the recoiling C¹⁴ atom may behave similarly to Doering and Knox's "carbene" (CH₂:) but that the recoiling atom, having a much larger energy associated with it, may be able to form additional products.⁵ The purpose of the work reported here has been to photolyze (by using both visible and uv light) C¹⁴-labeled diazomethane in the presence of benzene, and to determine the distribution of radioactivity between the methyl group and the ring of the resultant toluene. In addition, an attempt was made to form labeled "carbene" by the action of x-rays on the same system.

¹The work described in this paper was sponsored by the U. S. Atomic Energy Commission.

²Appointment supported by the International Cooperation Administration under a program administered by the National Academy of Sciences.

³A. P. Wolf, C. S. Redvanly, and R. C. Anderson, This Journal, 79, 3717 (1957), have thoroughly reviewed this type of experiment.

⁴R. M. Lemmon, F. Mazzetti, F. L. Reynolds, and M. Calvin, This Journal, 78, 6414 (1956).

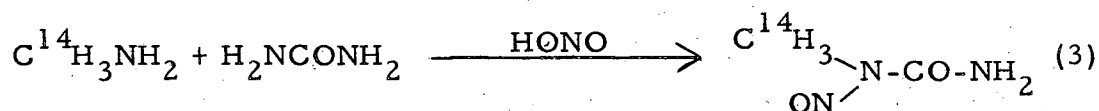
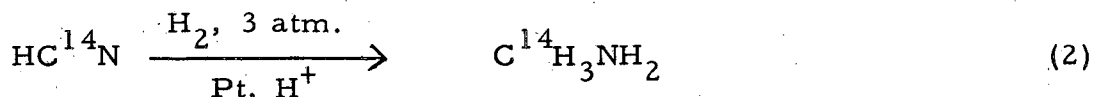
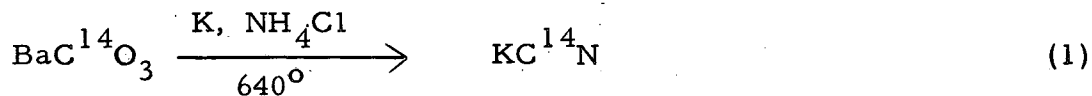
⁵A. P. Wolf, B. Gordon, and C. S. Redvanly, Abstracts of Papers, 131st Meeting of the American Chemical Society, Miami, Florida, April 1957, p. 12-0.

⁶W. von E. Doering and L. H. Knox, This Journal, 75, 297 (1953).

EXPERIMENTAL

N-methyl-N-nitrosourea-methyl-C¹⁴

Labeled methylnitrosourea was prepared according to the following reactions:



The labeled cyanide was prepared according to the method of Sixma et al.⁷ The conversion of the cyanide to diazomethane followed, in general, the methods described by Jones and Skraba.⁸ The specific activity of the labeled nitrosomethylurea which was used in the benzene experiments was 124 $\mu\text{C}/\text{mmole}$.

Benzene-C¹⁴H₂N₂ Irradiations

To 250 ml of reagent-grade benzene in a 500-ml flask was added about 40 ml of a 45% aqueous solution of KOH. The flask was cooled on an ice bath and a mixture of 36.5 mg of the labeled methylnitrosourea and 15.3 g of inactive N-methyl-N-nitroso-N-nitroguanidine was added slowly. The yellow benzene solution of diazomethane was decanted into another flask and the aqueous residue washed with 60 ml of benzene. The combined benzene solutions were dried for one hour with KOH pellets. The concentration of diazomethane was determined by titrating against benzoic acid. The yields of diazomethane varied from 75 to 80% and the average concentration in benzene was approximately 0.25 mole per liter.

Approximately 300 ml of the C₆H₆-C¹⁴H₂N₂ solution was placed in a 500-ml Pyrex flask. Most of the air was displaced from the flask by a stream of nitrogen. Nitrogen generated during the reaction was allowed to escape through a mercury valve which protected the flask's contents from atmospheric oxygen. The flask was irradiated with two 275-watt General Electric Reflector Sunlamps, one on each side. The distance between the lamps and the flask was about 20 cm. During the irradiation the flask and its contents were kept at approximately 20° by a stream of water running over the outside of the flask. After 18 hours of irradiation the solution was colorless and no further evolution of nitrogen could be observed.

⁷F. L. J. Sixma, H. Hendricks, K. Helle, U. Hollstein, and R. Van Ling, *Rec. trav. chim.* 73, 161 (1954).

⁸A. R. Jones and W. J. Skraba, *Science*, 117, 252 (1953).

The ultraviolet irradiations were performed in the same way except that the solution was contained in a quartz flask, and the two sunlamps were replaced by a water-cooled, 1-kw General Electric A-H-6 mercury vapor ultraviolet lamp. This lamp was also 20 cm from the reaction flask.

The x-ray irradiations were also performed on 30-ml portions of a 0.25 M solution of $C^{14}H_2N_2$ in benzene. The solutions were placed in cellophane-covered beakers and were irradiated in the dark by a Machlett OEG-60 50-kvp x-ray generator operated at 25 ma. The air in the beakers was replaced by nitrogen. The solutions were stirred and maintained at 0° during the irradiations. The total dosages ranged up to 3.6×10^7 r, delivered over 10 hours.

Separation of Reaction Products

After the irradiation the bulk of the benzene was distilled through a 15-plate vacuum-jacketed column (Glass Engineering Laboratories). From the initial 300 ml of solution, all but about 10 ml were distilled at a boiling temperature of 80° . The residue was then separated into toluene and cycloheptatriene fractions by distillation on a Podbielniak "whirling heli-band" fractionating column. The fractions were nearly quantitatively pure at this point. The fractions were further purified, and their identities unequivocally established, by gas-liquid partition chromatography (Wilkens "Aerograph", 5-ft column, polyethylene oxide substrate, 86° , He flow 30 to 50 cc per minute).

Determination of C^{14} Activity

The amounts of radioactivity in the purified toluene and cycloheptatriene fractions were determined by direct addition to a liquid scintillation solution (2,5-diphenyloxazole in toluene). The scintillation counter was described earlier.⁹

Distribution of Radioactivity in Toluene

The purified, labeled toluene was diluted with inactive, reagent-grade toluene to give, in the ultraviolet-light irradiation, a specific activity of 1.04×10^5 dpm/mmole. The toluene was then converted into benzoic acid by the addition of aqueous permanganate.¹⁰ In a reaction flask equipped with a heater, thermometer, magnetic stirrer, and a reflux condenser were placed 3.1 ml of the toluene and 200 ml of water. The contents were heated to 95° and, with vigorous stirring, 9.2 g of $KMnO_4$ was added in small portions. At the end of 10 hours, the solution was practically colorless. The MnO_2 was filtered from the hot solution, and benzoic acid was precipitated by cooling the solution to 10° and adding about 30 ml of conc. HCl. The benzoic acid was collected by filtration and purified by crystallization

⁹Elton M. Baker in Chemistry Division Quarterly Report, UCRL-3157, Sept. 1955, p. 51.

¹⁰F. Ullmann and J. B. Uzbachian, Ber. 36, 1797 (1903).

from about 60 ml of water. Its melting point was 122° and its elementary analysis was as follows: Calculated for $C_7H_6O_2$: C, 68.84, H, 4.95; Found: C, 68.72; H, 5.09. The specific activity was determined by combustion to $C^{14}O_2$ and counting in an ionization chamber.^{11, 12} It was found to be 1.04×10^5 dpm/mmole. The benzoic acid was then recrystallized in the same fashion and the specific activity redetermined. Its activity was unchanged.

About 600 mg of the benzoic acid was quantitatively decarboxylated by heating at 400° for 3 hours with 200 mg of cadmium powder in an evacuated tube.¹³ The benzene and CO_2 were separated, the CO_2 volume measured, and the CO_2 transferred into an ionization chamber by the use of the apparatus shown in Fig. 1. The decarboxylation tube, A, was attached to the vacuum line and cooled to -196° ; the entire system was then evacuated. Traps B and D were cooled by liquid nitrogen and Trap C was cooled in a dry ice-isopropyl alcohol bath. Stopcocks 1, 2, 3, and 5 were closed, the decarboxylation Tube A was broken by moving the ball joint, the liquid nitrogen bath was removed from Tube A, and the benzene and CO_2 were collected in Trap B. Stopcock 5 was opened and pumping was continued for a few minutes (to remove traces of CO formed during the decarboxylation). Stopcock 5 was closed, the liquid nitrogen bath removed from Trap B, and benzene collected in Trap C while CO_2 collected in Trap D. Trap C was closed off and the CO_2 volume was measured by removing the bath from Trap D and allowing the CO_2 to expand into the previously measured volume between Stopcocks 3 and 5. The CO_2 was then recondensed back into Trap D; this trap was then removed from the line and the CO_2 transferred into an ionization chamber for the radioactivity determination. The benzene in Trap C was then transferred into Trap E which was removed from the vacuum line. The benzene was purified by two passages through a gas-liquid partition chromatogram ("Aerograph", 5-ft column, paraffin substrate) and its radioactivity measured by liquid-scintillation counting.

Rearrangement Tests

In order to determine whether cycloheptatriene would rearrange into toluene under the conditions of the reaction, the following experiments were performed:

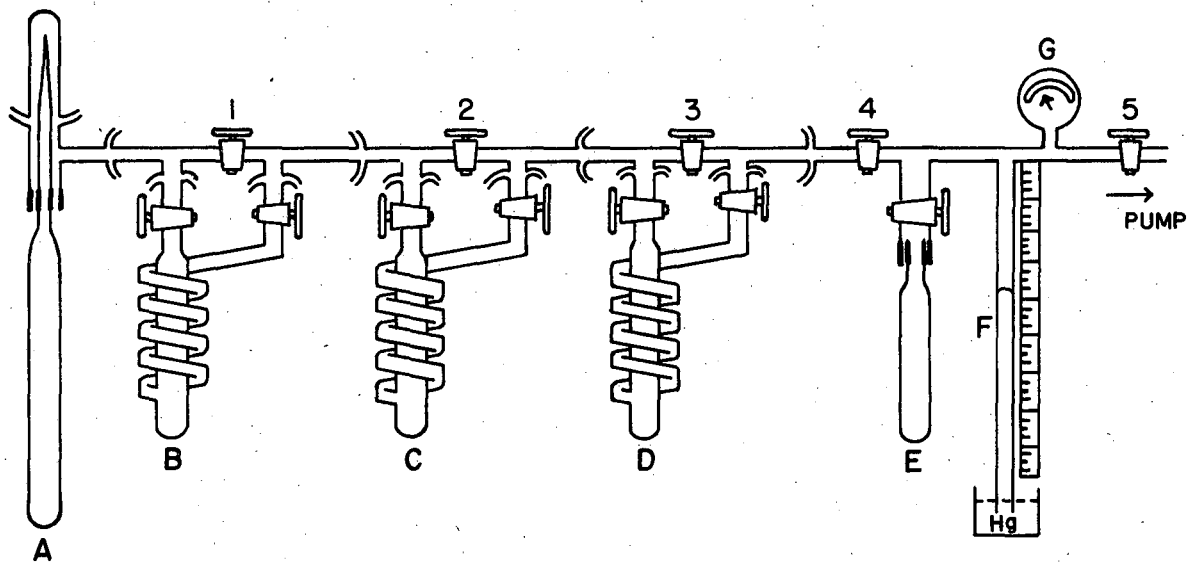
(a) Chromatographically pure cycloheptatriene (0.3 ml) was sealed in a Pyrex tube and heated at 130° for 50 hours. An aliquot portion was then chromatographed (polyethylene oxide) under conditions which would permit the detection of 0.5% of toluene. No toluene could be detected.

(b) Two other portions of cycloheptatriene were sealed in separate tubes; one tube (Pyrex) was irradiated with the sun lamps for 60 hours, the

¹¹K. E. Wilabach and W. Y. Sykes, *Science* 120, 494 (1954).

¹²B. M. Tolbert, *Ionization Chamber Assay of Radioactive Gases*, UCRL-3499, March 1956, p. 32.

¹³W. Moser, *Helv. Chim. Acta* 14, 971 (1931).



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Fig. 1. Vacuum line for transfer of products from benzoic acid decarboxylation.

- | | |
|-------------------------------------|-----------------|
| A. Combustion tube | E. Benzene trap |
| B. Benzene and CO ₂ trap | F. Manometer |
| C. Benzene trap | G. Vacuum gauge |
| D. CO ₂ trap | |

other (quartz) with the ultraviolet lamp for the same time. In neither case could any toluene be detected (i. e., any toluene formed was less than 0.5% of the cycloheptatriene).

RESULTS AND DISCUSSION

The x-ray irradiation produced no toluene or cycloheptatriene that could be detected by the gas-liquid partition chromatography. The chromatography was performed under conditions which would allow the detection of a yield of cycloheptatriene or toluene of as little as 0.1%.

Table I presents the results obtained from typical experiments using either the sun lamps or the ultraviolet lamp. With both types of irradiation the yields, based on diazomethane, of cycloheptatriene and toluene were approximately 30% and 8% respectively. The data were obtained from 600 ml of a 0.25 M solution of diazomethane in benzene. This solution was divided into two equal parts for the two irradiations, which were performed concurrently. The data of Table I show no significant differences between the visible- and ultraviolet-light irradiations.

The loss of about 18% of the radioactivity during the irradiations probably reflects a combination of "carbene" radicals to form ethylene and other low-molecular-weight hydrocarbons. More of this volatile material was removed during the benzene distillation, the bulk of it coming over in the first 50 to 100 ml. Gas chromatography (on polyethylene oxide) of the distilled benzene showed the presence of at least two compounds (probably polymers of "carbene") with retention times less than that of benzene. The same compounds appear to be present in both types of irradiations. No compounds other than toluene and cycloheptatriene were detectable (gas chromatography) after the removal of the benzene, i. e., of all compounds boiling below 80°.

In the ultraviolet irradiations reported here, the "carbene" from the photolyzed diazomethane may have an imparted energy as high as 6 ev (corresponding to the radiation of around 2000 Å transmitted through the quartz). Such an energy appears to be not high enough to permit the "carbene" to accomplish what a recoiling C^{14} atom, or radical, can accomplish--namely, to introduce activity into the benzene ring of toluene. These experiments therefore suggest the lower limit of energy, i. e., the recoiling C^{14} species probably has an energy above 6 ev when it interacts "chemically" with benzene.

Table I

	Sunlamp	Ultraviolet lamp
Results of visible- and ultraviolet-light irradiations of solutions of diazomethane-C ¹⁴ in benzene		
Percentages of total activity:		
C ¹⁴ H ₂ N ₂ -C ₆ H ₆ soln., before irradiation	100	100
C ¹⁴ H ₂ N ₂ -C ₆ H ₆ soln., after irradiation	82	83
Residue after removal of C ₆ H ₆	66	67

Cycloheptatriene/toluene ratio	3.5	3.5
Spec. act. cycloheptatriene, dpm/mmole	9.4 × 10 ⁵	9.4 × 10 ⁵
Spec. act. toluene, dpm/mmole	9.3 × 10 ⁵	9.3 × 10 ⁵

Toluene decarboxylation:		
Spec. act. toluene (after dilution), dpm/mmole	1.43 × 10 ⁵	1.04 × 10 ⁵
Spec. act. benzoic acid, dpm/mmole	1.42 × 10 ⁵	1.04 × 10 ⁵
Spec. act. CO ₂ , dpm/mmole	1.39 × 10 ⁵	1.01 × 10 ⁵
Spec. act. benzene, dpm/mmole	<2.0 × 10 ²	<1.5 × 10 ²
C ¹⁴ in methyl group	>99.8%	>99.8%
C ¹⁴ in ring	<0.2%	<0.2%