[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KAN.]

The Reactions of Recoil Tritium with Substituted Benzoic Acids

BY R. MILFORD WHITE AND F. S. ROWLAND[1]

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Recoil tritium atoms react with substituted benzoic acids to form tritiated benzoic acid when the substituent group is $-NH_2$, $-NO_2$, $-OH$, $-COOH$, $-F$, $-Cl$, $-Br$, $-I$. The ratio of the total radioactivity bound as benzoic acid to that as the parent molecule ranges from 0.02 for *m*-aminobenzoic acid to 0.58 for *o*-iodobenzoic acid. The ease of replacement increases rapidly as the bond strength of the substituent to the aromatic ring decreases. Intramolecular degradation of the benzoic acids shows that most of the tritium radioactivity substitutes into the position of the substituent. A smaller amount of the benzoic acid activity is always found in other positions than that formerly occupied by the substituent group. Labeled aniline was also isolated from irradiated aminobenzoic acids. The sensitivity to bond strength implies that chemical bonding is much more important than the physical mass of the bonded atoms or groups in determining the course of recoil tritium reactions. This sensitivity also implies that the energy at the time of reaction, while well in excess of thermal energies, is probably in the range of a few electron volts.

Introduction.—Ten to fifty percent of the recoil tritium atoms from the nuclear reactions $Li^6(n,\alpha)T$ or $He^3(n,p)T$ react as "hot" atoms with organic molecules to give labeled forms of the molecule attacked.[2] In certain cases (*e.g.*, acetone,[3] unsaturated hydrocarbons),[4] 10–15% of the "hot" tritium atoms also react with the substitution of T for CH_3 to give a labeled product of lower molecular weight than the parent[5] molecule. The relative difficulties of analysis for all possible radioactive products have so far limited most recoil tritium studies of non-hydrocarbons to the substitution in the parent molecule alone, or for certain specific "possible" products. The experiments reported here were designed to look for the occurrence of other reactions analogous to T for H and T for CH_3, in which the "hot" T atom might react with the replacement of other functional groups in a molecule. The parent molecules chosen were all substituted benzoic acids, such that the replacement of the substituent group by a recoil tritium would lead to labeled benzoic acid as the product. After isolation and purification, the active benzoic acid from each irradiated sample was degraded in order to determine the intramolecular tritium distribution.

Experimental

Irradiations.—All samples were irradiated as dry powders, thoroughly mixed with 3% by weight of Li_2CO_3 as the tritium source, and irradiated for the times and fluxes shown in the tables of results. The samples which were irradiated for only 12 minutes at 5×10^{12} n./cm.^{2}/sec. showed no visible radiation damage effects. The other samples all turned a light brown color while receiving a substantially larger neutron dose. By visual estimate of the color change, the extent of radiation damage seemed to be in the order *meta* < *para* < *ortho*.

Chemicals.—Technical grade substituted benzoic acids were purified by crystallization for use in these samples. Freedom from benzoic acid impurity was ensured by deliberate contamination of the substituted benzoic acids with 1% labeled benzoic acid (2×10^6 d.p.m./mg.). The purification was continued until the parent molecule had the correct melting point, *and* less than 20 d.p.m./mg. of residual tritium activity. This purificaton process failed to eliminate more than 90% of the labeled benzoic acid from *o*- and *m*-fluorobenzoic acids; for these samples, uncontaminated material, purified by the usual procedures, was used.

Purification after Irradiation.—Separate aliquots of each irradiated sample were taken for the purification of the substituted benzoic acid parent, and for the purification and degradation of the benzoic acid fraction. After adding sufficient inactive parent for convenience in chemical manipulations, (usually 20:1), substituted benzoic acid was freed from many trace impurities by decolorization with charcoal, and passage through a Dowex-1 column as the ammonium salt. The parent compound was then brought to radiochemical purity by recrystallization from several solvents.

After the addition of carrier benzoic acid to the irradiated sample (usually 10 parts carrier to 1 part irradiated material; 2:1 for 12-minute irradiations), the labeled benzoic acid was freed from the substituted benzoic acid parent by displacement chromatography on a Dowex-1 column. With the exception of *m*-hydroxybenzoic acid, all of the parent molecules are stronger acids than benzoic acid and are selectively adsorbed. The eluent was further purified by recrystallization from alcohol–water solutions. Frequently, the original benzoic acid eluent from the column was essentially radiochemically pure.

Carrier aniline hydrochloride (10:1 part irradiated material) was added to three of the aminobenzoic acid irradiations, hydrolyzed to aniline with NaOH and steam distilled three times from basic solution. The acetanilide and *p*-bromoacetanilide derivatives were formed from this purified sample.

Degradation.—The successive steps in the benzoic acid degradation are shown in Fig. 1.

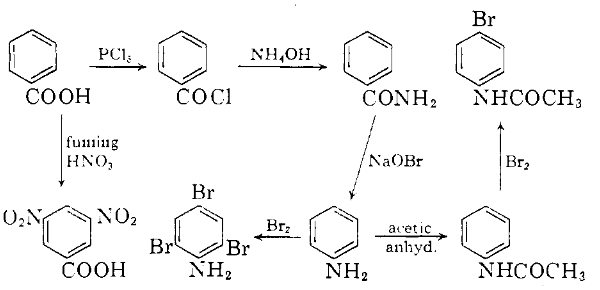

FIG. 1.

This degradation scheme, with the exception of the preparation of 3,5 dinitrobenzoic acid, was used earlier by Bonner in determining the distribution of deuterium in benzoic acid.[6]

All of these chemical steps must be free from tritium isotope effects and from hydrogen exchange in order for the ob-

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[1] The results presented in this paper are taken from a thesis presented by R. Milford White to the University of Kansas in partial fulfillment of the requirements for the Ph.D. degree. This work was presented in part at the 135th Meeting of the A. C. S., Boston, Mass., April, 1959, and was supported by Contract No. AT-(11-1)-407 with the United States Atomic Energy Commission.

[2] F. S. Rowland and R. Wolfgang, *Nucleonics*, **14**, No. 8, 58 (1956).

[3] W. J. Hoff, Jr., and F. S. Rowland, THIS JOURNAL, **79**, 4867 (1957).

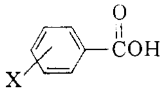
[4] D. Urch and R. Wolfgang, *ibid.*, **81**, 2025 (1959); J. K. Lee, B. Musgrave and F. S. Rowland, 134th Meeting of the A. C. S., Chicago, Ill., Sept., 1958.

[5] The term "parent" molecule has often been used in hot atom chemistry to describe the molecule in which an atom undergoes a nuclear reaction. This "parent" molecule, Li_2CO_3, is not involved here. We use the term for the molecule present in macroscopic quantities with which the recoil tritium atom reacts chemically.

[6] W. A. Bonner, THIS JOURNAL, **79**, 2469 (1957).

TABLE I

SPECIFIC RADIOACTIVITY OF BENZOIC ACIDS ISOLATED FROM IRRADIATED SUBSTITUTED BENZOIC ACIDS



Irradiated compound	Irradiation conditions[a]	Specific activities of benzoic acid and derivatives (d.p.m./μ mole)					
		Benzoic acid	Benzamide	Acetanilide	*p*-Bromoacetanilide	3,5 Dinitrobenzoic acid	Tribromoaniline
o-NH_2	A	24.9	24.1	24.9	24.8	22.8	1.8
o-NH_2	B	259	259	260	253	230	17
o-NO_2	B	350	331	342	313	311	34
o-OH	B	328	312	281	280	252	36
o-COOH	B	704	720	712	663	543	174
o-Br	B	2075	2055	2085	2000	1930	...
o-Br	C	....	....	822	810	745	91
o-I	B	3360	3330	3360	3150	3100	...
m-NH_2	A	9.3	11.0	10.0	9.3	1.5	8.6
m-NH_2	B	107	108	....	....	17	...
m-OH	B	308	318	313	289	54	252
m-Br	B	1060	1020	1040	910	138	...
m-I	B	2640	2530	2590	2310	374	...
p-NH_2	A	17.5	19.0	16.9	2.5	14.8	2.8
p-NH_2	B	214	200	205	25	180	24
p-OH	B	282	280	281	64	241	34
p-Cl	B	892	894	908	216	705	...
p-Br	B	1290	1150	1180	331	925	...

[a] A, Brookhaven reactor, 12 min. at 5×10^{12} n./cm.²/sec.; B, Brookhaven reactor, 2 hr. at 5×10^{12} n./cm.²/sec.; C, Argonne reactor, 11 hr. at $\sim 5 \times 10^{11}$ n./cm.²/sec.

served distribution of radioactivity to be valid. No primary isotope effects are possible in these reactions, for every tritiated position is completely removed if attacked at all. Since secondary isotope effects are quite small, and are further reduced by the high yields obtained in all reactions, no isotopic corrections are necessary.

Control experiments showed that less than 0.5% tritium exchange with the solvent occurred in any of the purification or degradation procedures. The chemical procedures are quite similar to those used by Bonner.[6] The precise procedures and the details of the control experiments for each are given in reference 7.

Preparation of 3,5-Dinitrobenzoic Acid.—Two ml. of fuming nitric acid was slowly added to 1 g. of benzoic acid in 7 ml. of concentrated sulfuric acid. This solution was heated for 6 hours on the steam-bath and then 15 minutes at 150°. The 3,5-dinitrobenzoic acid was precipitated from the solution with ice-water and was purified by recrystallization from alcohol (yield 80%). Nitration in tritiated sulfuric acid showed <0.1% tritium exchange; active 3,5-dinitrobenzoic acid showed no loss in activity in 24 hours heating in sulfuric acid at 150°.

Tritium Assay.—The tritium content of each compound was assayed by gas counting of the products (HT and CH_3T) from zinc–nickelic oxide combustion in the presence of a large excess of propane. Samples weighing up to 70 mg. were combusted and counted for some degradation products of low specific activity.[8] Difficulties with non-quantitative conversion of tritium in some aromatic compounds into volatile radioactivity have been essentially eliminated by the use of 5 mg. of paraffin (and no water) in each combustion tube.

Results

For each irradiated sample of a substituted benzoic acid, each of the six compounds listed in Table I was prepared according to the chemical procedures given above. Chemical purity was readily obtained by crystallization, and radiochemical purity was determined by assay of several crystallizations of the chemically pure compound. The data of Table I represent agreement within statistical error of counting (±1%) for two or more crystallizations.

The accuracy and dependability of the purification and degradation procedures can be readily checked by the agreement of benzoic acid–benzamide–acetanilide measurements with each other and with the sum of the tribromoaniline and 3,5-dinitrobenzoic acid activities.

The intramolecular tritium distributions were obtained from the specific radioactivity of the degradation products and are shown in Table II, together with the specific activity ratios of benzoic acid to parent molecule for each irradiation. The distribution of radioactivity among the *o*-, *m*- and *p*-positions of each molecule is estimated to be accurate to about ±3% of the total ring activity.

We have also included in Table II some approximate data from samples which were not satisfactorily radiochemically pure by the criteria above. Some of these (several from series C, which were chronologically first) were purified without the Dowex adsorption step; others were purified prior to discovery of the assay difficulty and were found not quite pure upon recounting. In each case, the parent compound was readily purified and the acetanilide assay gives a good upper limit on the benzoic acid activity. The general behavior of the specific activity during purification leads us to conclude that most of these samples were essentially radiochemically pure, although not demonstrably so, and that the upper limits are also good estimates of the actual values for the ratio of replacement of the substituent group to the replacement of hydrogen on the ring. The halogen-substituted benzoic acids (especially fluorobenzoic acids) follow through some of the purification steps rather readily, but are removed very well in the formation of acetanilide from benzamide, and in the nitration of benzoic acid.

Table II also lists the percentage of the calculated total tritium which was found as labeled par-

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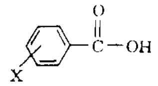
(7) R. Milford White, Ph.D. Thesis, University of Kansas, 1960.

(8) F. S. Rowland, J. K. Lee and R. Milford White, T.I.D.-7578, U.S.A.E.C., 1959, p. 39.

TABLE II

SPECIFIC ACTIVITY OF PARENT AND BENZOIC ACID AND INTRAMOLECULAR DISTRIBUTION OF TRITIUM IN BENZOIC ACID FOR $Li^6(n,\alpha)T$ REACTIONS WITH SUBSTITUTED BENZOIC ACIDS

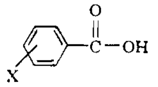


Irradiated compound	Irradiation conditions[b]	Total tritium found as parent, %	Specific activity of original sample (d.p.m./μg.) Parent	Benzoic acid[a]	Ratio of activity, benzoic acid to parent	Intramolecular distribution of tritium in benzoic acid *o*-	*m*-	*p*-
o-NH$_2$	A	32	4.60	0.20	0.044	92	7	1
o-NH$_2$	B	32	46.5	2.13	.046	91	6	3
o-NH$_2$	C	~26	23.0	<1.23	< .054	~88		
o-NO$_2$	B	28	39.0	2.80	.072	82	10	8
o-NO$_2$	C	~28	24.5	<1.72	.070	~73		
o-OH	B	41	59.7	2.30	.039	87	13	0
o-COOH	B	32	46.2	5.84	.126	69	24	7
o-Br	B	37	53.3	17.1	.32	89	7	4
o-Br	C	~35	31.0	<6.74	< .22	~89		
o-I	B	33	48.0	27.6	.58	84	9	7
o-F	B	57	83.0	<4.29	< .05	~64		
o-Cl	B	49	71.6	<10.7	< .15	~86		
m-NH$_2$	A	33	4.87	0.08	.017	7	86	7
m-NH$_2$	B	35	50.9	0.88	.017	[c]	84	←
m-NH$_2$	C	~26	22.6	<0.39	< .017			
m-NO$_2$	B	29	42.9	<2.38	< .056	13	80	7
m-NO$_2$	C	~29	25.4	<1.40	< .055			
m-OH	B	43	61.6	2.56	.042	10	82	8
m-Br	B	36	52.3	8.53	.163	1	87	12
m-Br	C	~32	28.1	4.06	.145	9	84	7
m-I	B	36	52.9	21.2	.40	2	86	12
m-F	B	44	64.4	<3.13	< .049		~82	
p-NH$_2$	A	39	5.59	0.14	0.025	2	12	86
p-NH$_2$	B	35	51.2	1.68	.033	0	12	88
p-NH$_2$	C	~35	31.4	<1.06	< .034			~81
p-NO$_2$	B	27	39.8	1.87	.047	3	19	78
p-NO$_2$	C	~26	22.9	~0.82	.036			
p-OH	B	31	45.6	2.30	.050	11	12	77
p-Cl	B	42	60.4	7.45	.123	2	22	76
p-Br	B	42	61.3	9.68	.158	6	22	72
p-Br	C	~34	29.8	<4.94	< .166			~72

[a] As measured by the acetanilide derivative. [b] A = 12 min. at 5×10^{12}, Brookhaven; B = 2 hr. at 5×10^{12}, Brookhaven; C = 11 hr. at $\sim 5 \times 10^{11}$, Argonne. [c] *o*- + *p*- = 16.

TABLE III

SPECIFIC ACTIVITIES OF PARENT AND ANILINE DERIVATIVES AND THE INTRAMOLECULAR DISTRIBUTION OF TRITIUM IN ANILINE FOR RECOIL TRITIUM REACTIONS WITH AMINOBENZOIC ACIDS



Irradiated compound	Irradiation conditions[a]	Calcd. total as parent, %	Specific radioactivity d.p.m./μg. of original sample Parent	Aniline	Ratio of activities aniline: parent	Intramolecular distribution of tritium in aniline *o*- and *m*-	*p*-
o-NH$_2$	B	32	46.5	2.23	0.048	96 ± 4	4 ± 4
m-NH$_2$	A	35	5.05	0.37	.072	88 ± 1	12 ± 1
p-NH$_2$	A	30	4.29	0.31	.073	25 ± 1	75 ± 1

[a] A, Brookhaven reactor, 12 min. at 5×10^{12} n./cm.^{2}/sec.; *different* samples from irradiation A of Tables I and II. B, Brookhaven reactor, 2 hr. at 5×10^{12} n./cm.^{2}/sec.; *same* sample as irradiation B of Table I and II.

ent molecule. The accuracy of these numbers is limited by uncertainty in the neutron flux—in the absence of individual monitoring of each sample, the error for a particular irradiation could easily be 10% or greater. Table III reports the purification and partial degradation of aniline from aminobenzoic acids. The distributions in Table III were obtained from the specific radioactivity of acetanilide and *p*-bromoacetanilide.

Discussion

Radiation Damage.—Most hot atom experiments of this type are confronted with the problem of macroscopic radiation damage during neutron irradiation. Much more of the damage in these systems is done by the recoiling tritons and alphas than by the background pile radiation, and the color change in longer irradiations indicates that such damage is not negligible. A 2-hour and a 12-minute irradiation at 5×10^{12} n./cm.^{2}/sec. correspond to 10 and 1% destruction, respectively, for a molecule with a *G*-value of 10 for decomposition. This value is probably too high for all of the molecules concerned, but provides a crude estimate of destruction in the absence of measured *G*-values

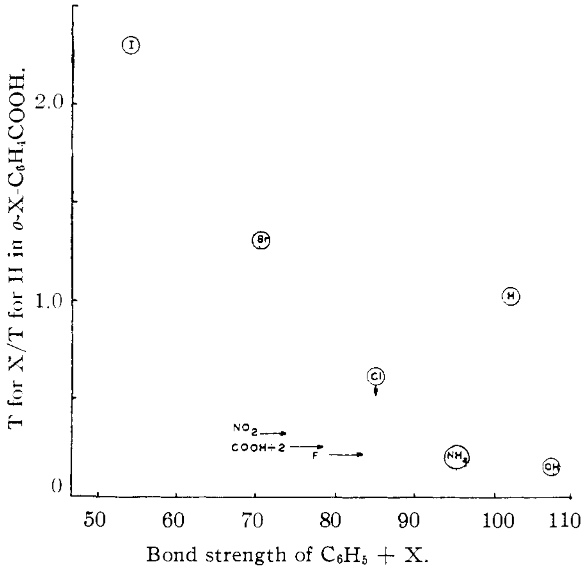
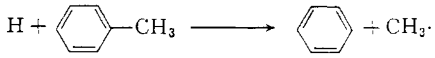


Fig. 2.—Relative ease of replacement of different *o*-substituted groups on benzoic acid.

under heavy ion bombardment. The shorter irradiations, however, give low specific activities, especially in the degradation products, (20 c.p.m./mg. for the benzoic acid from *m*-aminobenzoic acid irradiated for 12 minutes, and 2 c.p.m./mg. in the 3,5-dinitrobenzoic acid from it), and introduce statistical uncertainty in the counting procedures.

Since radiation damage effects can occur both by degradation of already-labeled molecules, and by recoil labeling of already-degraded molecules, calculation of expected levels of labeled impurities is not feasible. The best evidence concerning radiation damage effects in these experiments was obtained by varying the neutron dose, as in Table I and II. The *o*-aminobenzoic acids give the same distribution of tritium within the benzoic acid product, and the same ratio of total activity in benzoic acid to total activity in the parent molecule for 12-minute and 2-hour irradiations. The *m*-aminobenzoic acids also give consistent results. A discrepancy in the activity ratio was observed for *p*-aminobenzoic acid, but the difference is quite small compared to the change in radiation dose. This observed independence of dose rate indicates that the tritiated benzoic acid arises from tritium reactions with the parent molecule and not from reactions involving degradation of the parent molecule by the heavy particle irradiation.

Replacement of Substituent Groups by Tritium.—These experiments show clearly that a recoiling tritium atom is readily able to replace a wide variety of substituent groups, with no observed exceptions, on an aromatic ring. Similar substitution reactions have been suggested in gas phase reactions at elevated temperatures, as in (1) and (2)



(1)

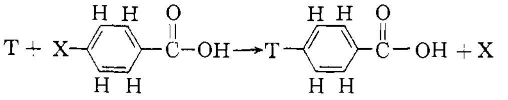
and

(2)

usually with the assumption that the reaction has a high activation energy.[9] Such a reaction can proceed with a recoil atom, for the required energy can readily be furnished from its own high kinetic energy. The substitutions of T for H in methane[10] and in cyclopropane[11] are examples of high activation energy processes proceeding in good yield, while the T for CH_3 substitutions in unsaturated hydrocarbons and acetone are also reactions of energetic atoms.[3,4]

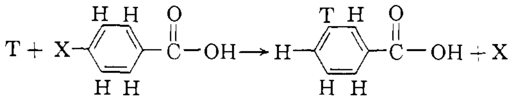
Although there is no direct evidence that these and other recoil tritium reactions in the solid state are actually occurring above thermal energies, there is ample indirect evidence. Experiments with other molecules have uniformly shown that a substantial percentage of recoil tritium atoms react above thermal energies,[2-4,10,11] while the experiments with acetone have shown very similar radioactivity distributions in gas, liquid and solid phase irradiations.[3,12] The implication is strong that the reaction mechanisms are the same or very similar in all phases for the "hot" reactions, and the high specific activity of the ring positions in mixed aliphatic-aromatic compounds (*e.g.*, isopropyl benzoate,[13] toluene[14] and cinnamic acids[15]) indicates that substitution at aromatic positions competes very well with the high energy aliphatic substitutions.

Intramolecular Tritium Distribution.—The intramolecular degradation of the isolated benzoic acids shows that the tritium atom is predominantly found in the position formerly occupied by the missing substituent group, as in reaction 3



(3)

However, the degradations also consistently show a significant amount of radioactivity in other positions of the molecule, as in (4)



(4)

This reaction is especially noticeable with *o*-phthalic acid, from which 24% of the benzoic acid activity is *meta* to the remaining –COOH group. The mechanism of such a reaction is not known, but could arise from substitution of T for H at an adjacent position, followed by an intramolecular hydrogen shift with displacement of the substituent group.

The yield of *o*-T from *p*-substituted molecules and *vice versa* is usually small, and less accurately known since it involves the small difference between

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(9) See E. W. R. Steacie, "Atomic and Free Radical Reactions," second edition, Reinhold Publishing Corp., New York, N. Y., 1954.

(10) M. El-Sayed and R. Wolfgang, THIS JOURNAL, **79**, 3286 (1957); M. El-Sayed, P. Estrup and R. Wolfgang, *J. Phys. Chem.*, **62**, 1356 (1958); P. Estrup and R. Wolfgang, THIS JOURNAL, **82**, 2661 (1960).

(11) J. K. Lee, B. Musgrave and F. S. Rowland, *ibid.*, **81**, 3803 (1959).

(12) J. K. Lee, Burdon Musgrave and F. S. Rowland, unpublished results.

(13) W. G. Brown and J. L. Garnett, *Intl. J. Appl. Rad. and Isotopes*, **5**, 114 (1959).

(14) M. Zifferero, *Energia Nucleare*, **4**, 479 (1957).

(15) R. M. White and F. S. Rowland, unpublished results.

two large numbers. This yield is a very minor percentage of the total tritium production and may well include radiation damage effects.

Variations in Ease of Substituent Replacement.—The fraction of the total radioactivity found as benzoic acid is strongly dependent on the identity of the substituent on the parent molecule. A useful basis for comparison of reactivity is the ratio of radioactivity as benzoic acid to that as parent molecule, as given in Table II. Such a ratio ignores intermolecular variations in hydrogen reactivity, and variations in relative reactivity of *o*-, *m*-, and *p*-positions within the molecule, but has the virtue of depending upon direct competition among positions in the same molecule. The variations in hydrogen reactivity among positions is much less than the variation in ratio for different substituents.[14,15]

The relative ease of replacement of substituents and hydrogen atoms in *o*-substituted benzoic acids is plotted against bond strength in Fig. 2. The bond strengths actually used are for the bond between the substituent and the aromatic ring in substituted benzenes, in the absence of data for substituted benzoic acids.[9,16] Data were not available for $-NO_2$, $-COOH$ and $-F$ bond strengths. With the exception of hydrogen, the available data fall on a smooth curve, corresponding to higher yields of labeled benzoic acid for weaker bonds between the substituent and the aromatic ring.

A reasonably smooth curve can also be obtained by plotting yield ratios *versus* the mass of the substituent group, or *versus* the mass of the atom bonded to the aromatic ring. In terms of "billiard-ball" theory, the maximum fraction of an energetic tritium atom's kinetic energy that can be lost in a single elastic collision is 1 for exactly equal mass and decreases rapidly as the inequality in mass increases (max. energy loss = $4mM/(m+M)^2$). The relative yields of labeled benzoic acid increase as the mass inequality increases.

The conclusion readily follows that the actual chemical bonding to the aromatic ring is much more important than the physical mass of the bonded atoms or groups in determining the course of recoil tritium reactions with substituents on an aromatic ring. The importance of bond strength in turn implies that the reacting recoil tritium does not have extremely high energies at the time of reaction—an energy range of at most a few electron volts at reaction seems indicated.

The relative ease of replacement of a particular substituent also depends on the location of the substituent on the ring, as can be seen by comparing isomers in Table II. The yields of labeled benzoic acid from *m*-aminobenzoic acid are much less than from either *o*- or *p*-aminobenzoic acid; isomeric differences are also noticeable for other substituents. While electron-donating or withdrawing power does not seem to be important in determining yields relative to the parent molecule, electronic distributions may have an effect on the decomposition of the tritium-plus-aromatic intermediate complex. Crystal structure, steric hindrance, etc., may also cause differences in particular cases. The present data do not seem adequate for isolation of the cause or causes of this isomeric variation.

Acknowledgments.—The coöperation of the service irradiation groups at the Argonne and Brookhaven National Laboratories is gratefully acknowledged.

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[16] A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths Publications, London, 1955.

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC., MURRAY HILL, N. J.]

Electrophilic Substitution at a Saturated Carbon by Electron Deficient Nitrogen

BY GERALD SMOLINSKY

RECEIVED FEBRUARY 29, 1960

Pyrolysis of 2,4,6-trimethyl-2′-azidobiphenyl (I) at 230° resulted in the formation of 2,4,9-trimethylcarbazole (IV) and 8,10-dimethylphenanthridine (V). Formation of V results from insertion of the aryl nitrogen into the C–H bond of the *o*-methyl group of I.

Loss of nitrogen from an organic azide would lead to an electron deficient species, $-\dot{\text{N}}:$, which would be expected to resemble a carbonium ion or a carbene in its reactions. The Curtius rearrangement,[1] the 1,2-shift of alkyl groups from carbon to nitrogen observed in the decomposition of cycloalkylazides,[2] and the formation of carbazoles from 2-azidobiphenyls[3] are reactions which in a loose sense illustrate the carbonium ion-like nature of this group. Again in a loose sense, the carbene-like character is illustrated by the formation of benzfuroxans from the decomposition of *o*-nitrophenyl azides,[4] and of arylazo compounds by photolysis of aryl azides.[5]

In view of the reactions discussed it appeared likely that in a suitably constituted molecule such as 2,4,6-trimethyl-2′-azidobiphenyl (I), it might prove possible to observe an insertion of the "nitrene," $-\dot{\text{N}}:$, into a C–H bond. This type of reaction is common in carbene chemistry[6] and has been observed recently with oxygen by Corey and White[7] who invoked a species equivalent to the isoelectronic cation, $-\ddot{\text{O}}:^{+}$, in the formation of 1,5-

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[1] See for example, J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Chap. 15.

[2] J. H. Boyer, F. C. Canter, J. Hamer and R. K. Putney, THIS JOURNAL, **78**, 325 (1956).

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