If uncertainties in S_f and σ^+ are ignored, one can predict *para* partial rate factors to within about 12% in this set. Here again the available data are as yet limited; moreover, the σ^+-constants are derived from one of the reactions, the solvolysis of phenyldimethylcarbinyl chlorides and the selectivity factors, S_f, derive from the reactions of *m*- and *p*-methyl reactants.

When a pair of linear correlations does not interrelate well, the validity of one or both is in doubt. In Fig. 5, for example, the Hammett least squares lines *1* and *2* may be taken as adequate. These generate lines *3* and *4*. If the Taft polar energy equation 1f applies and if his *o*-methyl and *o*-methoxy σ^*-values are satisfactory, *3* and *4* should fall close to the experimental data. They do not. Line *5*, which derives from *3* and *4*, also fails. For these reasons it was concluded that the Taft equation did not apply in this case. The foregoing suggests an internal consistency check or a validity test for new linear correlations.

For the field of linear correlations it is significant that in equation 13 two factors affect the property y of a system and become interlocked. This is clear from the expressions in 19. Also, the equation of one set of intercepts has the form

$$y_{1j} = rz_j + s = b_j \quad (x_1 = 0) \qquad (24)$$

That is, the spacings of the intercepts of one set at $x_1 = 0$ are proportional to related structural constants of the second set.[23] Any theoretical progress in the Hammett equation, say, can perhaps be carried over to any other equation which it will interrelate. Furthermore, our understandings of structural properties and line parameters which have heretofore developed independently, should become unified.[3]

There is, of course, nothing in equation 13 which restricts it to structure–reactivity problems. With the proper linear correlation and the generating procedure, we have satisfactorily predicted the boiling points of the esters R_iCOOR_j.[24] In chelate chemistry, linear correlations of pK_s (K_s = stability constant) with pK_a or pK_b of the ligand, with ionization potentials of the metal, with reciprocal metal radii, etc., probably could be treated by the methods of this paper.[25] There is a possible application in gas–liquid chromatography which involves separation factors *versus* other variables.[26] Indeed, whenever a data pattern appears similar to that formed by one set of lines as in Fig. 3, the possibility of a second linear correlation should at least be recognized.

Acknowledgment.—We wish to thank Prof. J. Berman of our Mathematics Department for a helpful discussion.

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(23) The absence of a continuous change in b_j with z_j reported for the chlorination of four series of compounds of the type p-$R_iC_6H_4OCH_2$-$C_6H_4R_j$ indicates a serious discrepancy in an otherwise excellent study.[3]

(24) Y. Ogata and M. Tsuchida, *Ind. Eng. Chem.*, **49**, 415 (1957).

(25) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice–Hall, Inc., New York, N.Y., Chaps. 4, 5, 1952; L. G. Van Uitert and W. C. Fernelius, THIS JOURNAL, **76**, 379 (1954).

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CHICAGO 16, ILL.

[CONTRIBUTION FROM THE RADIATION LABORATORY,[1] UNIVERSITY OF CALIFORNIA, BERKELEY]

The Distribution of Radioactivity in Toluene Formed from Benzene and Photolyzed Diazomethane-C^{14}

BY RICHARD M. LEMMON AND WALTER STROHMEIER[2]

RECEIVED MAY 26, 1958

Diazomethane-C^{14} was photolyzed (both by visible and 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 C^{14} 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.

A number of reports have appeared recently describing the irradiation of organic compounds with recoiling C^{14} atoms, derived from the N^{14} (n,p)C^{14} reaction,[3] or with C^{14} 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 25–50 e.v.) where a chemical bond formation can take place.

Wolf and co-workers[5] have shown that when toluene is formed from the irradiation of benzene with recoiling C^{14} atoms, not all of the C^{14} activity is present in the methyl group. 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 C^{14}-atom irradiation of toluene.

Doering and Knox[6] photolyzed diazomethane in the presence of benzene and formed toluene and cycloheptatriene. Wolf has concluded[5] that the recoiling C^{14} atom may behave similarly to Doering and Knox's "carbene" (CH_2:) but that the recoil-

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

(2) Appointment supported by the International Cooperation Administration under a program administered by the National Academy of Sciences; present address: Physikalisch Chemisches Institut der Universität Würzburg.

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

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

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

(6) W. von E. Doering and L. H. Knox, THIS JOURNAL, **75**, 297 (1953).

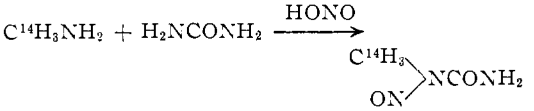
ing atom, having a much larger energy associated with it, may be able to form additional products. The purpose of the present work has been to photolyze (using both visible and ultraviolet light) C^{14}-labeled diazomethane in the presence of benzene, and to determine the distribution of reactivity between 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.

Experimental

N-Methyl-N-nitrosourea-methyl-C^{14}.—Labeled methylnitrosourea was prepared according to the reactions

$$BaC^{14}O_3 \xrightarrow[640°]{K,\ NH_4Cl} KC^{14}N \qquad (1)$$

$$HC^{14}N \xrightarrow[Pt,\ H^+]{H_2,\ 3\ atm.} C^{14}H_3NH_2 \qquad (2)$$



$$C^{14}H_3NH_2 + H_2NCONH_2 \xrightarrow{HONO} \begin{matrix} C^{14}H_3 \\ ON \end{matrix}\!\!>\!NCONH_2 \qquad (3)$$

The labeled cyanide was prepared following 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 nitrosomethyl-urea which was used in the benzene experiments was 124 μc./mmole.

Benzene-$C^{14}H_2N_2$ 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 75–80% and the average concentration in benzene was approximately 0.25 mole per liter.

Approximately 300 ml. of the C_6H_6–$C^{14}H_2N_2$ solution was placed in a 500-ml. Pyrex flask. Most of the air was removed 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.

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 100-ml. 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. This dosage is equivalent to a total energy absorption by the solution of 3×10^{22} e.v.

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. was 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 30–50 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 dis./min./mmole. The toluene was then converted into benzoic acid by the reaction with aqueous permanganate.[10] The benzoic acid was purified by crystallization from about 60 ml. of water. Its melting point was 122° and its elemental analysis was: Calcd. 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 dis./min./mole. The benzoic acid then was 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] After the tube was cooled it was connected to a vacuum line. The benzene was trapped at −80° and the CO_2 was trapped at −196° in a manner previously described.[14] The volume of CO_2 was measured on the vacuum line and the gas then was transferred into an ionization chamber for the radioactivity determination. The benzene was purified by two passages through a gas–liquid partition chromatograph (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 then was chromatographed (polyethylene oxide) under conditions that 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 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 gas–liquid partition chromatography. However, the solution absorbed only about 3×10^{22} e.v. Assuming that no energy is transferred from the benzene to the CH_2N_2, the latter molecules would absorb about 3×10^{20} e.v. Assuming a *G*-value for diazomethane decomposition of 10, this energy would lead to the formation of 3×10^{19} "carbene" radicals; this latter figure represents only about 1% of the total number of CH_2N_2 molecules present. The chromatography was performed under conditions which would allow the detection of a yield of cycloheptatriene or toluene of as little as

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

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

[9] E. M. Baker, University of California Radiation Laboratory Report No. UCRL-3157, September, 1955, p. 51.

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

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

[12] B. M. Tolbert, University of California Radiation Laboratory Report No. UCRL-3499, March 5, 1956, p. 32.

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

[14] R. M. Lemmon and W. Strohmeier, University of California Radiation Laboratory Report No. UCRL-8297, May, 1958, p. 6.

0.1%. It therefore appears that the X-rays have little effect in promoting the decomposition of diazomethane in benzene solution. Furthermore, the maximum possible *G*-value for "carbene" formation appears to be not greater than 1.

Table I

Results of Visible and Ultraviolet Light Irradiations of Solutions of Diazomethane-C^{14} in Benzene

	Sunlamp	Ultraviolet lamp
Percentages of total activity		
$C^{14}H_2N_2$-C_6H_6 soln., before irrad.	100	100
$C^{14}H_2N_2$-C_6H_6 soln., after irrad.	82	83
Residue after removal of C_6H_6	66	67
Cycloheptatriene/toluene ratio	3.5	3.5
Sp. act. cycloheptatriene, dis./min./mmole $\times 10^{-5}$	9.4	9.4
Sp. act. toluene, dis./min./mmole $\times 10^{-5}$	9.3	9.3
Toluene decarboxylation		
Sp. act. toluene (after diln.), dis./min./mmole $\times 10^{-5}$	1.43	1.04
Sp. act. benzoic acid, dis./min./mmole $\times 10^{-5}$	1.42	1.04
Sp. act. CO_2, dis./min./mmole $\times 10^{-5}$	1.39	1.01
Sp. act. benzene, dis./min./mmole $\times 10^{-2}$	<2.0	<1.5
C^{14} in methyl group, %	>99.8	>99.8
C^{14} in ring, %	< 0.2	< 0.2

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 50–100 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 e.v. (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 indicate a lower limit of energy, *i.e.*, the recoiling C^{14}-species probably has a kinetic energy above 6 e.v. when it interacts "chemically" with benzene.

Berkeley 4, Calif.

[Contribution from the Chemistry Department of Northwestern University]

Overlap Control of Carbanionoid Reactions. I. Stereoselectivity in Alkaline Epoxidation

By Howard E. Zimmerman, Lawrence Singer and B. S. Thyagarajan

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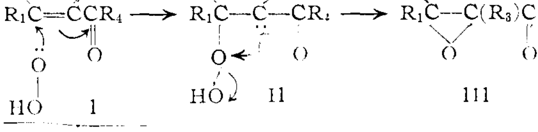
The alkaline epoxidation reaction of unsaturated carbonyl compounds has been found to be highly stereoselective. The energy of the carbanionic intermediate and that of the derived transition state is less responsive to ordinary steric interactions than to those diminishing electron delocalization. Overlap control favors the epoxide product with the unhindered carbonyl group. Thus epoxidation of α-phenylbenzalactone leads to the product with the large phenyl groups *cis* and the smaller acetyl group unhindered. The contrasting situation of epoxidation of α-phenylcinnamaldehyde, with an acyl group which can be planar even when *cis* to phenyl, and that of α-phenylcinnamonitrile, whose axially symmetric nitrile function has no conformational requirement, is discussed.

The epoxidation of polarized double bond compounds with alkaline hydrogen peroxide was first reported by Weitz and Scheffer[1] in 1921 and ever since this time has been the object of continued synthetic and mechanistic interest. In 1949, this mechanism was advanced by Bunton and Minkoff[2].



(1)

At first glance it might appear that the reaction, due to the intervention of the carbanionic intermediate II, would lead inevitably and prosaically to the more stable of the two possible stereoisomeric products. The literature affords little support for any other conclusion.

Thus the epoxidation reactions of known stereochemistry listed in Table I lead, with one exception,

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Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

(2) C. A. Bunton and G. J. Minkoff, *J. Chem. Soc.*, 665 (1949).