

methylpyrazolo[3,4-*d*]pyrimidine, 3 g. of thiourea, and 100 ml. of absolute ethanol was refluxed for 5 hr. The solid product was filtered and reprecipitated from dilute potassium hydroxide solution by glacial acetic acid to give 4.0 g. (73.6%) of white solid, m.p. >300°.

This preparation was found to be identical to the compound made by Method 1 on the basis of identical ultraviolet absorption spectra at pH 1 and pH 11.

*Preparation of 6-chloro-4-mercapto-1-methylpyrazolo[3,4-*d*]pyrimidine (XIV, R = CH₃).* To 200 ml. of 0.5*N* potassium hydrosulfide was added 5 g. of finely powdered 4,6-dichloro-1-methylpyrazolo[3,4-*d*]pyrimidine. The mixture was stirred at 0° for 15 min. and then allowed to stand at room temperature for 2 hr. The mixture was filtered and the filtrate acidified with glacial acetic acid. Four and one-half grams (46%) of white solid was obtained, m.p. 223° (dec.).

Anal. Calcd. for C₈H₈N₄SCl: N, 27.9. Found: N, 27.7.

*Preparation of 6-ethoxy-4-mercapto-1-methylpyrazolo[3,4-*d*]pyrimidine (XV).* To 100 ml. of absolute ethanol containing 2.0 g. of sodium was added 5.3 g. of powdered 6-chloro-4-mercapto-1-methylpyrazolo[3,4-*d*]pyrimidine (XIII). The mixture was allowed to stir at room temperature for 1 hr. followed by 30 min. of heating on the steam bath. Sodium chloride was filtered and filtrate acidified with dilute acetic acid to give 4.5 g. (81%) of small, yellow plates, m.p. 240° (dec.).

Anal. Calcd. for C₈H₁₀N₄S: C, 45.6; H, 4.8. Found: C, 45.2; H, 4.9.

*Preparation of 6-chloro-4-ethylthio-1-methylpyrazolo[3,4-*d*]pyrimidine (XIX).* Ten g. of finely powdered 4,6-dichloro-1-methylpyrazolo[3,4-*d*]pyrimidine was added to a solution of 12 g. of potassium hydroxide, 20 g. of ethylmercaptan, and 50 ml. of water. The mixture was stirred at room temperature for 3 hr. A white precipitate was obtained which was filtered and recrystallized from absolute ethanol to give 8.5 g. (76%) of white needles, m.p. 112–113°.

Anal. Calcd. for C₈H₈N₄SCl: C, 42.1; H, 4.0. Found: C, 42.4; H, 4.1.

*Preparation of 6-ethoxy-4-ethylthio-1-methylpyrazolo[3,4-*d*]pyrimidine (XX).* Five g. of 6-chloro-4-ethylthio-1-methylpyrazolo[3,4-*d*]pyrimidine was added to 100 ml. of absolute ethanol containing 2.0 g. of dissolved sodium. The mixture was allowed to stand at room temperature for 5 hr. It was then warmed on a steam bath for 3 min. and filtered. White needles, m.p. 92–93°, were obtained from the cooled filtrate. The yield was 3.0 g. (58%).

Anal. Calcd. for C₁₀H₁₄N₄OS: C, 50.5; H, 5.9. Found: C, 50.4; H, 6.1.

TEMPE, ARIZ.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

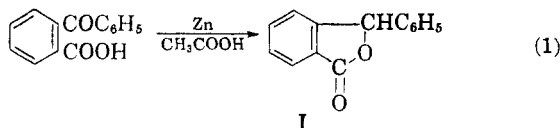
Condensations Involving the Metalation of the 3-Position of 3-Phenylphthalide by Means of Alkali Amides. Carbonation of Phthalide¹

CHARLES R. HAUSER, MARVIN T. TETENBAUM, AND DAVID S. HOFFENBERG

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3-Phenylphthalide was metalated at its 3-position by means of an alkali amide in liquid ammonia, and the resulting alkali derivative was employed in several types of carbon-carbon condensations in this medium or in ether. These condensations included carbonation, benzylation, benzoylation, and conjugate addition. The structure of the acid obtained on carbonation was established by the Hofmann rearrangement of the corresponding acid amide. The ketone produced on benzoylation was cleaved by means of potassium hydroxide solution.

Although 3-phenylphthalide (I) is readily prepared by the reduction of *o*-benzoylbenzoic acid by means of zinc and acetic acid (Equation 1),^{2,3} this active hydrogen compound appears not to have been employed previously in condensations involving the ionization of its 3-hydrogen (γ -hydrogen).

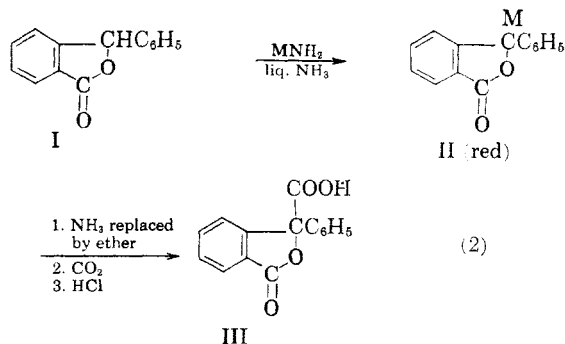


(1) Supported by the National Science Foundation.

(2) F. Ullmann, *Ann.*, 291, 23 (1896).

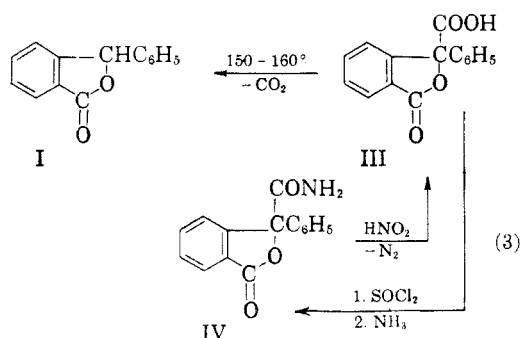
(3) Also, we have obtained a 48% yield of 3-phenylphthalide (I) along with a 25% yield of *o*-benzylbenzoic acid on reducing *o*-benzoylbenzoic acid with zinc-amalgam and hydrochloric acid (Clemmensen method). These two compounds were readily separated by means of sodium bicarbonate solution in which I was insoluble. Earlier workers [H. L. Bradlow and C. A. VanderWerf, *J. Am. Chem. Soc.*, 69, 1254 (1947)] have reported that, under certain conditions, this method produces *o*-benzylbenzoic acid in yields of 70–75%.

In the present investigation the 3-position of 3-phenylphthalide was metalated by means of alkali amides in liquid ammonia, and the resulting red alkali derivative employed in several types of carbon-carbon condensations. One of these reactions involved carbonation to form lactone acid III which was obtained in yields of 80–87% by means of potassium amide, sodium amide, or lithium amide (Equation 2, M = K, Na, or Li).



As indicated in Equation 2, the liquid ammonia over the red alkali derivative of 3-phenylphthalide (II) was replaced by ether before carbonation. The fact that intermediate salt II is stable during this interchange of solvents when its cation M is sodium or lithium as well as potassium is of interest, since only the potassium derivatives of di- and triphenylmethides are stable under similar conditions.⁴ Such an interchange of solvents over the sodium and lithium derivatives of di- and triphenylmethides causes them to revert to sodium and lithium amides and di- and triphenylmethanes.⁴ The greater stability of the sodium and lithium derivatives of 3-phenylphthalide (II = Na or Li) under these conditions appears to be ascribable to the presumably more weakly basic nature of 3-phenylphthalide carbanion (compared to di- and triphenylmethide carbanions).⁴

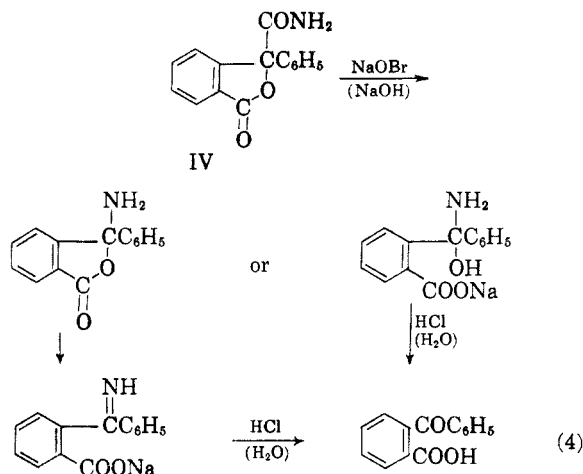
Although a sample of lactone acid III melting at 126–127° was isolated, this compound was generally obtained even after several recrystallizations as a white powder melting at 85–92°, which appeared to be essentially pure (see EXPERIMENTAL). Samples having either melting point were readily decarboxylated at 150–160° to form 3-phenylphthalide (I), and were converted to the corresponding amide (IV) from which lactone acid III was regenerated by means of nitrous acid (Equation 3).



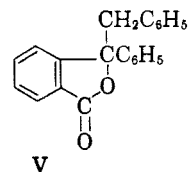
Since the carbanion of 3-phenylphthalide has several resonance structures involving the aromatic rings, its carbonation might conceivably have produced, instead of lactone acid III, a lactone acid having the carboxyl group attached to one of the aromatic rings. The corresponding lactone amide would then have the acid-amide group attached to the aromatic ring. That the lactone acid had structure III and the lactone amide, structure IV, was established by effecting the Hofmann rearrangement of the latter, which produced *o*-benzoylbenzoic acid in 89% yield (Equation 4).

Had the acid-amide group been attached to one of the aromatic rings, this rearrangement should have produced a relatively stable primary aromatic amine. No such amine was found.

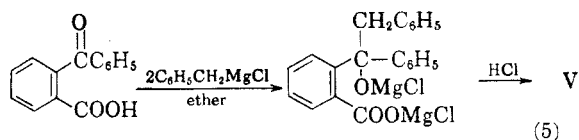
(4) See C. R. Hauser, D. S. Hoffenberg, W. H. Puterbaugh, and F. C. Frostick, *J. Org. Chem.*, **20**, 1531 (1955).



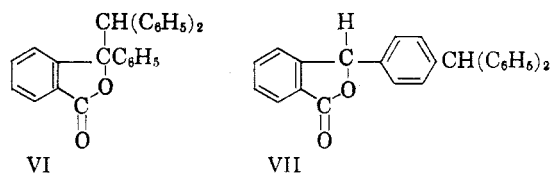
A second type of condensation of 3-phenylphthalide (I) involved its benzylation with benzyl chloride by means of sodium amide in liquid ammonia to form lactone V in 77% yield.



The structure of the benzylation product was established as V by an independent synthesis from *o*-benzoylbenzoic acid and excess benzylmagnesium chloride (Equation 5).⁵



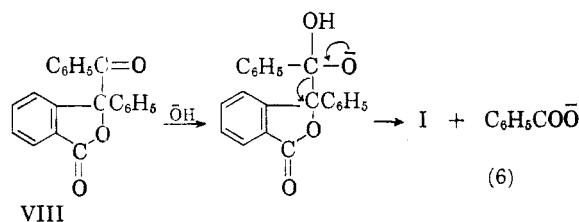
Similarly, 3-phenylphthalide (I) was benzhydrylated with benzhydryl bromide by means of potassium amide. By analogy with the benzylation, the product would be assigned structure VI but this structure was not established. Its unexpectedly high melting point might suggest structure VII, or possibly still another isomer.



A third type of condensation of 3-phenylphthalide (I) involved its benzylation with benzoyl chloride (after replacing the liquid ammonia with ether) to form lactone-ketone VIII in 74% yield. The structure of this product is supported by its cleavage by means of hot aqueous potassium hy-

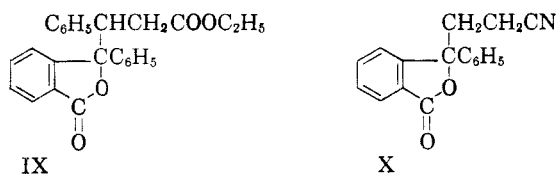
(5) W. R. Dunnivant in this laboratory performed this experiment (refluxed 20 hr.) to give a 20% yield of V, m.p. and mixed m.p. 103–104°.

dioxide to regenerate 3-phenylphthalide (95%) along with benzoic acid (93%). Such a cleavage would hardly be expected if the benzoyl group had been attached to the 3-phenyl ring. The mechanism of the cleavage presumably involves the attack of hydroxyl ion on the ketone carbonyl group and the elimination of the carbanion of 3-phenylphthalide (Equation 6). The alkali might also have opened (saponified) the lactone ring which would have been regenerated on acidification.



Lactone-ketone VIII reacted slowly with 2,4-dinitrophenylhydrazine reagent, losing the elements of water, to form a yellow product that was presumably the corresponding 2,4-dinitrophenylhydrazone. This reagent might possibly react with the lactone group,⁶ but its preferential reaction with the ketone group of VIII should be expected.

A fourth type of condensation of 3-phenylphthalide (I) involved its conjugate addition to ethyl cinnamate and acrylonitrile. The structures of the products may be assigned tentatively IX and X, respectively.



Carbonation of phthalide. Phthalide (XI) was carbonated to form lactone acid XII in 46% yield by means of potassium amide as described above for 3-phenylphthalide. Considerable resinous material was also obtained.



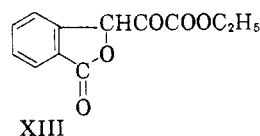
However, an attempt to effect the benzylation of phthalide (XI) with benzyl chloride under the conditions that produced a good yield with 3-phenylphthalide was unsatisfactory, much resinous material being produced.

These results might indicate that the amide ion attacks not only the 3-hydrogen of phthalide to

(6) W. Wislicenus [*Ber.*, **20**, 401 (1887)] reported that phthalide reacted with phenylhydrazine involving the opening of the lactone ring to form an alcohol-amide type of compound. Such an addition product was evidently not formed in our reaction of lactone-ketone VIII with 2,4-dinitrophenylhydrazine.

effect its ionization but also the carbonyl group resulting in the opening of the lactone ring, although the hydroxy-amide that should be formed from the latter reaction was not found. Hydroxide ion has been reported to attack the carbonyl group of phthalide (XI) to open the lactone ring.⁷

It should be mentioned that long ago Wislicenus⁸ effected the acylation of phthalide (XI) with diethyl oxalate by means of sodium dissolved in ethanol to form lactone-ester XIII, but no yield was given.



EXPERIMENTAL⁹

3-Phenylphthalide (I). This compound was prepared by the method of Ullmann² employing 10 times the quantities of reactants.

A mixture of 100 g. (0.44 mole) of *o*-benzoylbenzoic acid, 200 g. (3.8 g.-atoms) of zinc dust, 200 ml. of water, and 800 ml. of glacial acetic acid was refluxed for 2 hr. The supernatant liquid was removed and allowed to cool. The white needles of the lactone, which soon precipitated, were collected on a funnel. More solid was precipitated by the addition of water to the filtrate. The combined solid was carefully added to a solution of sodium bicarbonate, and the resulting mixture was filtered. The solid was recrystallized from ethanol to give 71 g. (77%) of 3-phenylphthalide (I), m.p. 115–116° (reported m.p. 115–116°).²

Carbonation of 3-phenylphthalide (I) to form lactone acid III. To a stirred suspension of potassium amide¹⁰ in 500 ml. of liquid ammonia was carefully added 21 g. (0.1 mole) of solid 3-phenylphthalide. The liquid ammonia was evaporated from the red solution on the steam bath as an equal volume of dry ether was added. The red ether solution was refluxed for 30 min., cooled, and excess crushed Dry Ice carefully added with stirring. When the excess Dry Ice had evaporated, water and ether were added. The alkaline aqueous layer was separated and combined with an alkali extract of the ether layer. After filtering to remove tarry material, the cooled solution was acidified with iced hydrochloric acid to precipitate a semisolid which soon almost completely solidified. After careful filtration, the solid was dissolved in chloroform, and ligroin (b.p. 60–90°) slowly added to precipitate 22 g. (87%) of 3-phenylphthalide-carboxylic acid (III) (white powder) melting at about 75°. Three more recrystallizations from the same solvents raised the melting point to 85–92° without much loss of the product. Further recrystallization generally failed to raise the melting point appreciably.

Anal. Calcd. for C₁₅H₁₀O₄: C, 70.86; H, 3.97. Found: C, 71.02; H, 4.08.

Although this product appeared to be essentially pure, a sample melting at 126–128° was isolated on two occasions by five or six recrystallizations from the chloroform-ligroin mixture.

Anal. Calcd. for C₁₅H₁₀O₄: C, 70.86; H, 3.97. Found: C, 70.86; H, 3.92.

(7) J. Hessert, *Ber.*, **10**, 1445 (1877); **11**, 237 (1878).

(8) W. Wislicenus, *Ann.*, **246**, 342 (1888).

(9) All melting points are uncorrected. Analyses are by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(10) See R. S. Yost and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 2325 (1947).

Similar results were obtained employing sodium amide or lithium amide instead of potassium amide.

Samples of the product melting at 85–92° and at 126–128° were decarboxylated, on heating to 150–160°, to give high yields (89%) of 3-phenylphthalide (I), m.p. 115–116°.

Also, similar results were obtained in certain other reactions with samples having the two different melting points (see below).

Conversion of III to lactone amide IV. A solution of 5 g. of lactone acid III (m.p. 85–92° or 126–128°) in 40 ml. of thionyl chloride was refluxed for 30 min. and the excess of the reagent then distilled. The residue was cooled and carefully poured into 40 ml. of iced ammonium hydroxide solution to give, after recrystallization from ethanol, 4.3 g. (87%) of white 3-phenylphthalidecarboxylic acid amide (IV), m.p. 225–227°.

Anal. Calcd. for $C_{15}H_{11}O_3N$: C, 71.14; H, 4.37; N, 5.53. Found: C, 71.18; H, 4.31; N, 5.68.

Reaction of lactone amide IV with nitrous acid. This reaction was carried out by an adaptation of the method of Baker.¹¹

To a mixture of 30 ml. of glacial acetic acid and 3 ml. of 70% sulfuric acid there was added 3.3 g. of lactone amide IV, and the solution cooled to 0°. A solution of 2 g. of sodium nitrite in 3 ml. of water was added dropwise, and the mixture gradually warmed to 50°. Water (70 ml.) was added to precipitate a white solid. After being cooled in an ice bath, the mixture was filtered, and the solid washed with cold sodium bicarbonate solution. There was obtained 2.7 g. (82%) of lactone acid III, m.p. 123–126°. A mixed melting point of this product with a sample of lactone acid III (m.p. 126–128°) was 125°.

Hofmann rearrangement of lactone amide IV. This reaction was carried out by the general method of Hoogewerff and Van Dorp.¹²

To an ice cold solution of sodium hypobromite, prepared from 3 ml. (0.06 g.-atom) of bromine and 12 g. (0.3 mole) of sodium hydroxide in 100 ml. of water, there was added with swirling 11.25 g. (0.05 mole) of the finely powdered lactone amide IV. The reaction mixture was warmed to 70–80° (solution was now complete) and kept there for 15–20 min. After cooling and filtering, the solution was acidified with 6*N* hydrochloric acid to give a dark oil, which solidified on cooling in a Dry Ice–carbon tetrachloride bath. The solid was dissolved in benzene (steam bath), and ligroin (b.p. 60–90°) was then added to precipitate an oil that quickly solidified. There was obtained 10 g. (89%) of *o*-benzoylbenzoic acid, m.p. 127°. This melting point was not depressed on admixture with an authentic sample of *o*-benzoylbenzoic acid.

Benzoylation of 3-phenylphthalide (I) to form lactone V. To a stirred suspension of 0.1 mole of sodium amide¹³ in 500 ml. of liquid ammonia was carefully added 21 g. (0.1 mole) of solid 3-phenylphthalide (I). The resulting dark red solution of the sodium derivative was stirred for 15 min., and 12.7 g. (0.1 mole) of benzyl chloride in an equal volume of anhydrous ether was added. The color was discharged, and a white precipitate was formed. After stirring for one hour, the liquid ammonia was evaporated on the steam bath as an equal volume of anhydrous ether was added. The resulting white suspension was refluxed for 30 min., cooled, and hydrolyzed with iced hydrochloric acid. The yellow ether layer was separated and combined with three ether extracts of the aqueous layer. After drying over Drierite, the ether was evaporated under reduced pressure on the steam bath to give 23 g. (77%) of white 3-benzyl-3-phenylphthalide (V) m.p. 99–102°. After two recrystallizations from ether, the product melted at 103–105°.

(11) R. H. Baker, *J. Am. Chem. Soc.*, **70**, 3858 (1948).

(12) See E. S. Wallis and J. F. Lane, *Org. Reactions*, **III**, 280 (1946).

(13) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **VIII**, 122 (1954).

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.94; H, 5.37. Found: C, 84.16; H, 5.66.

A 1-g. sample of this product was heated with 10 ml. of concentrated sulfuric acid on the steam bath for 30 min. the dark red mixture was cooled, and carefully poured onto ice. The resulting solution was extracted with ether overnight in a continuous liquid-liquid extractor. Evaporation of the yellow ethereal solution yielded 0.5 g. (40%) of an orange, water soluble powder that softened at 220° and decomposed at 240–250°. This product analyzed for a monosulfonated derivative of lactone V.

Anal. Calcd. for $C_{21}H_{16}O_6S$: C, 66.30; H, 4.24; S, 8.43. Found: C, 66.73; H, 4.26; S, 8.24.

Benzhydrylation of 3-phenylphthalide (I) to form lactone VII. To a stirred suspension of 0.1 mole of potassium amide¹⁰ in 500 ml. of liquid ammonia was carefully added 21 g. (0.1 mole) of solid 3-phenylphthalide (I). The resulting dark red solution of the potassium derivative was stirred for 15 min., and 24.7 g. (0.1 mole) of benzhydryl bromide in an equal volume of anhydrous ether was added. The color was mostly discharged. After stirring for one hour, the liquid ammonia was evaporated on the steam bath as an equal volume of anhydrous ether was added. The resulting yellow-green mixture was refluxed for 30 min., cooled, and hydrolyzed with iced hydrochloric acid. The yellow ether layer was separated and combined with three ether extracts of the aqueous layer. After drying over Drierite, the ether was evaporated under reduced pressure on the steam bath to give a theoretical yield of white 3-benzhydryl-3-phenylphthalide (VII) m.p. 247–249°. After two recrystallizations from a mixture of chloroform and ether, the product melted at 252–252.5°.

Anal. Calcd. for $C_{27}H_{20}O_2$: C, 86.15; H, 5.36. Found: C, 85.94; H, 5.28.

Benzoylation of 3-phenylphthalide (I) to form lactone-ketone (VIII). The sodium derivative of 3-phenylphthalide (0.1 mole) was prepared in liquid ammonia as described above, and the ammonia evaporated as an equal volume of dry ether was added. The resulting red ethereal solution was stirred and refluxed for 30 min., and 14.1 g. (0.1 mole) of freshly distilled benzoyl chloride in an equal volume of anhydrous ether was then added, the color being discharged. After refluxing for one hour, the mixture was cooled and filtered. Evaporation of the ether on the steam bath under reduced pressure left 23 g. (74%) of 3-benzoyl-3-phenylphthalide (VIII), m.p. 102–104°. This melting point was not changed by three recrystallizations from ether.

Anal. Calcd. for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49. Found: C, 80.16; H, 4.63.

A sample of this ketone was treated with 2,4-dinitrophenylhydrazine reagent for several days to give yellow crystals m.p. 193–194° after being recrystallized from ethanol. An analysis of these crystals agreed with that calculated for the 2,4-dinitrophenylhydrazone.

Anal. Calcd. for $C_{27}H_{18}O_6N_4$: C, 65.58; H, 3.67. Found: C, 65.62; H, 3.42.

Alkaline cleavage of lactone-ketone VIII. A 0.22-g. sample of this compound was refluxed with excess 40% aqueous potassium hydroxide for 2.5 hr. The resulting solution was cooled and acidified with cold 6*N* hydrochloric acid to precipitate a white solid which was collected on a funnel and washed thoroughly with hot water. The insoluble solid remaining on the funnel was 3-phenylphthalide (0.14 g., 95%), m.p. and mixed m.p. 116–117°. The aqueous filtrate was extracted with ether to give 0.08 g. (93%) of benzoic acid, m.p. and mixed m.p. 122°.

Conjugate addition of 3-phenylphthalide (I) with ethyl cinnamate to form IX. To a stirred solution of the sodium derivative of 3-phenylphthalide prepared from 0.1 mole each of sodium amide and the lactone I in 500 ml. of liquid ammonia, there was added 17.6 g. (0.1 mole) of ethyl cinnamate in an equal volume of anhydrous ether. After one hour, the liquid ammonia was replaced by ether, and the resulting suspension was refluxed for 30 min. The mixture

was hydrolyzed with iced hydrochloric acid, and the ethereal layer, after being combined with several ether extractions of the aqueous layer, was dried over Drierite. The solvent was removed and the residue washed with ether to give 18.5 g. (48%) of lactone-ester IX, m.p. 150–153°. One recrystallization from ether raised the melting point to 155–156°.

Anal. Calcd. for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74. Found: C, 77.56; H, 5.80.

Cyanoethylation of 3-phenylphthalide (I) to form X. To a stirred solution of the sodium derivative of 3-phenylphthalide prepared from 0.1 mole each of sodium amide and the lactone I in 500 ml. of liquid ammonia, there was added 5.3 g. (0.1 mole) of freshly distilled acrylonitrile in an equal volume of anhydrous ether. After stirring for 30 min., a few drops of excess acrylonitrile was added, causing the color to change from red to a deep, greenish black. After stirring for an hour longer, the liquid ammonia was replaced by ether during 15 min. on the steam bath. Some of the acrylonitrile appeared to polymerize. The reaction mixture was decomposed with iced hydrochloric acid, and the ethereal layer carefully separated and combined with several ether extracts of the aqueous layer. After drying over Drierite,

the solvent was removed to leave 14.5 g. (56%) of lactone-nitrile X, m.p. 176–180°. After two recrystallizations from ethanol, the product melted at 177–178°.

Anal. Calcd. for $C_{17}H_{13}O_2N$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.78; H, 4.80; N, 5.26.

Carbonation of phthalide (XI) to form lactone acid XII. This reaction was carried out as described above for 3-phenylphthalide (I), employing sodium amide. The intermediate sodium derivative which formed was deep orange. There was obtained, after recrystallization of the product from a mixture of chloroform and ligroin (b.p. 90–120°) and finally washing with cold ether, a 46% yield of 3-carboxyphthalide (XII) m.p. 152–153° (reported m.p. 150–151°).¹⁴

In an attempt to determine whether the amide ion was attacking the lactone ring, the phthalide was allowed to stir for 5 hr. with an equimolar portion of sodium amide before carbonation. Once again, an approximately 46% yield of acid XII was obtained along with considerable tar.

DURHAM, N. C.

(14) S. Ruhemann, *J. Chem. Soc.*, 2030 (1910).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Rearrangements of 2,6-Dimethyl- and 2,3,4,6-Tetramethylbenzyltrimethylammonium Ions with Sodium Amide and Reactions of the Products¹

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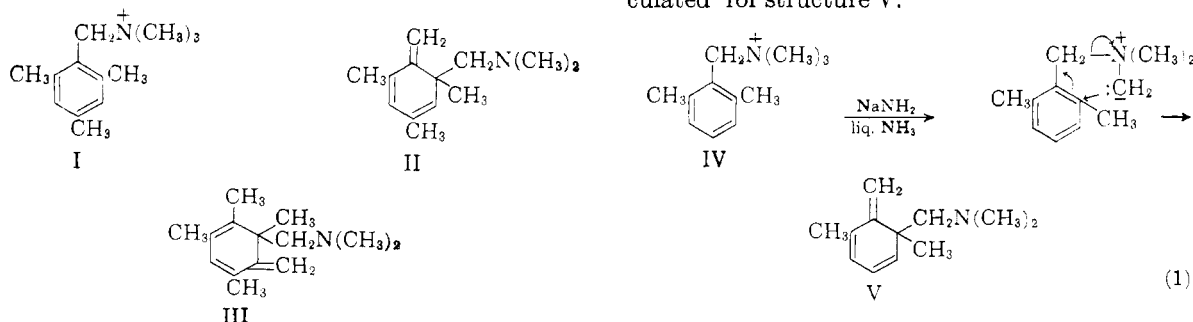
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2,6-Dimethyl- and 2,3,4,6-tetramethylbenzyltrimethylammonium ions were rearranged by sodium amide in liquid ammonia to form corresponding *exo*-methylene-cyclohexadienammines which exhibited characteristic reactions of such compounds. The methiodide of each of these *exo*-methyleneammines was converted by sodium amide in liquid ammonia to another *exo*-methyleneamine which also exhibited certain of the characteristic reactions. Evidence is presented that the unsymmetrical 2,3,4,6-tetramethyl quaternary ion underwent only one of the two possible courses of rearrangement.

The 2,4,6-trimethylbenzyltrimethylammonium ion (I) has previously² been rearranged by sodium amide in liquid ammonia to *exo*-methyleneamine II,² the methiodide of which was converted to another *exo*-methyleneamine (III)³ on further treatment with this reagent.

The corresponding reactions have now been car-

ried out with the 2,6-dimethyl- and 2,3,4,6-tetramethylbenzyltrimethylammonium ions. The former quaternary ion (IV) was rearranged by sodium amide in liquid ammonia to give *exo*-methyleneamine V, the mechanism being indicated in Equation 1. The ultraviolet absorption wave length maximum of the product agreed with the value calculated⁴ for structure V.



(1) Supported by the National Science Foundation.

(2) C. R. Hauser and D. N. Van Eenam, *J. Am. Chem. Soc.*, **79**, 5512 (1957).

(3) C. R. Hauser and D. N. Van Eenam, *J. Am. Chem. Soc.*, **79**, 6280 (1957).

Similar to *exo*-methyleneammines II and III, V

(4) For calculations of absorption maxima by Woodward's rules, see L. F. Fieser and M. Fieser, *Natural Products Related to Phenanthrene*, third ed., Reinhold Publishing Corp., New York, N. Y., 1949, pp. 185–188.