nine protons. The $AcH_2\cdot$ radicals are not seen because they have only a very low concentration compared to that of the observed radical ($\cdot$Cho$\cdot$). The observed radical reacts either with its cage (to propagate the decomposition reaction) or terminates with another radical that propagates into the vicinity.

The data points in Fig. 4 below 6% and for times less than 100 hr. give a reasonable fit to eq. IV of Fig. 10. The data at higher damage levels fall in the dose saturation region, and thus no kinetic information can be obtained from this region. The data at longer times fall in a separate group. Here, $k_1t/2$ is, presumably, no longer $<< 1$; *i.e.*, the simplifying assumptions for eq. IV are no longer valid. At the present time there are not sufficient data to solve for the rate constants in eq. III.

A steady state approximation gives:

$$AcH_2\cdot = \sqrt{k_1/k_4}\,(\cdot\mathrm{Cho}\cdot)^{1/2} \qquad \mathrm{I}$$

$$d(\cdot\mathrm{Cho}\cdot)/dt = -k_1(\cdot\mathrm{Cho}\cdot) - k_a\cdot\sqrt{k_1/k_4}\,(\cdot\mathrm{Cho}\cdot)^{3/2} \qquad \mathrm{II}$$

Integrating this, substitution in the propagation eq. 2 and integrating again gives

$$\mathrm{Cho} - \mathrm{Cho}_0 = \frac{k_1k_2t}{k_3} - 2\,\frac{k_2}{k_3}\log\left\{\left(\frac{k_3}{\sqrt{k_1k_4}}\right)(\cdot\mathrm{Cho}_0\cdot)^{1/2}\,(e^{k_1t/2} - 1) + e^{k_1t/2}\right\} \qquad \mathrm{III}$$

where Cho_0 = initial concn. of choline

$\mathrm{Cho}_0\cdot$ = initial concn. of $\cdot$Cho$\cdot$

In two limiting cases this simplifies

$$\text{where } \frac{k_1t}{2} \ll 1 \quad \mathrm{Cho} - \mathrm{Cho}_0 \approx -\left(k_2\sqrt{\frac{k_1}{k_4}}\,(\cdot\mathrm{Cho}_0\cdot)^{1/2}t\right) \qquad \mathrm{IV}$$

$$\text{where } \frac{k_1t}{2} \gg 1 \quad \mathrm{Cho} - \mathrm{Cho}_0 \approx \frac{-2k_2}{\sqrt{k_1k_4}}\,(\cdot\mathrm{Cho}\cdot)^{1/2} \qquad \mathrm{V}$$

Fig. 10.—Integration of the kinetic model for choline chloride radiation damage.

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

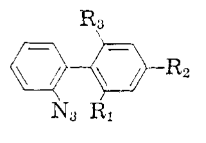
Thermal Reactions of Substituted Aryl Azides: The Nature of the Azene Intermediate

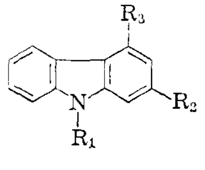
BY GERALD SMOLINSKY

RECEIVED DECEMBER 2, 1960

Six aryl azides were prepared and thermally decomposed. In two cases, *o*-azidocumene (XIX) and *o*-azidophenylcyclohexane (XX), the pyrolysis products were identified as 3-methyl-2,3-dihydroindole (XX) and hexahydrocarbazole, respectively. It is proposed that these products were formed by insertion of an azene group into the C–H bond of a primary and secondary carbon, respectively. The mechanism of these reactions is discussed in terms of a singlet or triplet azene intermediate.

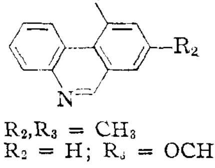
In an earlier paper it was reported that the decomposition of 2-azido-2′,4′,6′-trimethylbiphenyl (I) resulted in the formation of 2,4,9-trimethylcarbazole (II) and 8,10-dimethylphenanthridine (III), presumably *via* the azene intermediate IV.[1] The present work was undertaken with the hope of gaining some insight into the electronic nature of the reacting azene intermediate—specifically as to whether this species behaves as an electrophile having a paired electronic configuration ($-\ddot{N}:$) or as a diradical $-\ddot{N}.)\cdot$





I, $R_1,R_2,R_3 = CH_3$
VIII, $R_1 = OCH_3$; $R_2,R_3 = H$
X, $R_1 = OH$; $R_2,R_3 = H$
XII, $R_1,R_2,R_3 = OCH_3$
XIV, $R_1 = CH_3$; $R_2 = H$; $R_3 = OCH_3$

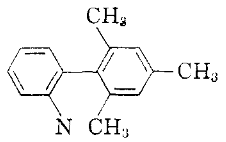
II, $R_1R_2R_3 = CH_3$
IX, $R_1,R_2 = H$; $R_3 = OCH_3$



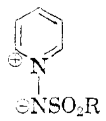
III, $R_2,R_3 = CH_3$
XVI, $R_2 = H$; $R_3 = OCH_3$

It appears that in the substitution reaction of aromatic nuclei by the azene formed from thermal decomposition of benzenesulfonyl azide, the intermediate reacts as an imino diradical.[2] Supporting this conclusion is the observation that methyl acrylate and acrylonitrile polymerized at 110° in the presence of small amounts of decomposing benzenesulfonyl azide; the polymerization of acrylonitrile was inhibited by the presence of traces of hydroquinone or *p*-benzoquinone.[3]

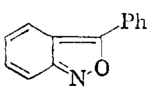
The following reactions can be explained by postulating an electrophilic azene intermediate. Decomposition of arenesulfonyl azides in pyridine



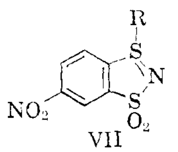
IV



V



VI



VII

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(1) G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 4717 (1960).

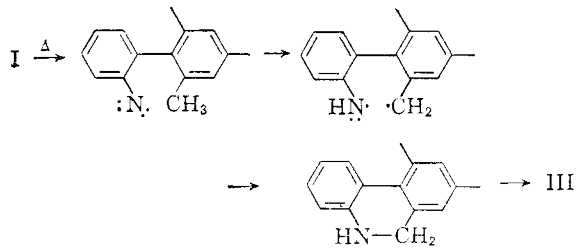
(2) J. F. Heacock and M. T. Edmison, *ibid.*, **82**, 3460 (1960); O. C. Dermer and M. T. Edmison, *ibid.*, **77**, 70 (1955); O. C. Dermer and M. T. Edmison, *Chem. Revs.*, **57**, 77 (1957).

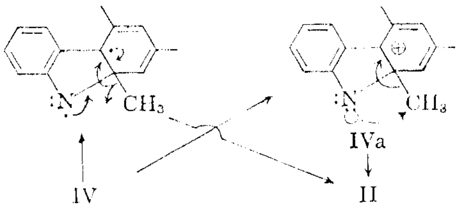
(3) K. Ziegler, W. Deparade and H. Kuhlhorn, *Ann.*, **567**, 151 (1950); K. Ziegler, W. Deparade and W. Meye, *ibid.*, **567**, 141 (1950).

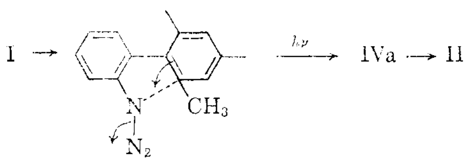
led to products of type V.[4] Smith, *et al.*, found that the decomposition of *o*-azidobenzophenone led to attack of the carbonyl oxygen by the azene to give 3-phenylanthranil (VI)[5a]; similarly, decomposition of *o*-nitro substituted aryl azides led to benzofuroxan derivatives.[5b] A recent paper by Wagner and Banholzer[6] reported that treatment of 3-nitro-6-mercaptobenzenesulfonamides with aqueous hypobromite led to the formation of products of type VII. These results may be rationalized by postulating azene formation followed by electrophilic attack on the adjacent sulfur atom.

One can invoke an electrophilic or biradical azene intermediate to explain the formation of carbazoles,[7] carbolines,[8] thienoindoles[8] and other heterocyclic compounds[5] by the decomposition of the appropriate *o*-substituted phenyl azide. However, it is likely that these reactions do not involve a discrete intermediate, and that loss of N_2 is concerted with ring closure. This may explain the observation that 2-azidobiphenyls having no substituents in the 2′-position will close to carbazoles under the influence of ultraviolet light[7a] while 2-azido-2′,4′,6′-trimethylbiphenyl (I) retains the azide group intact under similar conditions.[1] In the latter case, the *o*-methyl groups presumably interfere with any interaction between the azido group and the *o*-position in the adjacent ring.

In the case of the thermal decomposition of I, phenanthridine (III) formation can be pictured as proceeding by attack of an imino diradical intermediate on the adjacent methyl group giving benzyl and imino radicals which then couple. Carbazole (II) formation can be viewed as either an electrophilic attack of the azene on the adjacent aromatic ring or as a radical reaction. It is felt that a less likely alternative is that this reaction takes place with concerted loss of N_2

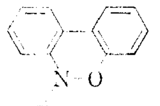






It seemed reasonable that by substitution of potential nucleophiles such as methoxyl and hydroxyl groups in place of the *o*-methyl groups in I, the electrophilic character of the azene would become more apparent. Accordingly, 2-azido-2′-methoxybiphenyl (VIII) was synthesized and then pyrolyzed at 220° in hexadecane. As expected[7b] only 4-methoxycarbazole (IX) was obtained (95%). When 2-azido-2′-hydroxybiphenyl (X) was heated in tetralin at 160°, 2-amino-2′-hydroxybiphenyl (XI) was obtained (30%) along with tars. Pyrolysis of the anion of X in diphenyl ether solution at 130° gave intractable tars from which it was possible to isolate and identify 10% of XI. Similar results were obtained in the case of 2-azido-2′,4′,-6′-trimethoxybiphenyl (XII) which when decomposed at 200° in diphenyl ether formed tars from which 2-amino-2′,4′,6′-trimethoxybiphenyl (XIII) was isolated (3%). On the other hand, when 2-azido-2′-methyl-6′-methoxybiphenyl (XIV) was pyrolyzed at 190° in hexadecane, in addition to 29% 2-amino-2′-methyl-6′-methoxybiphenyl (XV) there was obtained 16% of 10-methoxyphenanthridine (XVI).

The above results are far from being definitive, but some trends are apparent. Carbazole formation, when possible, seems to be the preferred course of the reaction except where a hydroxyl group or its anion is present in one of the 2-positions as in the case of X and its anion. Moreover, phenanthridine formation still occurs even when a methoxyl group is present in the 6′-position as in XIV. Although no identifiable products were obtained from the interaction of the azene with the several oxygen functions present in the 2′-positions of VIII, X, XII and XIV, it is not possible to rule out such a reaction, and it may be that the difficulty arises from the fact that the temperatures necessary for the decompositions were too high for any product such as XVII to survive.



XVII

Significantly, in all the above decompositions, except for that of VIII, reduction of the azide to the corresponding amine occurs; moreover, in those cases where the reaction was run in hexadecane or tetralin solution the amount of amine formed was relatively large (*ca.* 30%). Amine formation can be explained readily by postulating that the azene is a diradical and abstracts hydrogen atoms from its surroundings. In order to test this theory, *o*-azidocumene (XIX) was prepared and pyrolyzed in diphenyl ether.

If the amine were to result from reaction of the azene with the hydrocarbon solvent, then in the

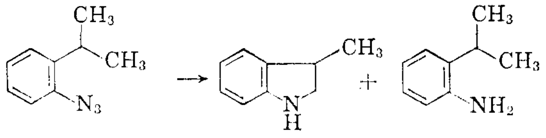
[4] G. L. Buchanan and R. M. Levine, *J. Chem. Soc.*, 2248 (1950); J. N. Ashley, G. L. Buchanan and A. P. T. Eason, *ibid.*, 60 (1957).

[5] (a) P. A. S. Smith, B. B. Brown, R. K. Putney and R. F. Reinisch, *J. Am. Chem. Soc.*, **75**, 6335 (1953); (b) J. H. Boyer and F. C. Canter, *Chem. Revs.*, **54**, 35 (1954).

[6] A. Wagner and R. Banholzer, *Angew. Chem.*, **71**, 311 (1959).

[7] (a) P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, **73**, 2435, 2438 (1951); (b) P. A. S. Smith, J. M. Clegg and J. N. Hall, *J. Org. Chem.*, **23**, 524 (1958).

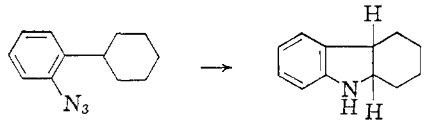
[8] P. A. S. Smith and J. H. Boyer, *J. Am. Chem. Soc.*, **73**, 2626 (1951)



XIX XX XXI

decomposition of XIX a significant yield of 3-methyl-2,3-dihydroindole (XX) should be obtained *via* intramolecular reaction. Although XX was formed (15%), it was accompanied by *o*-aminocumene (XXI, 37%) as well as considerable tarry material. The formation of XX establishes the fact that azenes can attack primary aliphatic hydrogens and is another example of an insertion reaction at a saturated carbon.[1]

When *o*-azidophenylcyclohexane (XXII) was pyrolyzed in diphenyl ether at 200° it smoothly lost nitrogen; hexahydrocarbazole was formed in



XXII XXIII, *cis* XXIV, *trans*

very high yield (86%) and was the only isolable product. The hexahydrocarbazole was separated into essentially equal amounts of the *cis* (XXIII) and *trans* (XXIV) forms.

A comparison of the yields and nature of the products obtained from the decomposition of XIX and XXII seems to support the view that the azenes behaved as diradicals. Compound XXII, in which the azene can abstract secondary hydrogens, gave a clean reaction with products arising mainly from this abstraction process. On the other hand, XIX in which the azene has only primary hydrogens readily available for reaction gave only a small yield of product arising from intramolecular reaction and much more material arising in other ways. Indeed, all the reactions presented in this paper make a stronger case for the azene reacting in the triplet state than in the singlet state; moreover, the postulation of the imino diradical intermediate readily explains the products formed in most azide decompositions.[1-3,5,7,8]

The azides employed in this work were all synthesized in a straightforward manner. *o*-Azidocumene (XIX) and *o*-azidophenylcyclohexane (XXII) were obtained *via* nitration of the appropriate alkylbenzene, catalytic reduction of the nitro group to the amine, diazotization and finally treatment with sodium azide. The biphenyl azides were prepared by condensing the appropriate methoxyiodobenzene derivative and *o*-bromonitrobenzene with copper powder and then catalytic hydrogenation of the nitro group and diazotization of the amine, etc. The condensation reactions proceeded quite satisfactorily except in the case of 2-nitro-2′,4′,6′-trimethoxybiphenyl (XXV) which proved difficult to separate from the by-products formed in the condensation reaction.

Experimental[9]

2-Iodo-3-methylanisole.—2-Nitro-3-methylanisole was prepared from 2-nitro-3-methylphenol according to the procedure of Haworth and Lapworth[10] and catalytically hydrogenated to the corresponding amine in ethanol with 5% palladized carbon. This amine (62.3 g., 0.455 mole) was dissolved in 75 ml. of sulfuric acid–400 ml. of water and diazotized at 5–6° with sodium nitrite (34.2 g., 0.497 mole) dissolved in 100 ml. of water. After the excess nitrous acid was destroyed with an aqueous sulfamic acid solution, an ice-cold solution of potassium iodide (225 g.) in 250 ml. of water was added rapidly to the well-stirred diazonium salt solution. A precipitate formed immediately and the reaction slowly warmed to about 35°. The next day, the dark oil which had formed was extracted with ether, the ether extracts washed with sodium sulfite, saturated sodium chloride, dried and evaporated. The residue was distilled at reduced pressure. The fraction boiling at 93–98° (1.5 mm.) weighed 91 g. (82%) and had a m.p. of 45° (lit.[11] m.p. 49°).

Iodo-2,4,6-trimethoxybenzene.—Phloroglucinol trimethyl ether was prepared from phloroglucinol using the procedure of Bennington, Morin and Cook.[12] The ether was then converted to the iodo compound by the method of Riedl.[13]

***o*-Aminophenylcyclohexane.**—Phenylcyclohexane was nitrated using the method of Mayes and Turner[14] and the resulting product twice fractionated through a 2-foot spinning band column. The fraction boiling 173.8–175° (17 mm). was hydrogenated in ethanol with a 5% palladized carbon catalyst.

***o*-Aminocumene (XXI).**—Cumene was nitrated according to the procedure of Brown and Bonner[15] and the product twice fractionated through a 2-foot spinning band column. The fraction boiling 135.9–137° (37 mm.), n^{21}_{D} 1.5242 (lit.[15] value n^{20}_{D} 1.5248) was hydrogenated in ethanol with a 5% palladized carbon catalyst.

2-Nitrobiphenyls (Table I).—The following is typical of the procedure used to prepare the nitrobiphenyls: Copper powder[16] (85 g.) was added in portions over a period of about an hour to a well-stirred solution of 2-iodo-3-methylanisole (85.5 g., 0.354 mole) and *o*-bromonitrobenzene (85 g., 0.413 mole) maintained at 180–185° in a nitrogen atmosphere. After all the copper had been added, stirring and heating were continued for an additional 2.5 hours. As the reaction proceeds, the copper loses its shiny appearance and the mixture becomes quite viscous. The cooled reaction mixture was thoroughly extracted with hot benzene, the benzene evaporated, and the residue distilled at reduced pressure.

In the above case, the product (XXVIII) boiled at 140–155° (0.3 mm.) and recrystallized from ethanol. In the case of 2-nitro-2′-methoxybiphenyl (XXVI) the product was collected at 150–170° (1.5 mm.) and recrystallized from ethanol. Trimethoxybiphenyl (XXV) was collected at 160–185° (0.5 mm.) and then fractionated through a 2-foot spinning band column (b.p. 156–159° (0.1 mm.)) and recrystallized from benzene–hexane. It was found that XXV was difficult to purify due to the presence of 2,4,6,2′,4′,6′-hexamethoxybiphenyl formed as a by-product in the reaction.

2-Nitro-2′-hydroxybiphenyl (XXVII) was prepared from the corresponding methoxy compound XXVI by hydrolysis in acetic acid with concentrated hydrobromic acid using the procedure of Colbert, Fox and Skinner.[17] The product was recrystallized from benzene.

2-Aminobiphenyls (Table I).—The aminobiphenyls were prepared from the corresponding nitro compounds by hydrogenation in a suitable solvent with 5% palladized carbon as catalyst. The 2′-methoxy-(XXVI), 2′-hydroxy-(XXVII) and the 2′-methyl-6′-methoxy-(XXVIII) nitrobi-

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[9] All melting points are corrected. Boiling points are uncorrected. Ultraviolet spectra were taken with a Beckman DK-2 recording spectrophotometer.

[10] R. P. Haworth and A. Lapworth, *J. Chem. Soc.*, 2993 (1923).

[11] Y. Sugii and H. Shindo, *J. Pharm. Soc. Japan*, **54**, 829 (1934).

[12] F. Bennington, R. D. Morin and L. C. Cook, *J. Org. Chem.*, **19**, 11 (1954).

[13] W. Riedl, *Ann.*, **597**, 148 (1955).

[14] H. A. Mayes and E. E. Turner, *J. Chem. Soc.*, 503 (1929).

[15] H. C. Brown and W. H. Bonner, *J. Am. Chem. Soc.*, **76**, 605 (1957).

[16] #450A available from Metal Disintegrating Co., Inc., Elizabeth 8, N. J.

[17] J. C. Colbert, O. Fox and W. A. Skinner, *J. Am. Chem. Soc.*, **75**, 2249 (1953).

TABLE I

SUBSTITUTED BIPHENYLS

2-Substituted biphenyl	2-Nitro-			2-Amino-			2-Azido-			
	Cpd.	Yield, %	M.p., °C.	Cpd.	Yield, %	M.p., °C.	Cpd.	Method	Yield, %	M.p., °C.
2′-Methoxy	XXVI^a	58	83	XXIX^f	70	80	VIII^j	A	87	48
2′-Hydroxy	XXVII^b	100	139	XI^g	73	94	X^k	A	89	Oil
2′-Methoxy-6′-methoxy	XXVIII^c	81	94	XV^h	72	88	XIV^l	A	82	43
2′,4′,6′-Trimethoxy	XXV^d	(30)^e	147	XIII^i	72	160	XII^m	B	84	117

[a] J. C. Colbert, O. Fox and W. A. Skinner, *J. Am. Chem. Soc.*, **75**, 2249 (1953); m.p. 82°. [b] *Ibid.;* m.p. 140°. [c] Calcd. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.31; H, 5.49; N, 5.86. [d] Calcd.for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.20; H, 5.05; N, 4.78. [e] Very difficult to purify. [f] L. Mascarelli and D. Gatti, *Atti Congr. Noz. Chim. Pure Appl.*, **4,** 503 (1932); m.p. 81°. [g] Calcd. for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.50. Found: C, 77.86; H, 6.11; N, 7.70. [h] Calcd. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 79.01; H, 7.19; N, 6.76. [i] Calcd. for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.52; H, 6.49; N, 5.51. [j] Calcd. for $C_{13}H_{11}N_3O$: C, 69.32; H, 4.92; N, 18.66. Found: C, 69.98; H, 4.72; N, 18.90. [k] Calcd. for $C_{12}N_9N_3O$: C, 68.23; H, 4.30; N, 19.90. Found: C, 68.26; H, 4.51; N, 19.81. [l] Calcd. for $C_{14}H_{13}N_3O$: C, 70.27; H, 5.48; N, 17.56. Found: C, 70.14; H, 5.54; N, 17.78. [m] Calcd. for $C_{15}H_{15}N_3O_3$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.33; H, 5.20; N, 14.90.

phenyls were hydrogenated in ethanol solution, while the 2′,4′,6′-trimethoxy-(XXV) nitrobiphenyl was hydrogenated in benzene solution. The 2′-methoxy-(XXIX) and 2′-methyl-6′-methoxy-(XV) aminobiphenyls were recrystallized from cyclohexane; the 2′,4′,6′-trimethoxyaminobiphenyl (XIII) from benzene. 2-Amino-2′-hydroxybiphenyl (XI) was best purified by sublimation (110° (0.1 mm.)), followed by recrystallization from benzene–cyclohexane if desired.

2-Azidobiphenyls (Table I).—The amines were converted to the corresponding azides using procedure A or B of Smith and Brown[7a] with the following modifications: When procedure B was employed, sodium nitrite was used in place of amyl nitrite. Furthermore, in each case the azide was isolated from the aqueous mixture by extraction with a suitable solvent. 2′-Methoxy-(VIII) and 2′-methyl-6′-methoxy-(XIV) azidobiphenyls were extracted with ether, 2′-hydroxy-(X) with cyclohexane, and 2′,4′,6′-trimethoxy-(XII) with benzene. The extracts were washed with water, dried and evaporated at reduced pressure at 40–45°.

Purification of the azides could be accomplished by passing a benzene solution through a column of Merck alumina (wt. ratio 50:1); in the case of 2-azido-2′-hydroxybiphenyl (X) Merck acid-washed alumina was used.

***o*-Azidocumene (XIX).**—*o*-Aminocumene (XXI) was converted to azide XIX in 68% yield using procedure B of Smith and Brown[7a] with the modifications listed above. The azide was purified by passing a hexane solution through Merck alumina (wt. ratio 50:1). The analytical sample was subjected to a short path distillation (50° (2 mm.)).

Anal. Calcd. for $C_9H_{11}N_3$: C, 67.05; H, 6.88; N, 26.07. Found: C, 67.01; H, 6.75; N, 26.28.

***o*-Azidophenylcyclohexane (XXII).**—*o*-Aminophenylcyclohexane was converted to azide XXII in 78% yield using procedure B of Smith and Brown[7a] with the modifications listed above. The azide was purified by passing a hexane solution through Merck alumina (wt. ratio 50:1). The analytical sample was subjected to a short path distillation (50° (0.1 mm.)).

Anal. Calcd. for $C_{12}H_{15}N_3$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.34; H, 7.25; N, 20.93.

Pyrolysis of 2-Azido-2′-methoxybiphenyl (VIII).—A solution of azide VIII (5.3 g., 0.0234 mole) in *n*-hexadecane (20 ml.) was added dropwise to stirred hexadecane (50 ml.) maintained at 220° in a nitrogen atmosphere. The decomposition was instantaneous, and gas evolution ceased shortly after the final addition, but heating was continued 5 minutes longer. The crystals which separated from the cooled solution were collected and found to weigh 3.85 g. (83%) and had a m.p. of 135–136°. Additional 4-methoxycarbazole (IX) was obtained by passing the hexadecane mother liquors through a column of 60 g. of Merck alumina. The hexadecane was eluted with petroleum ether, and an oily material with isopropyl alcohol–benzene. By seeding a solution of this oil in benzene–hexane with crystals of the carbazole, it was possible to obtain an additional 0.5 g. of material. The total yield of carbazole (IX) was 4.35 g. (94%).

The analytical sample was recrystallized from benzene–hexane and sublimed (105° (0.1 mm.)); m.p. 135–136°. The ultraviolet spectrum of this material in cyclohexane exhibited eight maxima and three shoulders, (): $\epsilon_{[illegible]}$ 30,600, (ϵ_{237} 46,500), ϵ_{242} 51,000, ϵ_{251} 16,000, ϵ_{274} 10,300, ϵ_{278} 11,500, ϵ_{284} 21,900, (ϵ_{304} 2,560), ϵ_{315} 5,800, (ϵ_{321} 4,000), ϵ_{328} 7,920.

Pyrolysis of 2-Azido-2′-hydroxybiphenyl (X).—A solution of azide X (4.2 g., 0.02 mole) in tetralin (10 ml.) was added dropwise to hot (160°) stirred tetralin (40 ml.) maintained in a nitrogen atmosphere. Gas evolution began immediately, but did not cease until about 0.75 of an hour after the final addition. Furthermore, the reaction solution became markedly discolored as the reaction proceeded. The cooled reaction solution was chromatographed on a column of 60 g. of Merck alumina. The tetralin was eluted with petroleum ether and the product with isopropyl alcohol–benzene. The total crude product was transferred to a sublimation apparatus and heated at 100° (0.1 mm.). The sublimate (1.2 g., 32%) was identified as slightly impure 2-amino-2′-hydroxybiphenyl (XI), from a comparison of its m.p. and infrared spectrum with that of an authentic sample.

Pyrolysis of the Anion of 2-Azido-2′-hydroxybiphenyl (X).—To a solution of 3.43 g. (0.0163 mole) of azide X in 60 ml. of diphenyl ether was added 8 ml. (0.0163 mole) of a 2.03 *M* solution of butyllithium in pentane. Butane was evolved smoothly and the solution became warm and darkened somewhat in color. After the butane evolution had ceased, the reaction solution was stirred and heated in a nitrogen atmosphere at 125–130° for about 0.5 hour. This resulted in a slow steady evolution of nitrogen accompanied by marked discoloration of the reaction solution.

Water was added to the cooled reaction mixture and extracted with benzene. The residue from the dried benzene extracts was placed on a column of 60 g. of Merck alumina. After the diphenyl ether had been eluted with petroleum ether, the product was eluted with isopropyl alcohol–benzene. The crude, dark, oily product was transferred to a sublimation apparatus and heated to 90–100° at 0.1 mm. The oily sublimate (320 mg., 10%) was shown to be impure 2-amino-2′-hydroxybiphenyl (XI) by an examination of its infrared spectrum and ultraviolet spectrum in neutral, alkaline and acidic ethanol.

Pyrolysis of 2-Azido-2′-methyl-6′-methoxybiphenyl (XIV).—A solution of azide XIV (5.3 g., 0.0222 mole) in hexadecane (10 ml.) was added dropwise to stirred, hot (190–200°) hexadecane (40 ml.) maintained in an atmosphere of nitrogen. Gas evolution was smooth and rapid and continued for about 5 minutes after the final addition. The cooled reaction solution was chromatographed on 120 g. of Merck alumina; hexadecane was eluted with petroleum ether, 2-amino-2′-methyl-6′-methoxybiphenyl (XV) (1.33 g., 29%) was eluted with 10% benzene–petroleum ether, 10-methoxyphenanthridine (XVI) (0.7 g., 16%) eluted with 50% benzene–petroleum ether, and finally a red oil was eluted with isopropyl alcohol–benzene.

The 10-methoxyphenanthridine (XVI) was recrystallized from benzene–hexane and sublimed (90° (0.1 mm.)) to give material of m.p. 104–105°. The ultraviolet spectrum of this compound in cyclohexane had nine maxima and one shoulder, (): ϵ_{247} 55,200, ϵ_{261} 18,300, ϵ_{271} 19,700, ϵ_{303} 6,100, (ϵ_{318} 1,650), ϵ_{322} 2,630, ϵ_{332} 2,550, ϵ_{337} 5,380, ϵ_{348} 2,740, ϵ_{352} 6,750.

Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.47; H, 5.30; N, 6.89.

Pyrolysis of 2-Azido-2',4',6'-trimethoxybiphenyl (XII).—A solution of azide XII (4.2 g., 0.0148 mole) in diphenyl ether (20 ml.) was added dropwise to hot (190–200°) stirred diphenyl ether (40 ml.) maintained in a nitrogen atmosphere. Nitrogen evolution was essentially instantaneous and ceased shortly after the final addition; however, heating was continued 10 more minutes. The cooled, darkly colored reaction solution was chromatographed on a column of 120 g. of Merck alumina. The diphenyl ether was eluted with petroleum ether, the product with chloroform. The crude, dark, oily product was transferred to a sublimation apparatus and heated to 100–120° (0.1 mm.) for 24 hours. The sublimate (110 mg., 3%) proved to be somewhat impure 2-amino-2',4',6'-trimethoxybiphenyl (XIII), as determined by m.p. and infrared spectrum.

Pyrolysis of *o*-Azidocumene (XIX).—A solution of 4.56 g. (0.0283 mole) of XIX in 20 ml. of diphenyl ether was added dropwise to 40 ml. of hot (200°) stirred diphenyl ether maintained in a nitrogen atmosphere. Gas evolution was instantaneous and the reaction darkened considerably. Heating was stopped when gas evolution ceased (~10 min.). The cooled reaction solution was chromatographed on 400 g. of Merck acid-washed alumina; the diphenyl ether was eluted with petroleum ether, the product with isopropyl alcohol–chloroform. The crude, dark-colored, ill-smelling product was subjected to a short path distillation (0.1 mm.). The almost colorless distillate (2.8 g.) was further separated by means of vapor phase chromatography[18] into three fractions (in the ratio 1:2.5:1.25): dihydroskatole (XX), *o*-aminocumene (XXI) and diphenyl ether. The diphenyl ether and *o*-aminocumene were identified by comparison of their respective infrared spectra with those of authentic samples. The identity of the dihydroskatole was established by preparing a picrate, m.p. 147–148° (lit.[19] m.p. 149–150°).

Anal. Calcd. for $C_{15}H_{16}O_7N_4$: C, 49.73; H, 3.90. Found: C, 49.77; H, 3.88.

Pyrolysis of *o*-Azidophenylcyclohexane (XXII).—To 50 ml. of hot (200–210°) stirred diphenyl ether maintained in an atmosphere of nitrogen was added dropwise a solution of 3.43 g. (0.0171 mole) of azide XXII in 10 ml. of diphenyl ether. Gas evolution was smooth and rapid and ceased shortly after the final addition. Heating was continued an additional 5 minutes and the reaction solution then cooled. The reddish-colored solution was chromatographed on 120 g. of Merck acid-washed alumina. Petroleum ether eluted the diphenyl ether, and isopropyl alcohol–benzene eluted the crude crystalline product (2.79 g., 95%). This material when subjected to sublimation (80° (0.1 mm.)) gave 2.55 g. (86%) of yellowish crystalline material which after several recrystallizations from hexane yielded 217 mg. of *trans*-hexahydrocarbazole (XXIV), m.p. 126–128° (lit.[20] m.p. 127°) and $\lambda_{\max}^{\mathrm{EtOH}}$ 287 mμ (lit.[20] value 286.5 mμ). The residue from the hexane mother liquors when recrystallized several times from ethanol yielded 115 mg. of *cis*-hexahydrocarbazole (XXIII), m.p. 97–98° (lit.[20] m.p. 99°) and $\lambda_{\max}^{\mathrm{EtOH}}$ 293 mμ (lit.[21] value 293 mμ). The *cis* and *trans* compounds had sufficiently different infrared spectra in carbon tetrachloride to have allowed an analysis of their relative proportions in the original reaction product. Four separate bands in each spectrum were used for the analysis. It was estimated that the pyrolysis gave 45–50% *cis*- and 40–45% *trans*-hexahydrocarbazole.

Dehydrogenation of Hexahydrocarbazole (XXIV).—Crude sublimed hexahydrocarbazole (100 mg.) obtained from the above reaction was heated at 200° for 17 hours in diphenyl ether (3 ml.) in the presence of 38 mg. of 10% palladized carbon while sweeping the mixture with nitrogen. The cooled reaction mixture was chromatographed on 8 g. of Woelm neutral alumina (activity grade 1). After the diphenyl ether had been eluted with petroleum ether, 102 mg. of crude carbazole (m.p. 210–220°, ultraviolet spectrum in ethanol essentially identical with that of an authentic sample) was eluted with benzene. One recrystallization from alcohol gave 65 mg. of carbazole of m.p. 246–247° (lit.[22] value m.p. 245°).

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(18) A. Beckman GC-2 gas chromatograph having a 40" column packed with Ucon Polar on Fluoropak was used. A temperature of 140° and pressure of 40 p.s.i. gave good separation.

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A Kinetic Study of the Reaction of a "Meso-ionic" Compound (Dehydrodithizone) with Haloacetates

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"Meso-ionic" compounds which possess very low pK'_a values but high polarizability would be expected to be excellent nucleophiles toward the sp^3 carbon but very poor nucleophiles toward the ester sp^2 carbon atom. This assumption has been shown to be valid in studies on the rates of nucleophilic displacement of halogen from α-haloacetates and p-nitrophenol from p-nitrophenyl acetate by the "meso-ionic" compound dehydrodithizone (I).

Introduction

The ability of a nucleophile to enter into an SN2 displacement at the sp^3 carbon is a function of both pK'_a and polarizability as expressed by the equation of Edwards.[2] Nucleophilicity toward

$$\log \frac{k_r}{k_{\mathrm{H_2O}}} = \alpha(E_0 + 2.60) + \beta(pK'_a + 1.74) \qquad (1)$$

the ester sp^2 carbon may be correlated by the Brönsted equation[3]

$$\log k_r = \alpha' pK_a + C \qquad (2)$$

where

$$C \neq \alpha(E_0 + 2.60) + \beta 1.74$$

"Meso-ionic" compounds possessing very low pK'_a values, such as dehydrodithizone (I), should, therefore, be very effective nucleophiles in those displacements in which $\alpha >> \beta$. In this category is found the SN2 displacement of halogen from α-haloacetates. We describe, herein, the kinetics of the reaction of I with α-iodo-, α-bromo- and α-chloroacetic acids and anions, as well as with bromoacetamide.

Results

The reagent I (red color, $\lambda_{\max}$ 250 mμ, $\epsilon \cong 24{,}000$) reacts as a sulfur nucleophile to yield colorless

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