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, $-\dot{\mathrm{N}}:$, 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," $-\dot{\mathrm{N}}:$, 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, $-\ddot{\mathrm{O}}:^+$, 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).

(3) P. A. S. Smith, J. M. Clegg and J. H. Hall, *J. Org. Chem.*, **23**, 524 (1958).

(4) P. A. S. Smith and B. B. Brown, THIS JOURNAL, **73**, 2435 (1951).

(5) L. Horner and A. Goss in A. Schoenberg, "Präparative Organische Photochemie," Springer-Verlag, Berlin, 1958, p. 192.

(6) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhri, THIS JOURNAL, **78**, 3224 (1956).

(7) E. J. Corey and R. W. White, *ibid.*, **80**, 6686 (1958).

dimethyl-6-oxabicyclo(3.2.1)octane from 1,3,3-trimethylcyclohexyl hydroperoxide. Coupling *o*-nitrobenzenediazonium chloride with mesitylene gave 2,4,6-trimethyl-2′-nitrobiphenyl (II); reduction of II to the corresponding amine III, followed by diazotization and treatment with sodium azide gave I.

Thermal decomposition at 230° of a hexadecane solution of I afforded three crystalline compounds.[8] One of them was identical to amine III, the other two, IV and V, had compositions $C_{15}H_{15}N$ and $C_{15}H_{13}N$, respectively. Their ultraviolet spectra bore a striking similarity to those of N-ethyl carbazole and phenanthridine, respectively (see Table I).

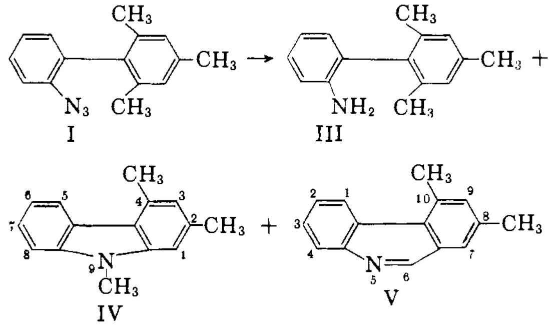
TABLE I

ULTRAVIOLET SPECTRA IN CYCLOHEXANE SOLUTION

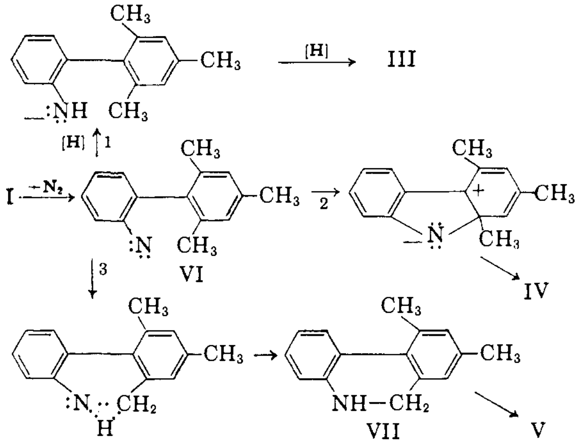
IV		N-Et carbazole		V		Phenanthridine	
λ_{max}, mμ	ε	λ_{max}, mμ	ε	λ_{max}, mμ	ε	λ_{max}, mμ	ε
		229	40,600	{247	58,300[b]	248	48,400
239	57,200	236	48,300	{251	57,800		
265	23,900	{259	21,200[b]	270	12,300	269	12,000
		{262		289	6,500	284	5,850
283	11,000	283	9,940	301	5,550	295	4,790
289	13,000	288	12,800	318	1,320	313	1,440
293	23,800	294	22,900	328[a]	1,040	321	829
313	2,130[a]	319	2,410[a]	333	2,180	327	2,080
325	4,270	328	3,940	342	1,020	335	625
340	5,150	344	5,520	349	2,580	343	2,170

[a] Shoulder. [b] Doublet.

Furthermore, the n.m.r. spectrum of IV showed three peaks (6.35, 7.21 and 7.54 τ[9]) of about equal intensity in the region characteristic of methyl absorption while the spectrum of V had only two peaks in this region (7.19 and 7.66 τ) as well as absorption at 1.1 τ which compares quite well with the value of 0.87 τ found for the C_6-hydrogen absorption of phenanthridine. The above evidence allows the assignment of structure 2,4,9-trimethylcarbazole to IV and 8,10-dimethylphenanthridine to V.



The results of this reaction can be rationalized by a mechanism involving the loss of N_2 to give a nitrene, VI, which can react to give the observed products *via* three paths. It can abstract a hydride ion from its surroundings, attack the adjacent aromatic ring, or form a bond with the carbon atom of the methyl group of the neighboring ring.



The insertion (path 3) appears to be the most favored reaction since V is obtained as the major product (50%); hydride ion abstraction (path 1) is second most favored (30%) while attack of the adjacent ring (path 2) is least favored (5%). Most likely V results from a concerted reaction in which hydrogen transfer and carbon–nitrogen bond formation occur simultaneously. The facile dehydrogenation of 5,6-dihydrophenanthridines[10] may explain why no 5,6-dihydro-8,10-dimethylphenanthridine (VII) is isolated from this reaction. Moreover, it is quite possible that VII could be the actual reducing agent in reaction path 1.[11]

In summary, the results reported in this paper emphasize the similar behavior of the isoelectronic species >C:,[6] -Ö:+,[7] and -N̈: as shown by their ability to insert into the C–H bond of a saturated carbon.

Experimental[14]

2,4,6-Trimethyl-2′-nitrobiphenyl (II) was prepared from diazotized *o*-nitroaniline (83 g., 0.6 mole) and mesitylene (150 g.) according to the procedure of Elks, Hawarth and Hey.[15] The fractionated product (29 g., 20%) had b.p. of 147–150° (2 mm.). The ultraviolet spectrum exhibited a shoulder at 240 mμ (ε 5300).

Anal. Calcd. for $C_{15}H_{15}NO_2$: C, 74.66; H, 6.27; N, 5.81. Found: C, 74.59; H, 6.05; N, 5.79.

2,4,6-Trimethyl-2′-aminobiphenyl (III).—A solution of II (15.5 g., 0.064 mole) in benzene (150 ml.) was hydrogenated at 50 p.s.i. using 5% palladized carbon (1.5 g.) as catalyst. After 24 hours, the mixture was filtered, the filtrate dried and evaporated to give an essentially quantitative yield of crystalline amine which could be recrystallized from hot hexane or 95% ethanol. An analytical sample was sublimed (75° (0.1 mm.)) to give material of m.p. 98–99° having a

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[8] Attempts at photodecomposition of hexane solutions of I in quartz vessels were unsuccessful. In no case was N_2 evolution observed and, after several hours, the solutions became dark and syrupy but still contained unchanged azide as evidenced by their I. R. spectra.

[9] The n.m.r. spectra were taken at 60 m.c. in carbon tetrachloride solution; τ-values are chemical shift values in p.p.m. relative to tetramethylsilane standard (τ = 10.0). Dr. Martin Saunders of Yale University took the spectra.

[10] A. Pictet and H. J. Ackersmit, *Ann.*, **266**, 151 (1891).

[11] One of the referees has noted that VI may not be a discrete intermediate and that the loss of N_2 may be concerted with the reactions postulated for the nitrene. Although one cannot rule out this possibility, invoking a nitrene intermediate allows for a more reasonable explanation of the products. Indeed, Bamberger[12] reported that the decomposition of aryl azides in aqueous media lead to the formation of hydroxylamines, and it has been found that the pyrolysis of phenyl azide produces some aniline as well as azobenzene.[13] Again, these results are best explained by the assumption of a nitrene intermediate.

[12] E. Bamberger, *Ann.*, **443**, 192 (1925); **424**, 233 (1921).

[13] A. Bertho, *Ber.*, **57**, 1138 (1924).

[14] All melting points are corrected. Ultraviolet spectra were determined in cyclohexane solution on a model 14 Cary recording spectrophotometer.

[15] J. Elks, J. W. Hawarth and D. H. Hey, *J. Chem. Soc.*, 1284 (1940).

maximum ($\epsilon_{291 \text{ m}\mu}$ 3,340) and a minimum ($\epsilon_{264 \text{ m}\mu}$ 985) in the ultraviolet spectrum.

Anal. Calcd. for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.35; H, 8.03; N, 6.55.

2,4,6-Trimethyl-2'-azidobiphenyl (I).—Amine III (11.07 g., 0.0524 mole) was converted to azide I using procedure B of Smith and Brown[4] with the one modification that 3.72 g. (0.054 mole) of sodium nitrite was used in place of amyl nitrite. The crude azide was extracted from the aqueous reaction mixture with petroleum ether; the extract was concentrated at 40° at reduced pressure and purification of the azide was effected by chromatography on 60 g. of Merck alumina. The yield of pale yellow oil was 11.4 g. (92%) and this material showed strong absorption in the infrared (neat) at 2120 cm.$^{-1}$—the characteristic absorption for the azide group.[16]

Anal. Calcd. for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.80; H, 6.21; N, 81.01.

Pyrolysis of I.—A solution of I (11.4 g., 0.0481 mole) in *n*-hexadecane (10 ml., previously purified by shaking with concentrated sulfuric acid, followed by distillation from sodium) was added dropwise to stirred hexadecane (150 ml.) maintained at 230° in a nitrogen atmosphere. The decomposition was practically instantaneous, and gas evolution ceased shortly after the final addition, but heating was continued 5–10 min. longer. The cooled solution was chromatographed on a column of 300 g. of Merck alumina. The hexadecane was eluted with petroleum ether, 0.91 g. of crude IV was eluted with 1:3 benzene–petroleum ether; 2.95 g. of crude III followed by 5.9 g. of V were obtained with 1:1 benzene–petroleum ether. A red oil (2 g.) was finally obtained with isopropyl alcohol–benzene. A rechromatograph of each fraction gave the following: 0.45 g. (4.5%) of IV, 2.9 g. (29%) of III and 4.8 g. (48%) of V.

The identity of III was established by m.p., mixed m.p., and infrared (CCl_4) spectrum.

Recrystallization of V from carbon tetrachloride followed by sublimation (100° (0.1 mm.)) gave material of m.p. 149–150° (evac. cap.).

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 87.02; H, 6.28; N, 6.84.

The carbazole IV, after recrystallization from 95% ethanol and sublimation (100°(1.5 mm.)) had a m.p. of 134°.

Anal. Calcd. for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.85; H, 6.96; N, 6.51.

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[16] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 230.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

Carbonium Ions. IX. Monoarylalkyl Cations[1,2]

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RECEIVED NOVEMBER 25, 1959

The electronic absorption spectra and the chemical and thermodynamic stabilities of monoarylalkyl cations have been examined as a function of cation structure.

A series of studies on triarylmethyl cations and diarylalkyl cations[2] led to the development of eq. 1, which relates the position of alcohol–cation (ROH—R^+) equilibria to the concentration of acid in water-strong acid systems. A similar equation, eq. 2, was developed for diarylolefin–diarylalkyl cation (Ol–R^+) equilibria. It was natural to anticipate that these two equations would be applicable to monoarylalkyl cation equillibria; this expectation was tested. For monoarylolefins, it was also necessary to test eq. 3, which although widely applicable to base-protonated base (B–BH^+) equilibria, was not obeyed in the protonation of diarylolefins,[2] and was thus expected to be inapplicable to monoarylolefins.

$$H_R = pK_{R^+} + \log c_{ROH}/c_{R^+} \qquad (1)$$

$$H_R - \log a_{H_2O} = pK'_{R^+} + \log c_{Ol}/c_{R^+} \qquad (2)$$

$$H_0 = pK_{BH^+} + \log c_B/c_{BH^+} \qquad (3)$$

A variety of compounds were prepared which are capable of forming monoarylalkyl cations in strong acid, but in no case were the equilibria sufficiently permanent to make precise quantitative measurements. The data in Table I summarize the quantitative data obtained and in general it can be said that monoarylalkyl cations obey the same equations as their triarylmethyl and diarylalkyl cation congeners. For alcohols that cannot dehydrate to arylolefins, the equilibria are between R^+ and ROH, and eq. 1 is obeyed. For alcohols that can dehydrate to arylolefins, the equilibria are between R^+ and olefin, and eq. 2 is obeyed.

Three basic ideas were utilized in an effort to inhibit the bimolecular destruction reactions (intermolecular self-alkylation, ether formation and hydride transfer) which are usually responsible for the transient nature of monoarylalkyl cation equilibria. The first was to replace hydrogens by methyl groups to form polymethylbenzyl cations of the types I and II. Second was to conjugate the extraordinary stability of the aliphatic bornyl cation with the monoarylalkyl system to form cations of undetermined structure which are isomeric with the 2-arylbornyl cations. These are designated series III. Third was to use cations of type IV which must rearrange through a bridge-head carbonium ion before several of the destruction routes become available. The results for series I–IV will be discussed separately.

Cations of Type I.—The equilibrium data on cation Ia fit eq. 1 to ±0.1 *pK* unit from 89–96% H_2SO_4. In the same range, *pK* calculated by either eq. 2 or 3 continuously changed by 1.2 *pK* units. A *pK* calculated on the assumption of an equilibrium between ROH_2^+ and R^+ ($pK = \log a_{H_2O} + \log c_{R^+}/c_{ROH_2^+}$) continuously varied by 1.1 *pK* units.

These results confirm the interpretation in terms of an ROH–R^+ equilibrium.[3] Further, any olefin

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[1] This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. This research also was supported in part by a grant from the National Science Foundation. Grateful acknowledgment is hereby made of this support.

[2] Previous paper in this series: THIS JOURNAL, **81**, 5790 (1959).

[3] N. Deno, J. Jaruszelski and A. Schriesheim, *ibid.*, **77**, 3044 (1955).