isopropyl-, *m*-diisopropyl- and 1,3,5-triisopropylbenzenes, which have been omitted from Fig. 1 to avoid crowding of data, lie close to the points for the ethyl analogs.

Thermodynamic Constants for the Argentation Reactions.—Values of $\Delta H°$ for a few of the argentation reactions have been calculated from equilibrium constants determined at 1.6 and 25.0°. These and the changes in free energy and entropy accompanying the interactions at 25° are recorded in Table III. These values encompass the process of silver ion desolvation which accompanies complex formation,[18] and only the changes in constants resulting from changes in donor structure are significant in this discussion.

In the absence of pronounced alkyl group steric effects, $\Delta H°$ for the interaction of halogens[1,2] with polyalkylbenzenes becomes increasingly negative as the number of donor substituents increases. Parallel decreases in $\Delta F°$ and $\Delta S°$ occur, and these changes are linear with those in $\Delta H°$. With the highly hindered donors, hexaethylbenzene and 1,3,5-tri-*t*-butylbenzene, $\Delta H°$, $\Delta S°$ and $\Delta F°$ are all abnormally small in magnitude. Apparently in these two cases the complexed halogen molecules are held outside the steric barrier at a distance such that they can interact only feebly with the electrons of the donor molecule.

TABLE III

HEAT, FREE ENERGY AND ENTROPY CHANGES ACCOMPANYING AROMATIC-SILVER ION COMPLEX FORMATION IN EQUIMOLAR WATER–METHANOL SOLUTION

Compound	$-(\Delta H°)$ at 1.6, 25.0°, kcal.	$-(\Delta F°)$ at 25.0°, kcal.	$-T(\Delta S°)$ at 25.0°, kcal.	$-(\Delta S°)$ at 25.0°, cal./deg.
Benzene	2.86	0.06	2.80	9.40
Toluene	2.72	.11	2.61	8.77
Mesitylene	2.93	− .14	3.07	10.3
1,3,5-Tri-*t*-butylbenzene	3.29	− 67	3.96	13.3
Hexamethylbenzene	3.45	− .27	3.72	12.5

The $-\Delta H°$ values for argentation reported in Table III show a slight upward trend with increasing alkylation of the donor nucleus which is paralled by a corresponding increase in $-\Delta S°$ values. The variations in $\Delta F°$ with $\Delta H°$ show no regularity. The coördination of silver ion with the highly hindered donor, tri-*t*-butylbenzene, is accompanied by a larger entropy loss than is that with less hindered donors. It seems likely, therefore, that in the argentation reaction, contrary to what is observed for halogen complex formation, as steric repression to interaction becomes more pronounced, the complex components are subject to more rigid spatial requirements. There is no indication that the distance of separation of silver ion and the aromatic nucleus in the complex is greatly dependent on the number and size of alkyl substituents on the donor ring.

Acknowledgment.—The authors are indebted to Research Corporation and to the National Science Foundation for grants in support of this research.

DAVIS, CALIFORNIA

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[18] S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Benzil–Ammonia Reaction

BY ERNEST WENKERT AND ARLEN B. MEKLER

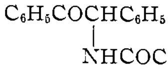
RECEIVED OCTOBER 29, 1955

The reaction of benzil with ammonia is interpreted as involving the ionic cleavage of benzil–ammonia complexes containing two benzil units. The structural elucidation of imabenzil, the one as yet unknown product of the reaction, is presented.

The action of ammonia on benzil, leading to a variety of products, has been known for over a century.[1] With the exception of imabenzil, a C_{35}-compound, the structures of all reaction products are well understood. Depending on the temperature, time and solvent of the reaction, various combinations of the following products have been isolated: ammonium benzoate (Ia), ethyl benzoate (Ib), benzamide (Ic), N-desylbenzamide (II), imabenzil and the three aromatic heterocycles 2,4,5-triphenyloxazole (IIIa), 2,4,5-triphenylimidazole (IIIb) and 2,3,5,6-tetraphenylpyrazine (IV).

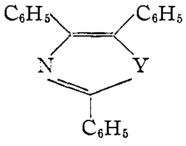
C_6H_5COY

Ia, $Y = O^{\ominus}, NH_4^{\oplus}$
b, $Y = OEt$
c, $Y = NH_2$

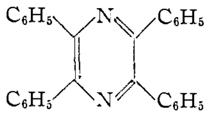


$$C_6H_5CO\underset{\displaystyle NHCOC_6H_5}{\underset{|}{C}}HC_6H_5$$

II



IIIa, Y = O b, Y = NH



IV

In previous discussions of the mode of formation of compounds I–III, it has been suggested that a solvolytic cleavage of the central carbon–carbon bond in benzil is reponsible for the production of the benzoic acid derivatives of structure I[1a,c] and that the accompanying benzaldehyde

$$C_6H_5COCOC_6H_5 + HY \longrightarrow C_6H_5COY + C_6H_5CHO$$

becomes the precursor of II and III because of its reaction with benzil and ammonia.[1a] An alternate proposal[1b] involved the solvolytic cleavage of a carbon–carbon bond in a benzil–ammonia complex, an "internal Cannizzaro reaction" of the interme-

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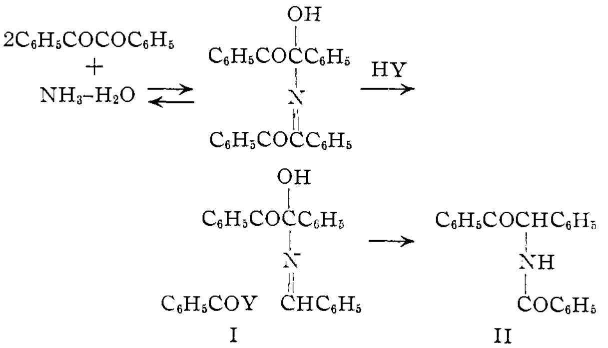
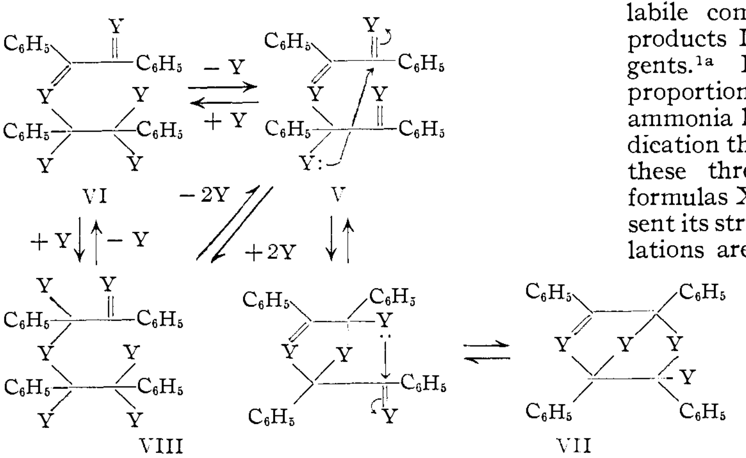
[1] (a) For a complete review of the literature *cf.* R. H. Wiley, *Chem. Revs.*, **37**, 415 (1945). For the most recent contributions on this subject *cf.* (b) D. Davidson, M. Weiss and M. Jelling, *J. Org. Chem.*, **2**, 319 (1937); (c) W. B. Leslie and G. W. Watt, *ibid.*, **7**, 73 (1942).

diate and the transformation of N-desylbenzamide (II) or its imine into III. Finally, the origin of IV has been ascribed to the possible presence of a benzoin impurity in benzil.[1c] However, in view of the mechanistically unprecedented nature of either of the suggested reaction paths the benzil–ammonia reaction requires reinterpretation.

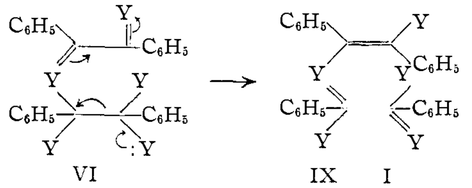


Davidson has indicated already[1b] that the type of products obtained suggests strongly that the reaction proceeds by way of disproportionations of complexes containing more than one benzil unit. In fact, Davidson's own complex of two benzil units (*vide supra*), expressed in general terms by V, is most suitable for the portrayal of the formation of all products by a *formally single, ionic mechanism.*[2]

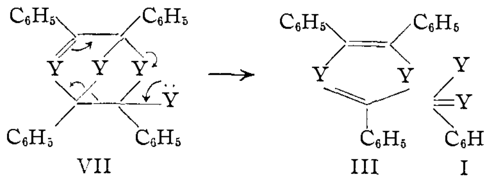
Just as benzil and ammonia are in ready equilibrium with V,[1b] the latter can be assumed to hold the same relationship with many solvent or ammonia adducts as well as many intermediates derived by intramolecular interaction of polar groups. Thus, from among the many variants, intermediates VI, VII and VIII can be cited for further consideration.



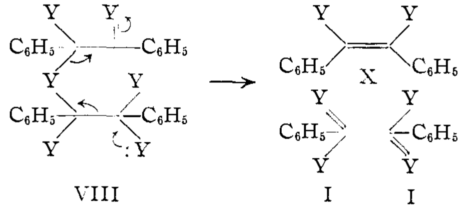
An irreversible disproportionation of complex VI leads to benzoic acid derivatives I as well as IX, a tautomer of N-desylbenzamide (II)



While N-desylbenzamide may be indeed the precursor of the heterocycles III, they are derivable by direct route through the decomposition of complex VII



Finally, the rupture of complex VIII leads to benzoic acid derivatives I again as well as X, a tautomer of benzoin or its nitrogen counterparts



Compounds X would yield the pyrazine IV on condensation with ammonia and benzil in close analogy to the known formation of a dihydropyrazine by the ammonolysis of benzoin.[3,4]

Imabenzil, the product of high molecular weight of the action of ammonia on benzil, was shown to possess the composition $C_{35}H_{28}O_3N_2$ and to be a very labile compound, readily decomposing into the products I–III in the presence of the mildest reagents.[1a] Its conversion by acids into equimolar proportions of N-desylbenzamide (II), benzil and ammonia has been interpreted in the past as an indication that it is basically a dehydrated complex of these three compounds.[1a,b] As a consequence, formulas XI–XIV have been put forward to represent its structure.[1a,b] Unfortunately all these formulations are suspect because they suffer from the common difficulty of containing two sites of lability, any one of which consists of a functional group more unstable than a hemiketal or carbinolamine. Thus, a reinvestigation of the chemistry of imabenzil became necessary.

It appeared at first that a repetition of some of the more crucial reactions of imabenzil, a study of its reducibility and an inspec-

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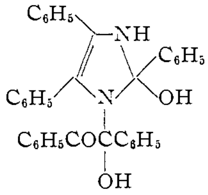
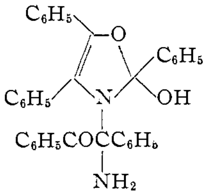
(2) The use of Y in place of O, OH, N, NH and NH_2 in the succeeding formulas has been introduced for the purpose of simplifying the discussion and emphasizing the generality of the described chemical changes. For further simplification all ionic charges have been omitted, but are to be understood to be involved in essentially all ensuing transformations and generally accompanied by hydrogen transfer reactions.

(3) D. Davidson, M. Weiss and M. Jelling, *J. Org. Chem.*, **2**, 328 (1937). Benzoindam, the $C_{28}H_{22}O_2N$ product of unassigned structure of the benzoin–ammonia reaction, is most probably didesylamine.

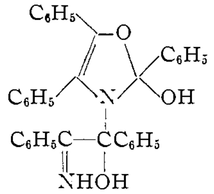
(4) It must be emphasized that complexes VI, VII and VIII have been chosen arbitrarily in order to depict most easily the irreversible processes leading to known products. This, however, may be done with impunity for the reasons that any variants of VI–VIII would have the same relation to V as do the latter and, furthermore, their break-up to products could be portrayed by pathways similar to those described above.



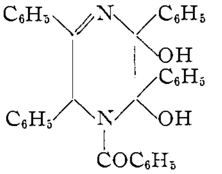
XI



XII



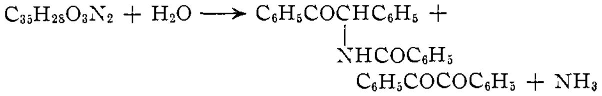
XIII



XIV

tion of its infrared absorption spectrum would aid greatly in the elucidation of its structure. Furthermore, it was felt that, if the compound be indeed a benzil–ammonia–N-desylbenzamide complex, it most likely would contain only one active site, such as a carbinolamine or hemiketal, which, however, on opening during a reaction, could liberate other such centers and thus completely unravel the compound.

In general conformity with previous results,[1a] aqueous sulfuric acid hydrolysis of imabenzil yielded 50% N-desylbenzamide (II) and 87% benzil, based on the stoichiometry

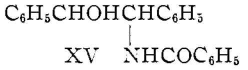


$$C_{35}H_{28}O_3N_2 + H_2O \longrightarrow C_6H_5CO\underset{NHCOC_6H_5}{\underset{|}{C}}HC_6H_5 + C_6H_5COCOC_6H_5 + NH_3$$

while a sodium hydroxide treatment produced a 75% yield of II, a 76% yield of benzil and a trace of the triphenyloxazole IIIa.

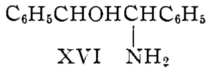
Data pertaining to the thermal decomposition of imabenzil also agreed in general with those of previous workers.[1a] Thus, pyrolysis of imabenzil without solvent yielded a mixture of N-desylbenzamide (II) and its cyclic derivatives IIIa and IIIb. When an ethanolic solution of imabenzil was refluxed for 15 hours, a mixture was obtained, consisting mostly of II and smaller amounts of Ic, IIIb and benzil. It was of interest that the yield of N-desylbenzamide (II) amounted to 112%, if based on the potential formation of one mole of II for every mole of imabenzil. If the hydrolysis data above are taken as a strong suggestion that imabenzil is indeed a complex of N-desylbenzamide, benzil and ammonia, then both the high yield of II and the apparently anomalous appearance of benzamide (Ic) in the decomposition reaction of imabenzil become apparent. The decomposition must lead not only to II but also to benzil and ammonia or a complex thereof which would be expected to disproportionate by pathways, already described, to more N-desylbenzamide (II) as well as benzamide (Ic).

Both sodium borohydride reduction and catalytic hydrogenation of imabenzil led to a mixture of two isomeric $C_{21}H_{19}O_2N$ compounds. They were recognizable as the epimeric 1,2-diphenyl-2-benzamidoethanols (XV) by the fact that they were identical with the two products obtained by catalytic hydrogenation of N-desylbenzamide (II). The compound melting at 239–240° proved to be the *erythro* product because of its ready acid-catalyzed conversion to the 215–216° product. The latter, consequently the *threo* product, was not affected by the same process.[5] Furthermore, both compounds could be hydrolyzed with alkali to the epimeric 1,2-diphenyl-2-aminoethanols (XVI), the former yielding the *erythro* product and the latter its *threo* counterpart.[6]



$$C_6H_5CHOH\underset{NHCOC_6H_5}{\underset{|}{C}}HC_6H_5$$

XV



$$C_6H_5CHOH\underset{NH_2}{\underset{|}{C}}HC_6H_5$$

XVI

The catalytic hydrogenation of imabenzil appeared anomalous at first in view of the uptake of nearly two moles of hydrogen per mole of starting material and the formation of more than 100% of the mixture of dihydro-N-desylbenzamides (XV), based on an expected 1:1 molar ratio of products to imabenzil. However, both facts can be rationalized by assuming that the benzil–ammonia complex, liberated during the reduction of the N-desylbenzamide moiety in imabenzil to its dihydro products XV, undergoes disproportionation to yield more imabenzil (or N-desylbenzamide) which by further reduction keeps repeating the cycle. Since the disproportionation requires the formation also of compounds I, the discovery of ethyl benzoate (Ib) as the third product of the hydrogenation lends strong support to the proposed reaction sequence. An alternate reaction path, *viz.*, decomposition of imabenzil to N-desylbenzamide (III) and benzil–ammonia, followed by the hydrogenation of the former and disintegration of the latter, was refuted when it was demonstrated that imabenzil remained intact on exposure to the catalytic hydrogenation conditions in the absence of hydrogen.

The infrared spectrum of imabenzil revealed a weak NH peak at 3.01 μ and maxima at 6.12, 6.22, 6.34, 6.55 and 6.65 μ, characteristic of benzamido and phenyl absorption. The presence of only a single band in the 2.8–3.2 μ region, implies that only one of the two dissimilar nitrogen atoms has a hydrogen attached to it. The complete superimposability of the 6.0–6.7 μ region on that of N,N-dimethylbenzamide would suggest that the benzamido nitrogen in imabenzil is dialkylated and hence that the "ammonia" nitrogen is part of the NH grouping. Finally, the lack of any 5.9 μ band indicates that the aromatic-ketonic functions of both the benzil and N-desylbenzamide moieties of imabenzil are masked.

The experimental data now permit the assignment of partial structure XVII to the C_{35}-compound. Thus, the N-desylbenzamide fraction (A) must have its ketonic group masked by two single-bonded oxygen atoms, in order to account for the formation of both diastereomeric dihydro-N-desylbenzamides (XV) and lack of formation of any di-

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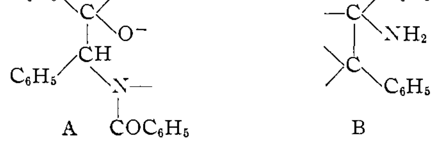
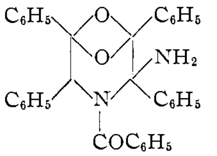
[5] For discussions relating to the acid-catalyzed interconversions of vicinal diastereomeric acylamino alcohols *cf. inter alia*, G. E. McCasland, R. K. Clark, Jr., and H. E. Carter, THIS JOURNAL, **71**, 637 (1949); L. H. Welsh, *ibid.*, **71**, 3500 (1949); G. Fodor, V. Bruckner, J. Kiss and G. Óhegyi, *J. Org. Chem.*, **14**, 337 (1949).

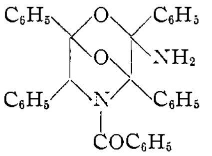
[6] For configurational assignments and physical constant data for the 1,2-diphenyl-2-aminoethanols *cf.* D. J. Cram and F. A. Abd Elhafez, THIS JOURNAL, **74**, 5828 (1952); A. McKenzie and D. C. Pirie, *Ber.*, **69B**, 876 (1936); and references contained in both papers.

nitrogenous compounds upon reduction of imabenzil. The benzamido group of fraction A must possess an unmasked carbonyl group and have its nitrogen bonded to fraction B. The latter structural requirement is based on spectral evidence as well as the fact that, were it not accepted, A and B would be attached to each other only *via* the ketal oxygens, a consequence of which would be a highly improbable structure for imabenzil. The benzil–ammonia portion B can hold only one function, *i.e.*, the amino group, in view of the use of the remaining three valences of the central two carbon atoms for bonding with fraction A of the molecule. A combination of parts A and B led to two possible structures for imabenzil, XVIII and XIX, of which the former is most unlikely (although not rigorously ruled out) not only because a four-membered cyclic dioxide is without analogs in organic chemistry but also because it would not be expected to be formed under the reversible carbonyl addition steps of the benzil–ammonia reaction.

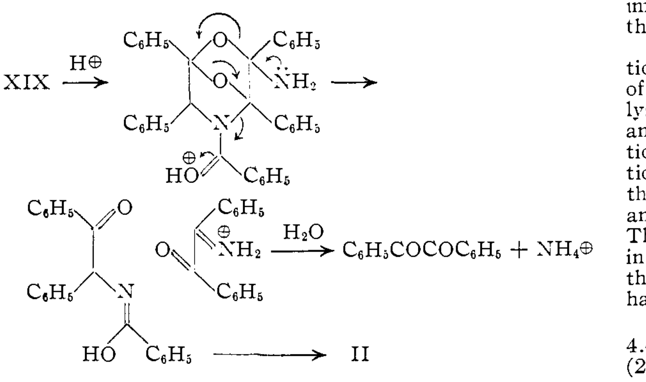

A B

XVII


XVIII


XIX

Structure XIX can accommodate all reactions of imabenzil. Thus, for example, its acid-catalyzed decomposition can be portrayed as



while most other reactions of the compound are simple variants of this process.

Whereas the mode of formation of imabenzil still remains obscure, two hypothetical paths can be suggested. One involves the formation of a benzil–ammonia complex, containing three benzil units and its disproportionation into I and XIX, while another requires the decomposition of a complex of ammonia and two benzil units (*cf.* V) to I and II and a combination of II and a monobenzil–ammonia complex by a route, formally the reverse of the above decomposition of imabenzil. The latter is undoubtedly the more attractive of the two possibilities.

Experimental

Imabenzil.—Davidson's[1b] mode of preparation of imabenzil was followed closely except that the reaction temperature was kept at 25–30°; 4.95 g. of pure product, m.p. 196–197°, could be obtained from 25 g. of benzil.

Anal. Calcd. for $C_{35}H_{28}O_3N_2$: C, 80.15; H, 5.34; N, 5.34. Found: C, 79.93; H, 5.59; N, 5.46.

Its infrared spectrum in Nujol or KBr pellet showed the following maxima: NH 3.01 μ (w); $C_6H_5CON<$ 6.12 μ (s), 6.22 μ (m), 6.55 μ (s), 6.65 μ (s). The shape of the infrared curve in the 6.0–6.7 μ region was identical with that of N,N-dimethylbenzamide.

Hydrolyses of Imabenzil.—(a) A solution of 1.00 g. of imabenzil in 50 ml. of methanol was added to 50 ml. of 30% H_2SO_4 and the mixture refluxed for four hours. Enough sodium bicarbonate was then added to neutralize the solution and the latter was extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulfate and evaporated to dryness. Chromatography on alumina of a benzene solution of the residue yielded 300 mg. of N-desylbenzamide,[1b] m.p. 139–140°, and 350 mg. of benzil, m.p. 95°.

(b) A mixture of 50 ml. of a methanolic solution of 750 mg. of imabenzil and 50 ml. of a 10% sodium hydroxide solution was refluxed for four hours. Extraction of the mixture with ether, followed by washing with water, drying over sodium sulfate and evaporation of the solvent yielded a solid residue whose benzene solution could be separated chromatographically on an alumina column to yield 340 mg. of N-desylbenzamide, m.p. 139–140°, 40 mg. of 2,4,5-triphenyloxazole,[1b] m.p. 115–116°, and 230 mg. of benzil, m.p. 95°.

Pyrolyses of Imabenzil.—(a) A solution of 3.44 g. of imabenzil in 100 ml. of ethanol was refluxed for 15 hours. The volume of the solution was concentrated and the following products then fractionally crystallized: 2.22 g. of N-desylbenzamide, m.p. 139–140°, 180 mg. of benzamide, m.p. 128°, 80 mg. of 2,4,5-triphenylimidazole,[1b] m.p. 272–273°, 30 mg. of benzil, m.p. 95°, and 60 mg. of starting material.

(b) A 580-mg. sample of imabenzil was heated for four hours at 150–155° in a nitrogen atmosphere. The resulting yellow oil could be fractionated as a benzene solution by chromatography on alumina yielding 300 mg. of N-desylbenzamide, m.p. 139–140°, 60 mg. of 2,4,5-triphenyloxazole, m.p. 115–116°, and 40 mg. of crude 2,4,5-triphenylimidazole (identical in infrared spectrum to that of an authentic sample).

Hydrogenation Products of N-Desylbenzamide.—A solution of 0.39 g. (1.2 mmoles) of N-desylbenzamide in 75 ml. of ethanol was hydrogenated over palladium-charcoal catalyst at room temperature and pressure. After two hours and an uptake of 29 ml. (1.3 mmoles) of hydrogen the reaction ceased. After filtration of the catalyst and evaporation of the filtrate to dryness, fractional crystallization of the residue yielded 0.26 g. of white flakes, m.p. 239–240°, and 0.11 g. of another crystalline solid, m.p. 215–216°. The infrared spectra of the two compounds were identical in the 2.5–7.0 μ region. A 2.81 μ peak had appeared and the 5.92 μ peak of the ketonic group in N-desylbenzamide had disappeared.

Anal. Calcd. for $C_{21}H_{19}O_2N$: C, 79.81; H, 5.99; N, 4.43. Found (239°): C, 80.01; H, 6.10; N, 4.14. Found (215°): C, 80.10; H, 6.17; N, 4.28.

1.00 g. of the 239° compound was refluxed in 50 ml. of 10% sodium hydroxide for four hours. Upon extraction of the reaction mixture with ether, drying and concentrating of the latter, and crystallization of the separating solid from methanol, 0.65 g. (99%) of *erythro*-2-amino-1,2-diphenylethanol, m.p. 163° (literature value[6] m.p. 163°), was obtained.

A like treatment on 1.03 g. of the 215–216° compound produced 0.60 g. (88%) of *threo*-2-amino-1,2-diphenylethanol, m.p. 129° (literature value[6] 129–130°).

erythro-2-Benzamido-1,2-diphenylethanol (the 239° product, 0.11 g.) in 50 ml. of 30% sulfuric acid was refluxed for four hours. The solution was neutralized, extracted with ether, the latter evaporated and the residue crystallized from methanol; 70 mg. (67%) of white flakes, m.p. 215–

216°, could be isolated. This product was shown to be the *threo* isomer by comparison of m.p., mixed m.p. and infrared spectrum.

When 0.13 g. of *threo*-2-benzamido-1,2-diphenylethanol (the 215–216° compound) was subjected to the same treatment, 0.10 g. of only impure starting material could be recovered. No higher melting product was detected.

Reductions of Imabenzil.—(a) Sodium borohydride (0.60 g.) was added with stirring to a solution of 0.34 g. of imabenzil in 75 ml. of ethanol and the mixture refluxed for four hours. Partial concentration of the solution and the addition of water produced a precipitate which on filtration was crystallized fractionally from methanol; 0.11 g. of a compound, m.p. 239–240°, and 80 mg. of another, m.p. 214–215°, were isolated. These products could be shown to be the *erythro*- and *threo*-2-benzamido-1,2-diphenylethanols, respectively, by comparison of their m.p., mixed m.p. and infrared spectra.

(b) A solution of 1.31 g. (2.3 mmoles) of imabenzil in 75 ml. of ethanol was hydrogenated over palladium–charcoal catalyst at room temperature and pressure. The reaction was complete at the end of 26 hours and the uptake of 103 ml. (4.6 mmoles) of hydrogen. After filtration of the catalyst and evaporation of the filtrate, fractional crystallization of the product from methanol gave 0.69 g. of white flakes, m.p. 239–240°, and 0.43 g. of a substance, m.p. 215–216°. These compounds were again shown to be the above two epimeric 2-benzamido-1,2-diphenylethanols by mixed m.p. and infrared spectra. Distillation of the oil, remaining after complete removal of methanol from the mother liquor, yielded 60 mg. of a liquid whose infrared spectrum was indistinguishable from that of ethyl benzoate.

When 0.65 g. of imabenzil was exposed to catalytic hydrogenation conditions identical to those above except for the absence of hydrogen gas, 0.54 g. of slightly impure starting material, m.p. 191–193°, was the only isolable product.

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Some Reactions of *o*-Halobromobenzenes with *n*-Butyllithium

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o-Fluorophenyllithium (I) and *o*-chlorophenyllithium (II) can be prepared in excellent yields at about −60 and −90°, respectively, by the interaction of the corresponding *o*-halobromobenzene with *n*-butyllithium. *o*-Bromophenyllithium (III) has been prepared in a 23% yield by employing a temperature of −100° and a reaction time of 7 minutes. The first two organolithium compounds on being allowed to warm to room temperature give 2-halo-2′-lithiobiphenyl and triphenylene (XIII). In the case of II at −65° only 2-chloro-2′-lithiobiphenyl (VII) and 2-(*o*-chlorophenyl)-2′-lithiobiphenyl (XI) have been derivatized whereas, at room temperature, only VII and XIII have been obtained. The possible routes of the reactions of I and II on warming and similarities to other reactions are discussed. In addition, 2-bromo-2′-carboxybiphenyl and 4-bromo-9,9-diphenylfluorene have been synthesized for comparison purposes.

Although *o*-fluorophenyllithium (I) had previously been considered too reactive to form derivatives as such,[1,2] we successfully obtained the benzophenone adduct in excellent yields.[3]

The inability of earlier workers to detect I can be ascribed to the reaction conditions employed. All of their reactions were carried out at temperatures in the vicinity of 0°, whereas all successful preparations of *o*-halophenyllithium compounds in this Laboratory were achieved below −50°. Attempts to prepare I and *o*-chlorophenyllithium (II) at −30° and 0° were unsuccessful.

In the course of our studies we have been able to carbonate I to *o*-fluorobenzoic acid (IV) in 83% yield at about −60° after adding the *o*-fluorobromobenzene to the *n*-butyllithium. In carrying out the addition in a reverse manner at the same temperature only a 42% yield of IV was obtained while a 15% yield of 2-fluoro-2′-carboxybiphenyl (X) was isolated. Furthermore, if the reaction mixture was allowed to warm to room temperature and then carbonated, the only acid isolated was X. In addition to this acid there was also obtained a 2.5% yield of triphenylene (XIII).

Similar results were obtained in the case of II although it appeared to be much more reactive than I, as was evidenced by the increased yield of coupling products under comparable conditions and also by the lower temperature required for its preparation in good yield. At −90°, II could be prepared in an almost quantitative yield as determined by carbonation. The method of carbonation, which was different from that used in the other runs, may be a promising one. Instead of pouring the mixture over a Dry Ice–ether slurry, powdered Dry Ice was added to the reaction mixture at −100° and then it was allowed to warm to room temperature.[4] The usual method, pouring of the reaction mixture into a Dry Ice–ether slurry, could not be used in this case since the temperature rise of the reaction mixture during carbonation was sufficient to give some 2-chloro-2′-carboxybiphenyl (IX). When the reaction was carried out employing conditions similar to those used for I, there was obtained about a 6% yield of *o*-chlorobenzoic acid (V) and an 18% yield of IX. With II the mode of addition was immaterial. By allowing II to warm to room temperature and then carbonating, a 22% yield of IX was obtained and a 7% yield of XIII was found in contrast to 2.5% of XIII obtained with I under similar conditions. By varying the reaction conditions it was possible to increase the yield of XIII to approximately 17%.

In any of the carbonations achieved below −30° in which coupling products appeared, there was obtained simultaneously on extraction of the ethereal layer with sodium hydroxide an acidic oil. Numerous attempts to obtain a pure compound from this oil failed, but it is believed that some 2-(*o*-chloro-

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[1] G. Wittig, G. Pieper and G. Fuhrmann, *Ber.*, **73**, 1193 (1940).

[2] G. Wittig and W. Merkle, *ibid.*, **75**, 1491 (1942).

[3] H. Gilman and R. D. Gorsich, THIS JOURNAL, **77**, 3919 (1955).

[4] The high yield of acid obtained by adding carbon dioxide to II is somewhat surprising in view of the high yield of ketones obtained by H. Gilman and P. R. Van Ess, THIS JOURNAL, **55**, 1258 (1933), by passing carbon dioxide over the organolithium compound.