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1,5-Hydrogen Transfer during Diazonium Ion Decomposition. II. Formation of Five- and Seven-Member Nitrogen Heterocycles[1,2]

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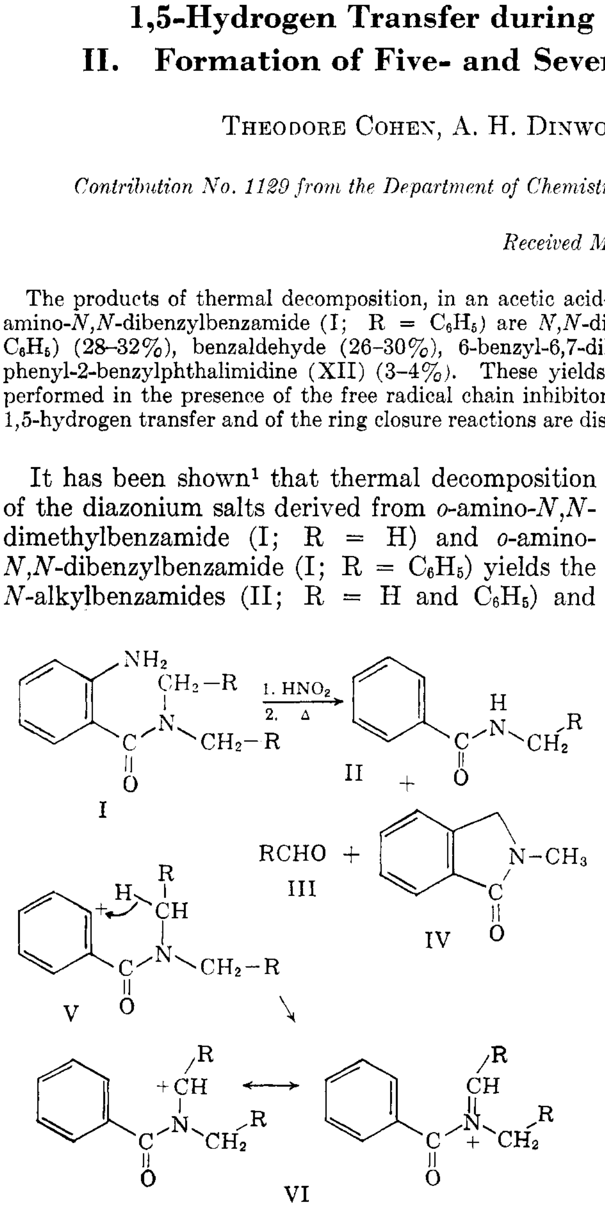
The products of thermal decomposition, in an acetic acid–sulfuric acid medium, of the diazonium salt derived from *o*-amino-*N*,*N*-dibenzylbenzamide (I; R = C_6H_5) are *N*,*N*-dibenzylsalicylamide (41–45%), *N*-benzylbenzamide (II; R = C_6H_5) (28–32%), benzaldehyde (26–30%), 6-benzyl-6,7-dihydro-5*H*-dibenz[*c*,*e*]azepine-7-one (XIV) (10–17%), and 1-phenyl-2-benzylphthalimidine (XII) (3–4%). These yields are not significantly changed when the decompositions are performed in the presence of the free radical chain inhibitors *m*-dinitrobenzene or benzenethiol. The mechanisms of the 1,5-hydrogen transfer and of the ring closure reactions are discussed in the light of these results.

It has been shown[1] that thermal decomposition of the diazonium salts derived from *o*-amino-*N*,*N*-dimethylbenzamide (I; R = H) and *o*-amino-*N*,*N*-dibenzylbenzamide (I; R = C_6H_5) yields the *N*-alkylbenzamides (II; R = H and C_6H_5) and aldehydes (III; R = H and C_6H_5). Another product from the diazotization of I (R = H) was shown to be *N*-methylphthalimidine (IV). In order to account for these and other cases[3] of *N*-dealkylation during thermally induced diazonium ion decomposition, it was proposed that the carbonium ion V, which results by loss of nitrogen from the diazonium ion, undergoes an intramolecular hydride ion transfer to produce the resonance stabilized ion VI. The latter may hydrolyze to yield the *N*-alkylbenzamide (II) and the aldehyde (III) or it may undergo an electrophilic ring closure to produce a phthalimidine of the type IV.



We have been impressed with the potential value of this reaction as a tool for the study of the mechanism of decomposition of diazonium ions and of the reactions of phenyl carbonium ions. Before pursuing isotopic and kinetic studies, it was deemed necessary to provide further evidence that the thermal reaction does indeed involve the transfer of a hydride ion to a phenyl carbonium ion rather than the transfer of a hydrogen atom to a free phenyl radical.[4]

The carbonium ion hypothesis appeared sound on the basis of the products isolated and of the known propensity of diazonium ions in acidic solu-

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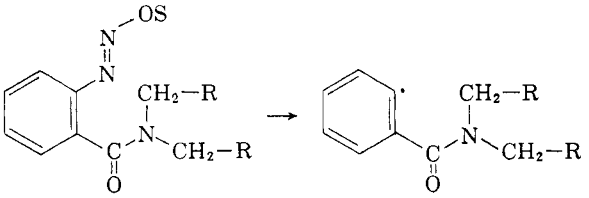
[1] The first paper in this series is taken to be Part I: T. Cohen, R. M. Moran, and G. Sowinski, *J. Org. Chem.*, **26**, 1 (1961).

[2] This work was supported by Grant NSF-G9475 from the National Science Foundation.

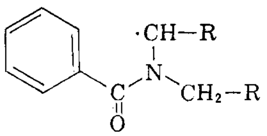
[3] For pertinent references, see the first paper of this series.[1]

[4] D. N. Brown, D. H. Hey, and C. W. Rees, *J. Chem. Soc.*, 3873 (1961).

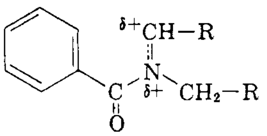
tion to decompose to carbonium ions.[5,6] Indeed, as has been pointed out by DeTar,[5] unimolecular decomposition of a diazonium ion could occur in a homolytic fashion only if the high energy radical-ion $\cdot N_2^+$ were released. A free radical would be much more likely to arise from a diazohydroxide (VII; S = H), a diazoacetate (VII; S = CH_3CO) or their equivalent, substances whose presence in substantial amounts in two or three normal sulfuric acid is very unlikely.[7] If small quantities of VII were present, however, its decomposition could produce the phenyl radical VIII in addition to nitrogen and the hydroxyl or acetoxyl radical. The new radical IX would result if VIII were to suffer an internal hydrogen atom transfer.



VII VIII + ·OS + N_2



IX



VI

In order to account for the aldehyde and amide products, it would be necessary to postulate (1) the reaction of IX with the hydroxyl or acetoxyl radical, (2) the abstraction of a hydroxyl or acetoxyl radical from VII by IX and the consequent initiation of an induced decomposition of VII, or (3) a chain propagation step involving the transfer of an electron from IX to the free diazonium ion to yield nitrogen, the radical VIII and the ion VI.

In view of the very low concentrations of the unstable radicals ·OS and IX, themselves derived from a substance (VII) whose concentration is negligible, the first alternative appears incapable of explaining the formation of amides and aldehydes in the rather substantial quantities reported.[1,8] The second possibility is no more attractive because of the necessity of a collision between two species (VII and IX) the concentrations of which are very low. The third alternative does not suffer from these disadvantages and it appears to be the most likely of the available free radical paths. The major objection to the third mechanism (and this applies to the second one as well) is the absence of products (*N*,*N*-dimethylbenzamide and *N*,*N*-dibenzylbenzamide) that would be expected if VIII or IX were to abstract a hydrogen atom from one of the many conceivable donors in the solution.

In order to confirm the absence of such products, we have performed a careful analysis of the mixture obtained in the thermal decomposition, in acetic acid 2 *N* in sulfuric acid, of the diazonium salt derived from *o*-amino-*N*,*N*-dibenzylbenzamide (I; R = C_6H_5), both in the absence and in the presence of the free radical scavengers *m*-dinitrobenzene and benzenethiol. While either of these might be expected to inhibit the chain mechanisms 2 and 3, thereby drastically reducing the concentrations of the hydrogen transfer products, the benzenethiol, because it is a ready source of hydrogen atoms, would produce large quantities of *N*,*N*-dibenzylbenzamide if either of these mechanisms obtain.

Improved reaction and work-up procedures now permit the accurate and reproducible determination of all of the major products. In addition to the products of deamination of I (R = C_6H_5) reported in the previous paper,[1] *N*,*N*-dibenzylsalicylamide, *N*-benzylbenzamide (II; R = C_6H_5), and benzaldehyde, two new products were obtained as an oily mixture resolvable by rechromatographing on alumina. The similarity of the position of the carbonyl absorption (1671 cm.$^{-1}$) in the infrared spectrum of one of these compounds to that (1678 cm.$^{-1}$) of *N*-methylphthalimidine (IV) indicated that this substance might be 1-phenyl-2-benzylphthalimidine (XII). This was confirmed by an independent synthesis consisting of the treatment of 3-phenylphthalide[9] (XIII) with benzylamine and benzylamine hydrochloride.

The formation of the phthalimidine XII from the thermal decomposition of this diazonium ion must be analogous to that of *N*-methylphthalimidine (IV) obtained from the decomposition of the diazonium salt derived from *o*-amino-*N*,*N*-dimethylbenzamide (I; R = H). Assuming the hydride ion transfer mechanism discussed above, it can be considered that the formation of XII involves electrophilic substitution of the partially positive carbon of the ion XI, formed from X, into the benzoyl ring.

The elemental analysis of the second component, melting point 115°, of this mixture indicated that it was an isomer of the phthalimidine (XII). The carbonyl absorption at 1618 cm.$^{-1}$ in its infrared spectrum identified it as a tertiary benzamide.[10] A consideration of the hydride transfer mechanism suggested two possible structures for this compound. These are 6-benzyl-6,7-dihydro-5*H*-dibenz[*c*,*e*]azepine-7-one (XIV), which could be produced directly

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[5] D. F. DeTar, "Organic Reactions," Vol. 9, J. Wiley and Sons, Inc., New York, 1957, p. 409.

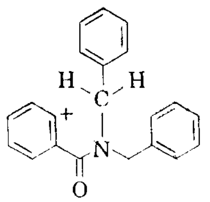
[6] J. F. Bunnett, *Quart. Rev.*, **12**, 1 (1958).

[7] H. Zollinger, "Diazo and Azo Chemistry," Interscience Publishers, Inc., New York, 1961, pp. 47–51.

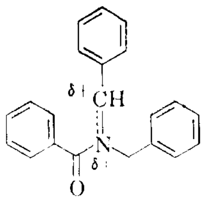
[8] This route cannot be completely ruled out, however, because the possibility exists that the loss of nitrogen from VII, the hydrogen atom transfer and the attack of ·OS on IX could all occur simultaneously or in very rapid succession. Nevertheless, the very low concentration of VII makes this route exceedingly unlikely.

[9] F. Rottering and T. Zinke, *Ber.*, **9**, 631 (1876).

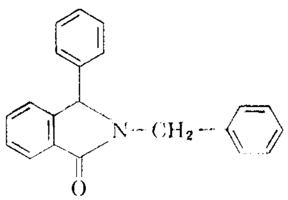
[10] We have found that *N*,*N*-dialkylbenzamides usually absorb in the vicinity of 1620 cm.$^{-1}$ while *N*-alkylbenzamides absorb in the vicinity of 1640 cm.$^{-1}$ (chloroform).



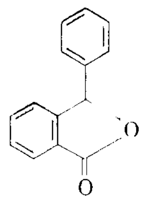
X



XI



XII



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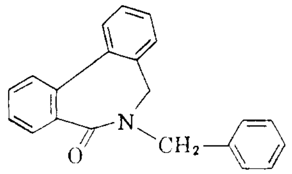

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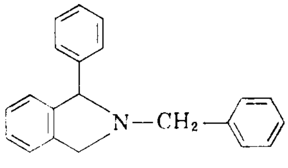

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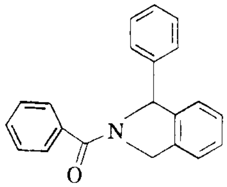
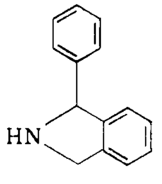
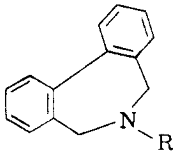


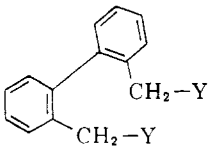
XVI



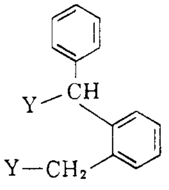
XVII



XVIII



XIX



XX

from X by electrophilic ring closure, and 1-phenyl-2-benzoylisoindoline (XVI), which could be formed by electrophilic ring closure into the benzyl ring in the presumed intermediate XI. These compounds would also be expected from free radical ring closures, in the event that the alternative hydrogen *atom* transfer obtains in this reaction. *A priori*, the first possibility appeared the less likely since seven-member ring formation in Pschorr type reactions is apparently unknown.[11] The belief that XVI represents the structure of the 115° material was strengthened by the isolation of benzoic acid from the hydrolysis of this compound in 9 *M* sulfuric acid. However, lithium aluminum hydride reduction of this substance gave a liquid base, the infrared spectrum of which was similar but not identical to that of the solid amine, 1-phenyl-2-benzylisoindoline (XV) obtained by similar reduction of XII. Confirming evidence that the unknown compound is not XVI was obtained by an independent synthesis of the latter proceeding from *o*-hydroxymethylbenzhydrol (XX; Y = OH), itself obtained by reduction of *o*-benzoylbenzoic acid. The glycol (XX; Y = OH) was converted by the use of thionyl chloride to the dichloride[17] (XX; Y = Cl), which yielded 1-phenylisoindoline (XVII) upon treatment with anhydrous ammonia. Benzoylation of XVII produced XVI, which was shown to differ from the unknown substance. The structure of XVI was verified by demonstrating that its reduction product was identical to XV, which had been obtained earlier from the reduction of the phthalimidine (XII). The possibility that the reduction of XII with lithium aluminum hydride had proceeded with rearrangement was precluded by preparing the reduction product XV independently from the dichloride XX (Y = Cl) and benzylamine.

The structure of the unknown product was finally established as the seven-member heterocyclic system XIV by demonstrating the identity of its lithium aluminum hydride reduction product, 6-benzyl-6,7-dihydro-5*H*-dibenz[*c,e*]azepine (XVIII; R = $C_6H_5CH_2$), to an authentic sample[12] prepared by the reaction of benzylamine with *o,o'*-bis(bromomethyl)biphenyl (XIX; Y = Br). The latter had been prepared previously by the action of *N*-bromosuccinimide on *o*-ditolyl,[12] but in this study it was obtained more conveniently by hydrogen bromide treatment of the glycol XIX (Y = OH), which results from the reduction of diphenic acid with lithium aluminum hydride. The only other amide capable of conversion to XVIII (R = $C_6H_5CH_2$) under these conditions is 6-benzoyl-6,7-dihydro-5*H*-dibenz[*c,e*]azepine (XVIII; R = C_6H_5CO). However, this substance was prepared by benzoylation of XVIII (R = H), obtained by treatment of XIX (Y = Br) with ammonia and it was shown to be distinctly different from the deamination product, the structure of which is thus rigorously established as XIV. The benzoic acid obtained by treatment of XIV with sulfuric acid must have resulted from the

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[11] For two recent reviews of the Pschorr reaction, see ref. 5 and P. H. Leake, *Chem. Rev.*, **56**, 27 (1956).

[12] W. Wenner, *J. Org. Chem.*, **17**, 1451 (1952).

TABLE I

PRODUCT YIELDS IN THE DECOMPOSITION OF THE DIAZONIUM ION DERIVED FROM I (R = C_6H_5)

Experimental conditions[a]	Yields, %					
	XII	XIV	II (R = C_6H_5)	Benzaldehyde[b]	Phenol	Total recovery[c]
45°	3	10	28	26	44	85
Steam bath	3	15	32	30	41	91
Steam bath, benzenethiol[d]	4	17	29	26	45	95
Steam bath, *m*-dinitrobenzene[e]	3	15	32	30	45	95

[a] In all cases, 5.0 mmoles of I (R = C_6H_5) was diazotized in 30 ml. of 2 *N* sulfuric acid in glacial acetic acid. [b] Estimated by correcting the yield of 2,4-dinitrophenylhydrazone for incomplete conversion to this derivative. [c] Since one mole of benzaldehyde is produced for each mole of amide (II), the yield of benzaldehyde is not included in the total recovery. [d] About 7 mmoles. [e] 1.0 mmole.

oxidation of the benzyl to a benzoyl group followed by hydrolysis.

This is apparently the first case of seven-member ring formation in a Pschorr type reaction.

The yields of the thermal decomposition products of the diazonium salt derived from *o*-amino-*N*,*N*-dibenzylbenzamide are shown in Table I. The product composition is essentially unaltered by the presence of either of the free radical chain inhibitors used. Furthermore, *N*,*N*-dibenzylbenzamide, the expected product of hydrogen atom abstraction by the radicals VIII or IX (R = C_6H_5) is not isolated even in the presence of 140 mole per cent of the powerful hydrogen atom donor, benzenethiol. It was demonstrated in separate experiments that this tertiary amide would have been detected had it been present in any appreciable quantity. The formation of the ring closed compounds, XII and XIV, might be a further indication of the ionic nature of the thermal reaction since preliminary experiments now underway in this laboratory indicate that these ring compounds are not formed when the decomposition of this diazonium ion is catalyzed by copper metal or cuprous chloride. The catalyzed reactions are usually considered to proceed *via* free radical intermediates,[13] and our isolation of substantial quantities of *N*,*N*-dibenzylbenzamide when the copper-catalyzed reaction is performed in the presence of benzenethiol lends support to this hypothesis.

The relative insensitivity of product composition to temperature is probably a reflection of the great instability of the phenyl cation[14] and the consequent low activation energies necessary for its various transformations.

The absence of 1-phenyl-2-benzoylisoindoline (XVI) among the reaction products is noteworthy. The ion XI might be expected to undergo an electrophilic ring closure at the *ortho* position of the benzyl ring rather than at the corresponding position of the deactivated benzoyl ring. That only the latter occurs could be attributed to the proximity of the *ortho* position of the benzoyl ring to the positive carbon atom. This proximity would be imposed by the planarity that is expected among the five atoms involved in ring formation, such planarity being necessary for effective resonance interaction. Another possibility is that the ring closure either very closely follows or is concomitant with the hydrogen transfer step. Experiments designed to distinguish between these possibilities are planned.

Experimental[15]

Deaminations of *o*-Amino-*N*,*N*-dibenzylbenzamide.—The preparation of this substance has been described.[1] The deaminations reported in the table were performed according to the following general procedure. The reaction medium, a solution of 2 *N* sulfuric acid in acetic acid, was prepared by diluting 27.8 ml. of concentrated sulfuric acid to 500 ml. with glacial acetic acid. A solution of 1.58 g. (5.0 mmoles) of pure *o*-amino-*N*,*N*-dibenzylbenzamide (m.p. 131.5–132.5°) in 30 ml. of this medium was diazotized at 16° by stepwise addition, with stirring of 0.345 g. (5.0 mmoles) of pulverized sodium nitrite. During the addition, the color of the solution changed from very pale yellow to pale yellow-green. The several crystals of sodium nitrite which remained undissolved at 16° went into solution as the latter was allowed to warm to room temperature. A very small quantity of urea was found to be sufficient to destroy excess nitrous acid. In runs in which a radical inhibitor was to be used, it was added at this stage. In the benzenethiol experiment. 20 drops (*ca.* 7 mmoles), was used. In the *m*-dinitrobenzene experiment, 0.168 g. (1.00 mmole) was used. The reaction mixture was then heated in a water bath at 45° or in a rapidly boiling steam bath. In the 45° run, nitrogen evolution was slow, and the reaction was allowed to continue for 4 hr., after which no noticeable gas evolution was occurring. In the steam bath experiments, gas evolution started slowly at 45° and was vigorous at 75°. The reaction was stopped after 1 hr., when gas was no longer being evolved.

After the reaction mixture had cooled to room temperature, water was added (about 20 ml.) to give a permanent cloudiness and the mixture was allowed to remain at room temperature for 1 hr. in order to hydrolyze any acetates. Enough sulfuric acid–acetic acid solution (10 ml.) to homogenize the suspension was added. To a one-fifth aliquot of this solution was added an excess of a freshly prepared saturated solution of 2,4-dinitrophenylhydrazine in acetic acid. After standing overnight, this was filtered and the precipitated 2,4-dinitrophenylhydrazone of benzaldehyde was dried and weighed; it had m.p. 237–239°. In the calculation of the yield of benzaldehyde, the weight of this derivative was corrected in accordance with the results of control runs in which it was determined that a 74% yield of the 2,4-dinitrophenylhydrazone could be isolated in this way from solutions in which the quantity of benzaldehyde was known.

A solution of the remaining four fifths of the reaction mixture, dissolved in 200 ml. of ether, was shaken with sufficient 0.5 *N* sodium hydroxide solution to neutralize all of the acids present. The aqueous phase was then shaken with

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[13] H. Zollinger, "Diazo and Azo Chemistry," Interscience Publishers, Inc., New York, 1961, pp. 159–168.

[14] E. S. Lewis, *J. Am. Chem. Soc.*, **80**, 1371 (1958).

[15] Melting points were determined on a Kofler block with a stage calibrated thermometer and they are therefore corrected. Infrared spectra were determined with a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. Microanalyses were performed by Alfred Bernhardt, Max-Planck-Institut für Kohlenforschung, Mulheim, Ruhr, Germany, and by Galbraith Laboratories, Knoxville, Tennessee.

four portions of ether, acidified with sulfuric acid, and extracted with four more portions of ether. All of the ether extracts were combined, dried over sodium sulfate, and evaporated under reduced pressure. The red oily residue was dissolved in the minimum quantity of benzene and adsorbed on an alumina column (1.5 × 40 cm., 110 g. Fisher alumina).

In the benzenethiol run, the additive was oxidized, presumably during the alkaline treatment in the work-up procedure, to diphenyldisulfide, which was eluted from the column with benzene. When *m*-dinitrobenzene was used, it was also eluted by benzene before any of the other reaction products. Elution with ether–benzene (4:1) gave a colorless oily fraction. Elution with ether containing 1% of ethanol, gave a colorless solid, m.p. 95–105°, of *N*-benzylbenzamide, identified by comparison of its infrared spectrum with that of an authentic sample[1] and a melting point of the recrystallized (benzene–petroleum ether) product, m.p. 104.5–105.5°, alone or mixed with the authentic sample of the same melting point. Further elution with ethanol, followed by 50% aqueous ethanol yielded fairly pure (according to its infrared spectrum) *N*,*N*-dibenzylsalicylamide,[1] m.p. 140–145°. The latter was contaminated with a trace of orange oil.

The colorless oily fraction which had been eluted first was rechromatographed on a similar column of Fisher alumina and eluted with successive 100-ml. portions of 10, 20, 30, and 40% ether in benzene. The more easily eluted, and minor, component was a colorless solid, m.p. 123–124°, alone or mixed with the authentic sample of 1-phenyl-2-benzylphthalimidine (XII), prepared as below. The infrared spectrum of this compound (carbonyl band at 1671 cm.$^{-1}$ in chloroform) was identical to that of the authentic specimen. The more difficultly eluted, major component of this oil had m.p. 90–110°. Recrystallization from ether gave colorless needles, m.p. 115–116°, shown below to be 6-benzyl-6,7-dihydro-5*H*-dibenz[*c,e*]azepine-7-one (XIV).

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.24; H, 5.73; N, 4.68. Found: C, 84.07; H, 5.88; N, 4.74.

The infrared spectrum of this material exhibited a strong absorption at 1620 cm.$^{-1}$. A solution of bromine in chloroform was not decolorized by the compound. A suspension of 40 mg. of this substance in 3 ml. of 9 *M* sulfuric acid was heated on a water bath for 3 hr. The mixture was then made alkaline by the addition of excess 5% aqueous sodium carbonate solution and extracted with ether. The aqueous layer was reacidified and extracted with ether. The latter extract was dried with sodium sulfate and evaporated to yield 16 mg. of crude white solid which was recrystallized from hot water to give 13 mg. (80% yield) of benzoic acid, m.p. 121–122°, alone or mixed with an authentic sample, m.p. 121–122°. The ether extract from the basic layer yielded an oil exhibiting a strong infrared band at 1634 cm.$^{-1}$.

Reduction of 6-Benzyl-6,7-dihydro-5*H*-dibenz[*c,e*]-azepine-7-one (XIV).—A solution of 147.0 mg. (0.492 mmole) of XIV in 10 ml. of anhydrous tetrahydrofuran was added dropwise to a stirred suspension of 0.15 g. (3.98 mmoles) of lithium aluminum hydride in 20 ml. of tetrahydrofuran and the mixture was refluxed for 2 hr. The pale purple color of the refluxing mixture disappeared upon cooling to room temperature. The excess hydride was destroyed by the addition of 5 ml. of saturated sodium chloride solution. After the addition of a further 25 ml. of water, the mixture was filtered and the filtrate extracted with two portions of ether. After drying with potassium carbonate, the ether was evaporated under vacuum to yield 141 mg. of pale yellow oil. The infrared spectrum of this oil no longer exhibited an amide carbonyl band and was identical to that of an authentic sample of 6-benzyl-6,7-dihydro-5*H*-dibenz[*c,e*]azepine prepared as below.

The hydrobromide of this base was prepared by adding several drops of 47% hydrobromic acid to a solution of the oil in 20 ml. of ether. The colorless precipitate which formed immediately had m.p. 205–207°, after recrystallization from ethanol–ether. The melting point was undepressed on admixture with an authentic specimen of the same melting point (see below) and the infrared spectra (Nujol) of the two samples were identical.

***o,o'*-Bis(hydroxymethyl)biphenyl (XIX; Y = OH).**—A solution of 2.21 g. (9.1 mmoles) of diphenic acid in 200 ml. of anhydrous ether was added dropwise to a magnetically stirred slurry of 1.00 g. (26.4 mmoles) of lithium aluminum hydride in 80 ml. of ether. During this addition and the subsequent reflux period of 2.5 hr., a nitrogen atmosphere was maintained over the mixture. The excess reducing agent was destroyed with excess sodium chloride solution, and the mixture was filtered through Celite on a sintered glass funnel. The filtrate was extracted with two portions of 3 *N* sodium hydroxide solution. Acidification of these extracts yielded no unchanged starting material. The ether layer was washed once with water, dried over sodium sulfate and evaporated to dryness. The colorless solid residue was recrystallized from benzene to give 1.21 g. (5.65 mmoles, 62% yield) of pure glycol, m.p. 104–106°, the infrared spectrum of which exhibited no carbonyl absorption.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.46; H, 6.58. Found: C, 78.32; H, 6.51.

6-Benzyl-6,7-dihydro-5*H*-dibenz[*c,e*]azepine (XVIII; R = C_6H_5—CH_2).—A mixture containing 1.00 g. (4.7 mmoles) of *o,o'*-bis(hydroxymethyl)biphenyl and 20 ml. of 47% aqueous hydrobromic acid was heated on a steam bath for 16 hr. and finally heated at reflux for 1 hr. After cooling to room temperature, the mixture, which contained no solid, was extracted with two portions of chloroform. Evaporation of the dried (sodium sulfate) extracts produced 1.58 g. of crude *o,o'*-bis(bromomethyl)biphenyl (XIX; Y = Br) as a colorless oily solid. This was converted to 0.63 g. (2.2 mmoles, 47% yield) of pale yellow oily XVIII (R = C_6H_5—CH_2) by the method of Wenner[12] using 2.0 ml. of benzylamine in 20 ml. of benzene. The hydrobromide was prepared as above. Recrystallization of this salt from ethanol–ether provided colorless crystals, m.p. 205–207° (lit.,[12] m.p. 196–197°, uncor.).

6-Benzoyl-6,7-dihydro-5*H*[*c,e*]azepine (XVIII; R = C_6H_5CO).—Another sample (1.22 g.) of the crude *o,o'*-bis(bromomethyl)biphenyl was mixed with 30 ml. of anhydrous ammonia in a stainless steel bomb which had been cooled in a Dry Ice–acetone mixture. The bomb was sealed and heated in a steam bath for 1 hr. After cooling, the bomb was opened and the excess ammonia was allowed to evaporate. The solid residue was equilibrated between water and ether, and the mixture was filtered to remove a small quantity of insoluble tan solid. The aqueous phase was discarded and the ether phase was extracted with two portions of 1.0 *N* hydrochloric acid. The combined acidic extract was made basic and extracted with three portions of ether. Evaporation of the dried (sodium sulfate) extracts yielded 0.40 g. of crude 6,7-dihydro-5*H*-dibenz[*c,e*] azepine (XVIII; R = H) as a pale yellow oil. The latter was shaken vigorously with 1 ml. of benzoyl chloride suspended in 20 ml. of 3 *N* sodium hydroxide. Extraction of this mixture with three portions of ether yielded 0.61 g. of a yellowish solid. Recrystallization from ether–benzene gave 0.57 g. of colorless XVIII (R = C_6H_5CO), m.p. 144.5–146°, exhibiting a carbonyl band in its infrared spectrum in chloroform at 1613 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.48; H, 5.72; N, 4.68. Found: C, 84.72; H, 6.01; N, 4.40.

A mixture with a sample of the amide, m.p. 115–116°, isolated from the thermal decomposition of the diazonium salt, had m.p. 100–105°. The infrared spectra of the two substances were distinctly different.

1-Phenyl-2-benzylphthalimidine (XII).—A solution of 1.041 g. (4.96 mmoles) of 1-phenylphthalide[9,16] and 0.710

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(16) A. Pernot and A. Willemart, *Bull. soc. chim. France*, 321 (1953).

g. (4.95 mmoles) of benzylamine hydrochloride in 10 ml. of freshly distilled benzylamine was refluxed under nitrogen for 48 hr. After the solution had cooled to room temperature, excess dilute hydrochloric acid was added and the mixture was extracted with three portions of methylene chloride. Evaporation of the extract produced 5.0 g. of a yellow-brown oil. This was dissolved in a minimum quantity of benzene and chromatographed on Fisher alumina (100 g.), using benzene–ether (3:2) as eluent. The white crystalline material obtained in this way was recrystallized from benzene–petroleum ether to yield 0.597 g. (1.99 mmoles, 40%) of 1-phenyl-2-benzylphthalimidine, m.p. 123–124°.

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.24; H, 5.73; N, 4.68. Found: C, 84.05; H, 5.59; N, 4.53.

Reduction of 1-Phenyl-2-benzylphthalimidine (XII).—A solution of 3.62 g. (12.1 mmoles) of XII in 20 ml. of dry tetrahydrofuran was added dropwise to a slurry of 2.07 g. (55 mmoles) of lithium aluminum hydride in 100 ml. of tetrahydrofuran, and the mixture was heated at reflux for 2 hr. An excess of saturated aqueous sodium chloride was added, dropwise at first, to the cooled reaction mixture and it was then filtered. Extraction of the filtrate with ether yielded a dark red solid, the infrared spectrum of which indicated that the reduction was very incomplete. A portion of this substance was dissolved in ether and extracted with dilute hydrochloric acid. The aqueous layer was made basic and extracted with ether. Evaporation of the dried (sodium sulfate) extract produced a green solid, m.p. 65–96°. After one recrystallization from *n*-pentane and one from ethanol–water, the m.p. was 94–97.5°. The analytical sample, m.p. 97–99°, was prepared by two further recrystallizations from the same solvent.

Anal. Calcd. for $C_{21}H_{19}N$: C, 88.37; H, 6.71; N, 4.91. Found: C, 88.50, 88.45; H, 6.69, 6.82; N, 4.90, 4.93.

The infrared spectrum was identical to that of a sample of 1-phenyl-2-benzylisoindoline (XV) prepared as described below.

2-Hydroxymethylbenzhydrol (XX; Y = OH).—A solution of 6.8 g. (30 mmoles) of *o*-benzoylbenzoic acid in 100 ml. of anhydrous ether was added dropwise to a slurry of 1.5 g. (40 mmoles) of lithium aluminum hydride in 75 ml. of anhydrous ether. The magnetically stirred mixture was allowed to reflux in a nitrogen atmosphere for 3.5 hr. After the careful addition of an excess of saturated sodium chloride solution, the metal salts were removed by filtration through Celite on a sintered glass funnel. The solution was extracted with three portions of ether. The combined extract was washed with aqueous sodium hydroxide, dried over sodium sulfate, and evaporated. The residual, yellowish, oily solid was recrystallized twice from carbon disulfide to yield 4.46 g. (21 mmoles, 70% yield) of colorless crystals, m.p. 71–72° (lit.,[12] m.p. 76°).

1-Phenyl-2-benzoylisoindoline (XVI).—A solution of 3.25 g. of crude 2-chloromethylbenzhydryl chloride (XX; Y = Cl), prepared from 3.24 g. (15 mmoles) of the above glycol (XX; Y = OH) by the method of Pernot and Willemart,[17] in 30 ml. of anhydrous ammonia was heated in a stainless steel bomb on a steam bath for 1 hr. The bomb was cooled in a Dry Ice–acetone mixture, it was opened, and the ammonia was allowed to evaporate. The residue was equilibrated between water and ether and the aqueous layer was extracted with two further portions of ether. The organic phase was extracted with two portions of 1 *N* hydrochloric acid. The clear acidic solution was made basic with 3 *N* sodium hydroxide, and the cloudy mixture was extracted with three portions of ether. The dried (sodium sulfate) extract was evaporated to yield 1.91 g. of green oil. Benzoylation by the Schotten-Baumann method gave a brown-green solid which, after recrystallizations from benzene, ethyl acetate, and ether, yielded 1.04 g. (3.5 mmoles, 23% yield) of 1-phenyl-2-benzoylisoindoline, m.p. 149.0–149.5°. It exhibited a carbonyl absorption at 1631 cm.$^{-1}$ in its infrared spectrum (chloroform).

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.48; H, 5.72; N, 4.68. Found: C, 84.51; H, 5.69; N, 4.68.

1-Phenyl-2-benzylisoindoline (XV).—A solution containing 0.99 g. (4.0 mmoles) of 2-chloromethylbenzhydryl chloride (preparation described directly above) and 2 ml. of benzylamine in 10 ml. of chloroform was heated at reflux for 45 min. and then cooled. The mixture, containing precipitated benzylamine hydrochloride, was vigorously shaken for 0.5 hr. with 5 ml. of benzoyl chloride and excess 10% aqueous sodium hydroxide. The mixture was extracted with two portions of ether and the organic extract was extracted with two portions of 1.0 *N* hydrochloric acid. The acidic solution was made basic with 3.0 *N* sodium hydroxide solution and extracted with three portions of ether. Evaporation of the dried (sodium sulfate) ether and recrystallization of the colorless residue from ethanol gave 0.28 g. (0.98 mmole, 25% yield) of XV, m.p. 94–97°.

Reduction of 1-Phenyl-2-benzoylisoindoline (XVI).—A solution of 240 mg. (0.80 mmole) of 1-phenyl-2-benzoylisoindoline in 25 ml. of dry tetrahydrofuran was added dropwise during a 5-min. period to a refluxing suspension of 300 mg. (7.9 mmoles) of lithium aluminum hydride in 50 ml. of the same solvent. The magnetically stirred mixture was allowed to reflux in a nitrogen atmosphere for 1 hr. Saturated aqueous sodium chloride solution was added cautiously to the cooled mixture in order to decompose the excess reducing agent. The metal salts were removed by filtration through Celite on a sintered glass funnel. The filtrate was extracted with three portions of ether, and the ether extract with two portions of 1.0 *N* hydrochloric acid. The acid solution was made basic with 3.0 *N* sodium hydroxide solution and extracted with three portions of ether. Evaporation of the dried (sodium sulfate) extract produced a small quantity of solid which was recrystallized from ethanol to give a few milligrams of colorless 1-phenyl-2-benzylisoindoline, m.p. 94–97°. Its infrared spectrum was identical to those of the two independently prepared samples.

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(17) A. Pernot and A. Willemart, *Bull. soc. chim. France*, 324 (1953).