calcium fluoride prism and the higher accuracy of these data (± 1 cm.$^{-1}$) is indicated in Table II.

Comments

The observations presented here supplement and substantiate the general conclusions developed in the previous publications and do not necessitate an extensive discussion. It may be considered firmly established that for complex molecules in solution the stretching vibration of the carbonyl group is influenced only by the molecular structure in its immediate vicinity. Unless the carbonyl group forms part of a conjugated system this influence normally does not extend beyond one carbon atom. Two carbonyl groups only interact on one another if they are separated by not more than two saturated linkages, and if such interaction occurs it causes a displacement of both the absorption bands to higher frequencies.[3] In this paper it has also been shown that the carbonyl stretching band is considerably disturbed by introduction of an alpha bromine atom. The situation in the 6-ketosteroids is also of interest, since it suggests that a carbon atom adjacent to a center of stereochemical inversion may be influenced by the steric configuration at that point. In cyclic ketones the position of the carbonyl band is also influenced by the ring size.

These correlations between structure and infrared absorption spectra are summarized in Table III. They parallel observations on the stretching frequency of the carbon–carbon double bond, which are reported separately,[10] and are proving of considerable value in the elucidation of the structure of ketosteroids. In certain instances it has been possible by this means to recognize and locate the carbonyl functions in newly isolated steroids where the quantities of material available are of the order of 25 to 50 micrograms.

Acknowledgments.—The authors wish to thank the several investigators listed individually in a footnote to Table I who kindly made available many of the compounds. The technical assistance of Miss E. Packard and Mr. D. Keir is also gratefully acknowledged.

This investigation was aided by grants from the American Cancer Society (on recommendation of the Committee on Growth of the National Research Council), Ayerst, McKenna and Harrison Ltd., the Jane Coffin Childs Memorial Fund for Medical Research, the Commonwealth Fund, the Anna Fuller Fund, the Lillia Babbitt Hyde Foundation, the Albert and Mary Lasker Foundation and the National Cancer Institute, U. S. Public Health Service.

Summary

Measurements of the position of the carbonyl stretching vibration in the infrared spectra of carbon disulfide solutions of an additional 180 steroids are reported. The compounds include steroid carboxylic acids, γ-lactones, δ-lactones, p-toluenesulfonate esters, 6-ketosteroids and a variety of α-brominated 3-ketosteroids. The results substantiate the previously reported observation that the position of the maximum of this absorption band is characteristic for the type of carbonyl group and its position in the steroid molecule.

These correlations between structure and infrared absorption spectra are being utilized in the determination of the structure of new steroids isolated from urine.

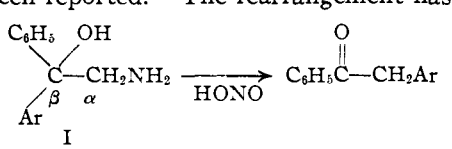
NEW YORK, N. Y.
OTTAWA, CANADA RECEIVED AUGUST 17, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Stereospecificity in the Rearrangement of Amino Alcohols

BY PETER I. POLLAK AND DAVID Y. CURTIN

The rearrangement with nitrous acid of a number of amino alcohols with the general formula (I) has been reported.[1] The rearrangement has generally been assumed to be closely related to the pinacol rearrangement and the "relative migratory aptitudes" suggested by this series of rearrangements are at least qualitatively in the order obtained by Bachmann, Moser and Ferguson[2] in the acid-catalyzed rearrangement of a series of symmetrically substituted tetraphenylethylene glycols. For instance, in each case p-tolyl, p-anisyl and 1-naphthyl have been reported to migrate faster than phenyl.



I

In striking contrast to the results obtained with the series of amino alcohols above were those reported[3] with a series of compounds (II) differing from series (I) only in the presence of an additional phenyl on the α-carbon. Here, for example, phenyl was reported to migrate faster than p-anisyl or p-tolyl.

(1) (a) Luce, *Compt. rend.*, **180**, 145 (1925); (b) McKenzie, Mills and Myles, *Ber.*, **63**, 904 (1930); (c) Orekhoff and Roger, *Compt. rend.*, **180**, 70 (1925); Tiffeneau, Orekhoff and Roger, *Bull. soc. chim. France*, **49**, 1757 (1931).

(2) Bachmann and Moser, THIS JOURNAL, **54**, 1124 (1932); Bachmann and Ferguson, *ibid.*, **56**, 2081 (1934).

(3) (a) McKenzie and Mills, *Ber.*, **62**, 1784 (1929); (b) McKenzie and Wood, *ibid.*, **71**, 358 (1938).

TABLE I

DEAMINATION OF DIASTEREOISOMERIC *dl*-1,2,-DIPHENYL-1-ARYL-2-AMINOETHANOLS

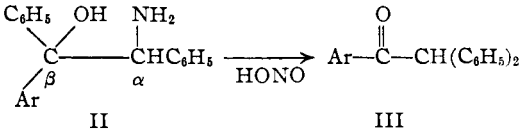
dl-1,2-Diphenyl-1-aryl-2-aminoethanol Aryl =	Racemate	M. p., °C.	Yield, %	Ref.	Deamination product	M. p., °C.	Yield, %	Ref.
p-Anisyl	α	159–160	60	3a	*p*-Anisyl benzhydryl ketone	130–131	97(97)[b]	5
p-Anisyl	β	145–146	54	[a]	*p*-Methoxybenzhydryl phenyl ketone	87–88	67(97)	3a
p-Tolyl	α	151–152	88	1b	Benzhydryl *p*-tolyl ketone	99–100	35(87)	1b
p-Tolyl	β	155–156	85	3b	*p*-Methylbenzhydryl phenyl ketone	96–97	33(83)	6

[a] *Anal.* Calcd. for $C_{21}H_{21}O_2N$: C, 78.97; H, 6.63; N, 4.39. Found: C, 78.82; H, 6.41; N, 4.23. Hydrochloride m. p. 216–217° d. *Anal.* Calcd. for $C_{21}H_{22}O_2NCl$: C, 70.88; H, 6.23; N, 3.94. Found: C, 70.88; H, 6.31; N, 4.38. [b] The figure in parentheses indicates the yield on the basis of unrecovered starting material.

TABLE II

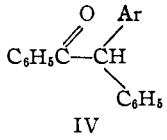
OXIDATION PRODUCTS OF DIASTEREOISOMERIC *dl*-1,2-DIPHENYL-1-ARYL-2-AMINOETHANOLS

dl-1,2-Diphenyl-1-aryl-2-aminoethanol Aryl =	Diaster.	Acid	M. p., °C.	Yield, %	Ketone	M. p., °C.	Yield, %	Ref.
p-Anisyl	α	Benzoic	119–120	20	*p*-Methoxybenzophenone	60–62	11	7
p-Anisyl	β	Benzoic	120–121	21	*p*-Methoxybenzophenone	61–62	10	7
p-Tolyl	α	Benzoic and *p*-benzoyl benzoic	119–120 194–196	17 19	....	... ...	.. ..	 8
p-Tolyl	β	Benzoic and *p*-benzoyl benzoic	118–119 195–196	15 14	....	... ...	.. ..	 8



II III

The compounds of series (II) differ from those of series (I) in having a second asymmetric center and thus existing in two diastereoisomeric forms. In only two cases were both diastereoisomers examined. McKenzie, Richardson and Dennler[4] observed that the α-racemate of 1,2-diphenyl-1-(1′-naphthyl)-2-aminoethanol (II, Ar = 1-naphthyl) on treatment with nitrous acid rearranged with migration of phenyl to benzhydryl 1-naphthyl ketone (III, Ar = 1-naphthyl) whereas the β-racemate rearranged under identical conditions to α-(1-naphthyl)-desoxybenzoin (IV, Ar = 1-naphthyl).[3b]



IV

McKenzie and Wood,[3b] however, reported that the rearrangement of either the α- or the β-racemate of 1,2-diphenyl-1-*p*-tolyl-2-aminoethanol (II, Ar = *p*-tolyl) yielded the same product, benzhydryl *p*-tolyl ketone (III, Ar = *p*-tolyl).

We have repeated the work of McKenzie and Wood[3b] on the rearrangement of the α- and β-racemates of 1,2-diphenyl-1-*p*-tolyl-2-aminoethanol with results which are only partially in agreement with theirs. Table I summarizes our results. *dl*-α-1,2-Diphenyl-1-*p*-tolyl-2-aminoethanol (α-II, Ar = *p*-tolyl) rearranged to benzhydryl *p*-tolyl ketone (III, Ar = *p*-tolyl) in agreement with the previous work. From the rearrangement of the β-racemate of this compound, however, we could isolate only *p*-methylbenzhydryl phenyl ketone (IV, Ar = *p*-tolyl) in a yield of 83% based on unrecovered starting material.

The α-racemate of 1,2-diphenyl-1-*p*-anisyl-2-aminoethanol (α-II, Ar = *p*-anisyl) was prepared and found to rearrange to *p*-anisyl benzhydryl ketone (III, Ar = *p*-anisyl) as previously described.[3a] The β-racemate of 1,2-diphenyl-1-*p*-anisyl-2-aminoethanol which had not been previously reported was synthesized and treated with nitrous acid. The only product isolated was *p*-methoxybenzhydryl phenyl ketone (IV, Ar = *p*-anisyl).

The amino alcohols used in this work were prepared by the method previously used by McKenzie and Mills[3a] as shown in Chart I.

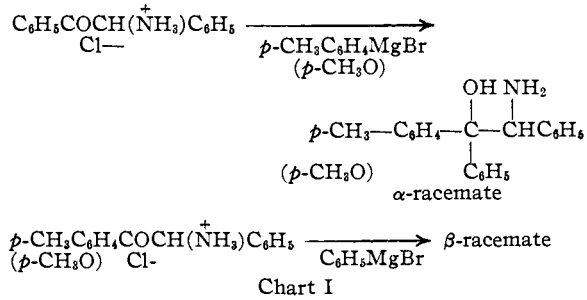


Chart I

That the two pairs of amino alcohols (α- and β-II, Ar = *p*-tolyl or *p*-anisyl) differed only in stereochemical configuration was confirmed by oxidative cleavage with alkaline permanganate. From either isomer, identical products were iso-

(4) McKenzie and Richardson, *J. Chem. Soc.*, **123**, 79 (1923); McKenzie and Dennler, *ibid.*, **125**, 2105 (1924).

(5) La Grave, *Ann. Chim. Phys.*, [10] **8**, 363 (1927).

(6) McKenzie, Roger and Widdows, *J. Chem. Soc.*, 2600 (1932).

(7) Remie, *J. Chem. Soc.*, **41**, 37 (1882).

(8) Meyer, *Monatsh.*, **28**, 1224 (1907).

TABLE III

CLEAVAGE OF KETONES BY 25% METHANOLIC POTASSIUM HYDROXIDE

Ketone	Acid	M. p. °C.	Yield, %	Hydrocarbon	Identified as	M. p., °C.	Yield, %	Ref.
p-Anisyl benzhydryl ketone	*p*-Anisic	184–185	96	Diphenylmethane	2,2′,4,4′-Tetranitrodiphenylmethane	173–174	76	9
p-Methoxybenzhydryl phenyl ketone	Benzoic	119–120	98	*p*-Methoxydiphenylmethane	*p*-Methoxybenzophenone	60–61	70	7
Benzhydryl *p*-tolyl ketone	*p*-Toluic	179–180	71	Diphenylmethane	2,2′,4,4′-Tetranitrodiphenylmethane	173–174	58	9
p-Methylbenzhydryl phenyl ketone	Benzoic	120–121	76	*p*-Methyldiphenylmethane	*p*-Benzoylbenzoic acid	195–197	91	8

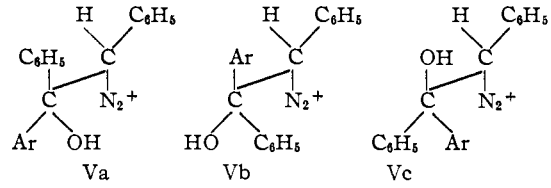
lated in each case. The results are shown in Table II.

The structures of the ketonic rearrangement products (III and IV) were confirmed by the cleavage with methanolic potassium hydroxide used by Bachmann and Chu.[10] The results are summarized in Table III.

Discussion

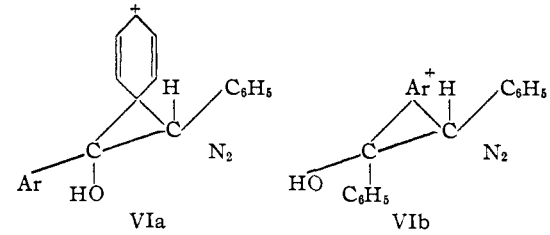
The results described here together with those previously reported for the α- and β-racemates of 1,2-diphenyl-1-(1′-naphthyl)-2-aminoethanol (α- and β-II, Ar = 1-naphthyl)[3b,4] indicate that the course of these reactions is primarily determined by the geometry of the rearranging molecule. The commonly accepted mechanism for the nitrous acid rearrangement of amino alcohols involves primary formation of a diazonium ion.[11] The diazonium ion may undergo loss of nitrogen to give a carbonium ion which subsequently rearranges or may undergo an internal one-stage displacement of nitrogen by the migrating group.[12] It has been demonstrated in one case that the configuration of the α-carbon is inverted in this type of rearrangement.[13] The retention of optical activity in the rearrangement of optically active amino alcohols closely related to those under discussion[14] has provided evidence that migration occurs simultaneously with or immediately after the elimination of nitrogen.

The geometry of the reacting molecule can influence the reaction in one or more of several possible ways. Molecules with the general formula V have three staggered configurations which are presumed initially to be in equilibrium with one another. Should Va have a sufficiently lower free energy to be present in appreciably greater concentration than Vb, a larger fraction of rearranging molecules would have the correct configuration for the replacement of nitrogen by phenyl rather than by aryl.



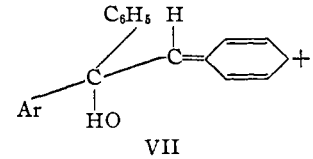
Va Vb Vc

Furthermore, if the diazonium ion V loses nitrogen with simultaneous migration of phenyl, the transition state has the configuration VIa while migration of aryl leads to transition state VIb. It seems possible that VIa may be of sufficiently lower energy than VIb to influence the relative rates of the two migrations.



VIa VIb

In addition to the steric effects considered above, steric inhibition of resonance in the transition state may play a part since resonance structures of type (VII) demand approximate coplanarity of the non-migrating rings. Models suggest that such coplanarity can be approached only in the case of transition state VIa.



VII

It is impossible at present to decide what the relative magnitudes of these effects may be in directing the course of the rearrangement. Other reactions have been reported to show behavior which may have a steric origin similar to that discussed here.[15]

The considerations above have led to the assignment of configuration VIIIa to molecules in the α-series and of configuration VIIIb to those in

(9) Schoepf, *Ber.*, **27**, 2318 (1894).

(10) Bachmann and Chu, THIS JOURNAL, **58**, 1118 (1936).

(11) M. J. S. Dewar "The Electronic Theory of Organic Chemistry," Oxford Press, London, England, 1949, p. 210.

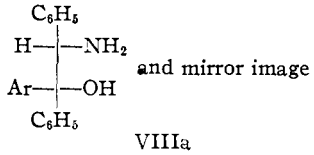
(12) For a discussion of this point in connection with other rearrangements see Winstein, Abstracts of Eleventh Organic Chemistry Symposium of the American Chemical Society, Madison, Wisconsin, June, 1949; Cram, THIS JOURNAL, **71**, 3863 (1949).

(13) Bernstein and Whitmore, *ibid.*, **61**, 1324 (1939).

(14) McKenzie, Roger and Wills, *J. Chem. Soc.*, 779 (1926); McKenzie, Roger and McKay, *ibid.*, 2597 (1932).

(15) Fodor, Bruckner, Kiss and Óhegyi, *J. Org. Chem.*, **14**, 337 (1949); Reulos and Collin, *Compt. rend.*, **216**, 774 (1943), **218**, 795 (1944); Winstein and Seymour, THIS JOURNAL, **68**, 119 (1946).

the β. An experimental test of this conclusion is now being carried out in these laboratories.



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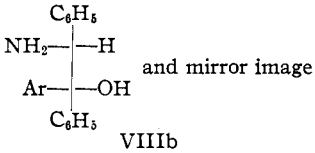
VIIIa



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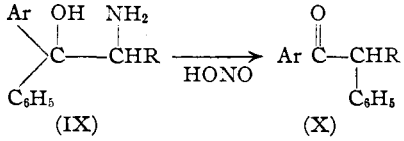
VIIIb

Two other series of compounds (IX, R = CH_3)[15a] and (IX, R = $C_6H_5CH_2^-$)[16] have been reported to show similar unexpected relative migratory aptitudes. A statement by Tiffeneau that in one case both the α- and β-racemate gave the same product (X) on rearrangement is unsupported by experimental detail. In the other cases only one of the two possible racemates was studied. We feel that these reactions need further investigation.



(IX) (X)

Our results point out the desirability of examining the rearrangement of both racemates before interpreting the results of rearrangements of molecules in which this type of diastereoisomerism is possible.

Experimental[17]

Synthesis of Desylamine Hydrochlorides.—Desylamine hydrochloride itself and the two 4-substituted analogs were prepared by reduction of the corresponding α-oximinodesoxybenzoins[18] with stannous chloride in ethanolic hydrogen chloride solution in accordance with a procedure described by Pschorr and Brueggemann.[19] Since the reduced tin complex of 4-methoxydesylamine did not crystallize from the reaction mixture after two weeks in the icebox, their procedure was modified in this case. The reduction mixture was decomposed directly by pouring into 30% cold sodium hydroxide solution followed by extraction with ether and treatment of the dried solution with anhydrous hydrogen chloride. The yield of *dl*-4-methoxydesylamine hydrochloride, m. p. 216–218°, from 94 g. of α-oximino-4-methoxydesoxybenzoin was 31 g. (30%). Upon recrystallization from 95% ethanol it melted at 237–238°.

Anal. Calcd. for $C_{15}H_{16}O_2NCl$: C, 64.86; H, 5.81; N, 5.04. Found; C, 64.92; H, 5.64; N, 5.54.

Several attempts were made to prepare *dl*-4-methoxydesylamine from the hydrochloride, but the isolation of a sample of the free base was unsuccessful.

Synthesis of the Diastereoisomeric *dl*-1,2-Diphenyl-1-aryl-2-aminoethanols (Table I).—The α-racemates of the amino alcohols were obtained by reaction of one molar equivalent of *dl*-desylamine hydrochloride, m. p. 232–233°, with six molar equivalents of arylmagnesium bromide in accordance with directions by McKenzie and co-workers.[1b,3a,3b]

The β-racemates of the aminoalcohols were prepared by reaction of one molar equivalent of *dl*-4-substituted desylamine hydrochlorides with six molar equivalents of phenylmagnesium bromide. The Grignard reaction mixtures were in all cases decomposed with a mixture of ammonium chloride, concentrated ammonia and ice.

Deamination of Diastereoisomeric *dl*-1,2-Diphenyl-1-aryl-2-aminoethanols (Table I).—Three grams of the *dl*-α- or *dl*-β-1,2-diphenyl-1-aryl-2-aminoethanol was dissolved in 200 ml. of 50% acetic acid at room temperature. The solution was poured into a 500 ml. three-necked round bottom flask equipped with stirrer and dropping funnel, and was cooled to 0°. Three moles of sodium nitrite per mole of amino alcohol was dissolved in 30 ml. of water and added slowly with agitation to the solution over a period of eight to twenty-four hours. The resulting precipitate was filtered and recrystallized from 95% ethanol to yield the deamination product. The mother liquor was made alkaline to yield unreacted starting material.

When 3.00 g. of *dl*-β-1,2-diphenyl-1-*p*-tolyl-2-aminoethanol was subjected to these conditions only 0.18 g. (7%) of *p*-methylbenzhydryl phenyl ketone was obtained, while the major product (0.42 g.) was a white solid, m. p. 212–213°, which contained nitrogen, was difficultly soluble in hot ethanol, but soluble in hot water. The analysis agreed with an acetate salt of *dl*-β-1,2-diphenyl-1-*p*-tolyl-2-aminoethanol having two moles of water of crystallization.

Anal. Calcd. for $C_{23}H_{25}O_3N \cdot 2H_2O$: C, 69.15; H, 7.32; N, 3.51. Found: C, 69.20; H, 6.51; N, 3.80.

Upon refluxing with 25% methanolic potassium hydroxide for forty-eight hours the acetate salt was reconverted to the original triarylaminoethanol.

In order to increase the yield of ketonic deamination product the above procedure for the deamination was altered in the case of *dl*-β-1,2-diphenyl-1-*p*-tolyl-2-aminoethanol. In a 500 ml. three-necked round bottom flask equipped with a stirrer and two dropping funnels, was placed 50 ml. of 50% acetic acid. To this solution, which was cooled to 0°, were added slowly and simultaneously a solution of 3.03 g. (0.01 mole) of *dl*-β-1,2-diphenyl-1-*p*-tolyl-2-aminoethanol in 200 ml. of 50% acetic acid and a solution of 2.07 g. (0.03 mole) of sodium nitrite in 30 ml. of water. After twenty-four hours agitation the reaction mixture was worked up following the usual procedure to yield 0.90 g. (33%) of *p*-methylbenzhydryl phenyl ketone.

In the deamination of *dl*-α-1,2-diphenyl-1-*p*-tolyl-2-aminoethanol a water-soluble solid was similarly isolated, which is believed to be the analogous acetate salt. It was not further investigated.

In order to test the stability of the aminoalcohols to the reaction medium, 3.00 g. of *dl*-β-1,2-diphenyl-1-*p*-tolyl-2-aminoethanol was dissolved in 200 ml. of 50% acetic acid and agitated at 25° for forty-eight hours. The starting material was recovered in 97% yield.

Alkaline Cleavage of Ketonic Deamination Products (Table II).—One-half gram of ketonic deamination product was treated for fifty hours under reflux with 15 ml. of 25% methanolic potassium hydroxide in a modified procedure of Bachmann and Chu.[10] The reaction mixture was diluted with 100 ml. of water and extracted with ether. The alkaline aqueous layer was concentrated on the steam-bath and acidified to yield the acidic cleavage product. The ether layer was dried and evaporated to yield the hydrocarbon cleavage fragment.

Structure of Diastereoisomeric *dl*-1,2-Diphenyl-1-aryl-2-aminoethanols (Table III).—On oxidative fission of the diastereoisomeric aminoethanols identical fragments were obtained from either racemate. A 4% solution was prepared from 0.28 g. (0.0018 mole) of potassium perman-

(15a) Mills and Grigor, *J. Chem. Soc.*, 1568 (1934); Tiffeneau, Levy and Ditz, *Bull. soc. chim. France*, [5] **2**, 1871 (1935).

(16) Mills, *J. Chem. Soc.*, 1565 (1934).

(17) All melting points are corrected. Elemental analyses were carried out by the Clark Microanalytical Laboratories, Urbana, Illinois.

(18) Hartung and Munch, THIS JOURNAL, **51**, 2262 (1929); Hartung and Crossley, "Organic Syntheses," Coll. Vol. II, p. 363; Foster and Dunn, *J. Chem. Soc.*, **95**, 4311 (1909).

(19) Pschorr and Brueggemann, *Ber.*, **35**, 2740 (1902).

ganate. It was mixed with 0.40 g. (0.0013 mole) of *dl*-α- or *dl*-β-1,2-diphenyl-1-aryl-2-aminoethanol and heated on the steam-bath until discoloration was complete (three to four hours). The mixture was acidified, the manganese dioxide reduced with sodium bisulfite, and the solution extracted with ether. The ether layer was in turn extracted with 10% sodium bicarbonate solution, which upon concentration and acidification yielded the acidic fragments. The ether layer was evaporated to dryness and the resulting ketones recrystallized from petroleum ether.

In an attempted oxidation with periodic acid[20] 96% of the starting material was recovered and traces of benzaldehyde could be identified as the 2,4-dinitrophenylhydrazone, m. p. 235–236°.

(20) R. Adams, Ed., "Organic Reactions," John Wiley and Sons, New York, N. Y., 1944, Chapt. VIII; Karrer and Hirohata, *Helv. Chim. Acta*, **16**, 495 (1933).

Summary

The course of the rearrangement with nitrous acid of certain unsymmetrically substituted triphenylethanolamines has been shown to be determined by the stereochemistry of the rearranging molecule.

A possible interpretation of this observation has been discussed and relative configurations have tentatively been assigned to the pairs of racemates studied.

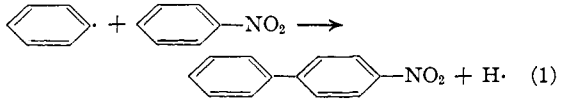
NEW YORK 27, N. Y. RECEIVED AUGUST 9, 1949

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY OF CORNELL UNIVERSITY]

The Mechanism of the Cyclization Reaction in the Decomposition of Diazonium Salts[1]

BY DELOS F. DETAR AND SENOL V. SAGMANLI

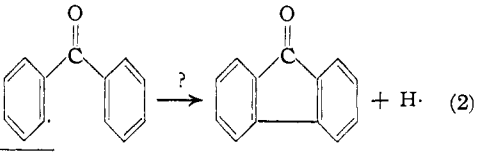
The work of Hey and Waters[2] has shown that a close relationship exists among the following three reactions which lead to the formation of biphenyl derivatives: (1) the decomposition of diazonium salts under alkaline conditions in the presence of an aromatic solvent by the method of Gomberg and Bachmann,[3] (2) the thermal decomposition of nitrosoacylanilides[4] in an aromatic solvent, and (3) the thermal decomposition of diacyl peroxides in an aromatic solvent. Hey and Waters have amassed a considerable body of evidence to indicate that free radicals are involved in all of these reactions. In order to account for the formation of symmetrical biaryls, they have postulated a reaction scheme which includes a radical substitution step.[2,5] Equation 1, for example, is postulated to be a common step



(1)

in the decomposition in the presence of nitrobenzene of benzenediazohydroxide,[6a] nitrosoacetanilide,[4] or benzoyl peroxide.[6b] This step is formally analogous to the usual electrophilic substitution reactions such as the nitration of benzene[7] and it is also analogous to the less common nucleophilic substitution reactions such as the amination of pyridine.[8]

Direct evidence about the possibility of the radical substitution step (Eq. 1) in aromatic systems is not available, but indirect evidence discussed later suggests that radical substitution reactions are not of general occurrence. The purpose of the present program has been to obtain additional evidence about the occurrence of radical substitution by a study of systems which are especially favorable for this reaction. Because the possibility of closing a five- or a six-membered ring constitutes a considerable driving force in a chemical reaction,[9] a study of the products obtained from the reaction of a radical which can form a five- or a six-membered ring by radical substitution (Eq. 2) should give the desired information. The presence of the cyclized compound among the reaction products would con-



(2)

(1) From a thesis presented by Senol V. Sagmanli to the Graduate School of Cornell University, June, 1949, in partial fulfillment of the requirements for the degree of Master of Science.

(2) (a) Hey and Waters, *Chem. Revs.*, **21**, 169 (1937); (b) Waters, "The Chemistry of Free Radicals," Oxford University Press, London, 1946, p. 148, p. 165.

(3) Bachmann and Hoffman, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 224.

(4) Grieve and Hey, *J. Chem. Soc.*, 1797 (1934).

(5) A variation of this mechanism has been proposed by Price, "Mechanisms of Reactions at Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 53. Price postulates that the substitution is a two-step process. In general, evidence about the direct substitution step (Eq. 1) is also applicable to this variation.

(6) (a) Gomberg and Bachmann, THIS JOURNAL, **46**, 2339 (1924); (b) Hey, *J. Chem. Soc.*, 1966 (1934).

(7) (a) Gillespie and Millen, *Quart. Revs.*, **2**, 277 (1948); (b) *cf.* also Bartlett in Gilman, "Organic Chemistry," 2d ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 205; (c) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 309.

(8) M. T. Leffler, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 91; *cf.* ref. 7b, p. 211; Russell and Telibens, *Org. Syntheses*, **22**, 35 (1942).

(9) For example, although benzophenone in common with other benzene derivatives containing *m*-directing substituents is unreactive toward Friedel-Crafts substitution, nevertheless anthraquinones are readily formed from *o*-benzoylbenzoic acids by an internal Friedel-Crafts substitution into a ring containing the deactivating benzoyl group. The driving force which makes this reaction possible is the formation of the six-membered ring. The cyclization even occurs in the presence of two deactivating groups, for 2,4'-benzophenonedicarboxylic acid cyclizes to 2-anthraquinonecarboxylic acid.[10]

(10) Limpricht, *Ann.*, **309**, 96 (1899).