Metalation of N-Methylbenzamide with Excess *n*-Butyllithium. Condensations with Electrophilic Compounds to Form *ortho* Derivatives. Cyclizations[1]

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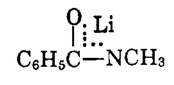
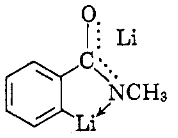
In contrast to N,N-dimethylbenzamide, N-methylbenzamide underwent *ortho* metalation as well as N-metalation with excess *n*-butyllithium to form dilithioamide II, which was condensed with benzophenone, acetophenone, *p*-chlorobenzophenone, and benzonitrile to form the corresponding *ortho*-substituted amides. The carbinol amides from the first two ketones were cyclized to phthalides. II was condensed with fluorenone, benzaldehyde, cyclohexanone, and cyclohexene oxide, and the resulting intermediate carbinol amides were cyclized to afford the corresponding lactones. These reactions furnish useful methods for the synthesis of such compounds. Attempts to effect *ortho* metalation of benzamide were unsuccessful.

It is well-known that N,N-dialkylamides undergo addition reactions with Grignard[3] and lithium[4] reagents leading to the formation of ketones. We have observed such an addition reaction of N,N-dimethylbenzamide with *n*-butyllithium in tetrahydrofuran–hexane to form valerophenone (70%).

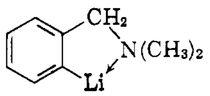
It seemed possible, however, that N-methylbenzamide, which would undergo an initial N-metalation with *n*-butyllithium to form monolithioamide I, might exhibit *ortho* metalation with excess of this reagent to give dilithioamide II, since the carbonyl group in I should be deactivated towards an addition reaction. This was realized. The somewhat related *ortho* metalation of benzyldimtheylamine with *n*-butyllithium in hexane–ether to form lithioamine III has been achieved recently.[5]



I



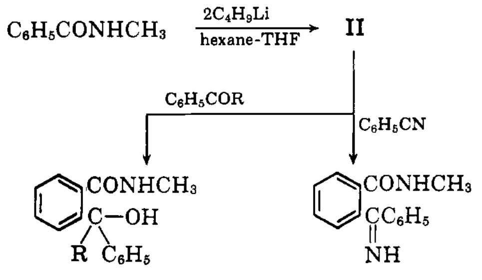
II



III

The formation of *o*,N-dilithioamide II was established by condensations with electrophilic compounds. Thus, II was condensed with benzophenone, acetophenone, *p*-chlorobenzophenone, and benzonitrile to form IVa–c and V in yields of 81, 43, 51, and 53%, respectively (Scheme A).

SCHEME A



IVa, R = C_6H_5
b, R = CH_3
c, R = p-ClC_6H_4

The metalation of N-methylbenzamide was generally effected with 2.5 molecular equivalents of *n*-butyllithium in refluxing hexane–tetrahydrofuran (15 min.). The condensations were usually carried out at the reflux temperature of the solvent mixture, but that with acetophenone was realized in much better yield at 0° (see Experimental). The general conditions were chosen on the basis of preliminary experiments with benzophenone (Table I).

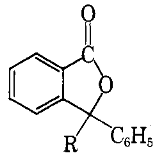
TABLE I

METALATION OF N-METHYLBENZAMIDE (A) WITH *n*-BUTYLLITHIUM (B) IN MIXTURE OF HEXANE AND ANOTHER SOLVENT. CONDENSATION WITH BENZOPHENONE (C)

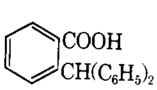
Mole ratio, B:A[a]	Other solvent[b]	Metalation time, hr.[c]	Mole ratio, C:A[d]	Condensation time, hr.[c]	IVa, yield %
2:1	Ether	5	2.2:1	3	45
2:1	Monoglyme	0.25	2.2:1	3	0
2:1	THF[e]	4[f]	2.2:1	3	42
2:1	THF	1	2.2:1	3	33
2:1	THF	0.25	2.2:1	3	57
3:1	THF	0.25	3.2:1	3	77
3:1	THF	0.25	3.2:1	0.5	81
2.5:1	THF	0.25	1.6:1	0.5	81

[a] *n*-Butyllithium (1.5 *M*) in hexane and 0.05 mole of A were used. [b] Volume equal to that of hexane. [c] At refluxing temperature of the solvent mixture. [d] Dissolved in volume of ether equal to that of hexane. [e] Tetrahydrofuran. [f] At room temperature.

The structures of the carbinol amides IVa–c and of the imine amide V were supported by analyses and by their infrared spectra, which showed peaks at 3350–3280 cm.$^{-1}$ for a secondary amide,[6] and at 1650–1620 cm.$^{-1}$ for an amide carbonyl group.[7] Structures IVa and b were confirmed by cyclization in refluxing toluene or xylene to evolve methylamine and give the known phthalides VIa and b. Moreover, VIa was



VIa, R = C_6H_5
b, R = C_6H_5



VII

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(1) Supported in part by a National Institutes of Health grant.

(2) National Science Foundation Science Faculty Fellow, on leave from Thiel College.

(3) See E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1954, p. 582.

(4) An example of the use of a lithium reagent for ketone synthesis has involved metalation of 2-phenyl-5-methylpyrrocoline with *n*-butyllithium, followed by condensation with N,N-dimethylbenzamide: V. Boekelheide and R. J. Windgassen, *J. Am. Chem. Soc.*, **80**, 2020 (1958).

(5) F. N. Jones, M. F. Zinn, and C. R. Hauser, *J. Org. Chem.*, **28**, 663 (1963).

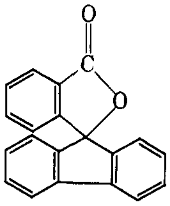
(6) See L. H. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 207.

(7) Ref. 6, p. 209.

hydrolyzed and reduced to form the known acid VII. The structure of imine amide V was confirmed by hydrolysis to *o*-benzoylbenzoic acid.

It should be pointed out that carbinol amides IVa–c cyclize so readily that methylamine was evolved on attempted recrystallization from refluxing ethanol. However, they were recrystallized satisfactorily at lower temperatures (see Experimental). Baeyer[8] reported that the carbinol acid corresponding to IVa could not be isolated because of its tendency to cyclize to the phthalide.

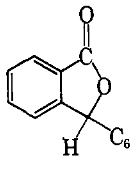
Likewise dilithioamide II was condensed with fluorenone, but the resulting carbinol amide underwent cyclization even at room temperature to form spirophthalide VIII in 58% yield (based on I).



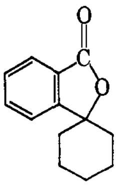
VIII

Structure VIII was supported by analysis, by agreement of its melting point with the reported value, and by its infrared spectrum, which showed a peak at 1760 cm.$^{-1}$ for the five-membered lactone,[9] but no absorption between 3000-2500 cm.$^{-1}$, indicating the absence of aliphatic hydrogen.[10]

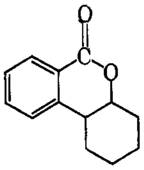
Similarly, dilithioamide II was condensed with benzaldehyde, cyclohexanone, and cyclohexene oxide to form presumably the corresponding carbinol amides, which were isolated as their lactones, IX, X, and XI, in yields of 42, 27, and 11%, respectively. The intermediate carbinol amides were not isolated since, in contrast to carbinol amides IVa–c, they did not precipitate on decomposing the reaction mixtures with water. Their isolation was not attempted because of their tendency to cyclize. As in the condensation with acetophenone, those with benzaldehyde and cyclohexanone were best effected at relatively low temperatures. Apparently the lower temperature minimized ionization of α-hydrogen of the ketones and hydride ion reduction of the aldehyde (see Experimental).



IX



X



XI

The melting point of phthalide IX agreed with the reported value. Structures X and XI, which are isomeric, were supported by their analyses and by their infrared spectra, which in X showed a peak at 1760 cm.$^{-1}$ for the five-membered lactone,[9] and in XI exhibited absorption at 1720 cm.$^{-1}$ for the six-membered lactone.[11]

The condensations of N-methylbenzamide through metalation furnishes a convenient method for the synthesis of such *ortho*-substituted derivatives as IVa–c and V, all of which appear to be new. This direct method generally should be preferable to the possible indirect route involving the ring opening of an appropriate phthalide with methylamine, a type of reaction employed previously with phthalide itself.[12]

The present reactions appear useful for the synthesis of certain phthalides such as VIa, and especially the spirophthalides VIII and X and the isocoumarin derivative XI. This route seems preferable to that employed earlier for VIII involving oxidation of 9-hydroxy-9-(*o*-tolyl)fluorene.[13] However, other methods are more convenient for phthalides VIb[14] and IX.[15]

In contrast to N-methylbenzamide, benzamide failed to undergo *ortho* metalation with excess *n*-butyllithium under similar conditions. Possibly the N-lithiobenzamide formed initially was too insoluble in the solvents employed. However, precipitation of N-lithio-N-methylbenzamide (I) did not prevent *ortho* metalation. Incidentally, benzamide is known to react with excess Grignard reagents to form ketones.[16]

Experimental[17]

Metalation of N-Methylbenzamide with *n*-Butyllithium to Form Dilithioamide II.—To a solution of 6.76 g. (0.05 mole) of N-methylbenzamide[18] in 80 ml. of tetrahydrofuran (freshly distilled from lithium aluminum hydride) in a dry flask under nitronitrogen was added, during 10 min., 80 ml. (0.125 mole) of 1.56 *M* *n*-butyllithium in hexane. During the addition the mixture refluxed and deposited a white precipitate which turned orange as the last of the *n*-butyllithium was added. The resultant mixture was then refluxed for 15 min. to give a dark red solution containing a tacky red precipitate. Heating was stopped and the mixture, containing dilithioamide II, was then employed as described below.

Condensation of II with Certain Ketones and Benzonitrile (Scheme A).—These reactions were effected under nitrogen as described below. The results are summarized in Table II.

(A) **With Benzophenone.**—To the stirred mixture containing II was added, during 8 min., a solution of 14.6 (0.08 mole) of benzophenone in 80 ml. of dry ether. The resulting mixture was refluxed for 0.5 hr. to give a clear red solution. This solution was cooled in an ice bath, and 100 ml. of water was added. The resulting precipitate was collected on a funnel and rinsed with water and ether. After drying *in vacuo*, a portion was dissolved in tetrahydrofuran at room temperature and cooled in the refrigerator to give an analytical sample of IVa.

Presumably because of its ease of cyclization, the melting point of IVa was not necessarily indicative of its purity. Thus, in certain experiments, product IVa obtained after drying *in vacuo* but not recrystallized exhibited a melting point from 133–136° dec. to 161–164° dec., yet the infrared spectra of these materials were essentially identical with that of the analytical sample. Moreover, the crude product was converted in 90% yield to pure phthalide VIa (see below). Similar observations were made also with IVb and IVc.

(B) **With Acetophenone.**—The mixture containing II was cooled in an ice bath for 5 min., and a solution of 9.6 g. (0.08 mole) of acetophenone in 80 ml. of ether was added during 20 min. The ice bath was removed, and the mixture was stirred for 30 min. and then poured into a mixture of 70 ml. of 2 *M* hydro-

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[8] A. Baeyer, *Ann.*, **202**, 36 (1880).

[9] Ref. 6, p. 186.

[10] Ref. 6, p. 14.

[11] Ref. 6, p. 185.

[12] A. Thielacker and H. Kolenda, *Ann.*, **584**, 87 (1953).

[13] H. D. Tubbs and S. H. Tucker, *J. Chem. Soc.*, 2939 (1951).

[14] F. N. Jones and C. R. Hauser, *J. Org. Chem.*, **27**, 3364 (1962).

[15] F. Ullman, *Ann.*, **291**, 23 (1896).

[16] S. S. Jenkins, *J. Am. Chem. Soc.*, **55**, 703 (1933).

[17] Melting points were taken on a Fisher-Johns melting point stage which had been calibrated with standard samples. Analyses were by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were taken on a Perkin-Elmer Model 237 Infracord in potassium bromide pellets.

[18] P. van Romburgh, *Rec. trav. chim.*, **4**, 388 (1885).

TABLE II

CONDENSATIONS OF DILITHIOAMIDE II WITH KETONES AND NITRILES

Ketone or nitrile	Product	Yield %	M.p., °C.[a]	Empirical formula	Calcd., %			Found, %		
					C	H	N	C	H	N
Benzophenone	α,α-Diphenyl-α-hydroxy-N-methyl-*o*-toluamide (IVa)	81	162.5–163	$C_{21}H_{19}NO_2$	79.47	6.03	4.41	79.27	6.03	4.60
Acetophenone	*o*-(1-Hydroxy-1-phenylethyl)-N-methylbenzamide (IVb)	43[b]	157–159	$C_{16}H_{17}NO_2$	75.27	6.71	5.49	75.14	6.69	5.35
p-Chlorobenzophenane	α-(4-Chlorophenyl)-α-hydroxy-α-phenyl-N-methyl-*o*-toluamide (IVc)	51	177–177.5	$C_{21}H_{18}ClNO_2$[c]	71.69	5.16	3.98	71.75	5.09	3.74
Benzonitrile	*o*-Benzimidoyl-N-methylbenzamide (V)	53	183–185[d]	$C_{15}H_{14}N_2O$	75.60	5.92	11.76	75.45	6.01	11.67

[a] Of the analytical sample. Melted with decomposition unless otherwise noted. [b] Condensation effected at 0° (see Experimental). [c] *Anal.* Calcd.: Cl, 10.08. Found: Cl, 9.92. [d] Melted without decomposition.

chloric acid and 50 g. of ice. The layers were separated and the organic layer (which contained a suspension of some of the product) was washed with 60 ml. of water and combined with an ether extract of the aqueous layers. After washing with saturated sodium chloride solution, the organic layer was filtered to remove the first crop of IVb. The solvents were removed from the filtrate under reduced pressure (rotary evaporator). The residue was triturated with 25 ml. of ether, and the mixture cooled and filtered to give more IVb. A sample of the combined product was recrystallized from hot methanol with rapid cooling to afford the analytical sample of IVb.

When the condensation of II with acetophenone was effected at the reflux temperature (0.5 hr.), there was obtained much polymeric material along with a 46% recovery of N-methylbenzamide and a 53% recovery of acetophenone.

(C) **With *p*-Chlorobenzophenone.**—This condensation was effected as described under A employing 17.3 g. (0.08 mole) of *p*-chlorobenzophenone. After filtering the product IVc that had precipitated on adding water, a second crop of IVc was obtained by the evaporation of solvents and addition of ether to the residue as described under B. The product was recrystallized as described under A.

(D) **With Benzonitrile.**—This condensation was effected as described under A employing 17.0 g. (0.165 mole) of benzonitrile, except that the reaction mixture was decomposed by pouring it into a solution of 8.6 g. (0.16 mole) of ammonium chloride in 120 ml. of ice–water. The resultant mixture was cooled and scratched to induce crystallization. The solid was collected on a funnel and recrystallized from benzene to give V.

Cyclization of IVa and b to Form Phthalides VIa and b. (A) **Cyclization of IVa.**—A mixture of 12.6 g. (0.04 mole) of crude IVa, m.p. 144–148° dec., and 75 ml. of toluene was heated at reflux for 30 min. A vigorous evolution of methylamine took place and all material eventually dissolved. The toluene was evaporated under reduced pressure and the residue was recrystallized from hexane–ethanol to give 10.2 g. (90%) of 3,3-diphenylphthalide (VIa), m.p. 116–117° (lit.[14] m.p. 116–116.5°). The melting point was not depressed on admixture with an authentic sample.[14] The infrared spectra were identical.

(B) **Cyclization of IVb.**—Similarly, 1.1 g. (0.0043 mole) of crude IVb, m.p. 151–152° dec., was refluxed for 30 min. in 25 ml. of xylene. The xylene was removed under reduced pressure and the residue was recrystallized from hexane–ethanol to give 0.7 g. (73%) of 3-methyl-3-phenylphthalide (VIb), m.p. 76.5–77° (lit.[19] m.p. 76.8–78°).

Hydrolysis and Reduction of VIa to VII.—This was effected essentially as described previously[8] by refluxing a mixture of 3.5 g. (0.012 mole) of VIa and a solution of 13.4 g. (0.24 mole) of potassium hydroxide in 30 ml. of water and 50 ml. of ethanol for 7 hr. The ethanol was evaporated from the resulting solution and 1.6 g. (0.072 mole) of zinc dust was added. After refluxing for 17 hr. the mixture was cooled, washed with ether, and the aqueous layer acidified to yield 1.3 g. (37%) of 2-benzhydrylbenzoic acid, m.p. 155–159°, and 159–160.5° after recrystallization from 95% ethanol (lit. m.p. 155–157°,[8] 158–162°[20]).

Condensation of II with Fluorenone to Form Phthalide VIII.—A solution of 14.4 g. (0.08 mole) of fluorenone in 80 ml. of ether was added during 10 min. to the mixture containing II. After stirring for 15 min. without heating, the reaction mixture was cooled in an ice bath and then poured into 70 ml. of 2 *M* hydrochloric acid and 30 g. of ice. The layers were separated and the organic layer was washed with water and combined with an ether extract of the aqueous layers. The organic layer was washed with saturated sodium chloride solution, and the solvents were then evaporated under reduced pressure at room temperature to leave a semisolid residue. This was triturated with 35 ml. of methanol, then cooled, and filtered to give 8.3 g. (58%) of spiro-[fluorene-9,1′-phthalan]-3′-one (VIII), m.p. 222.5–224°. Recrystallization from methanol–benzene gave VIII, m.p. 224–224.5° (lit. m.p. 226°,[13] 219–220°[21]).

Anal. Calcd. for $C_{21}H_{17}NO_2$: C, 84.15; H, 4.11. Found: C, 84.49; H, 4.25.

Partial evaporation of the first filtrate above yielded 4.3 g. of recovered fluorenone, m.p. 80–82.5°.

When the condensation of II with fluorenone was effected in the usual manner (refluxed 0.5 hr.), the reaction mixture darkened and the yield of VIII was slightly lower (49%).

Condensation of II with Other Electrophilic Compounds to Form Lactones. (A) **With Benzaldehyde.**—The mixture containing II was cooled in an ice bath and a solution of 8.4 g. (0.08 mole) of benzaldehyde in 80 ml. of ether was added during 30 min. The mixture was stirred for 20 min., then for 45 min. with the cooling bath removed, and poured into 80 ml. of 2 *M* hydrochloric acid and 40 g. of ice. The layers were separated and the organic layer was washed with water and combined with an ether extract of the aqueous layers. After washing with saturated sodium chloride solution and drying over sodium sulfate, the solvents were evaporated and the residue was distilled *in vacuo.* There was obtained 1.6 g. (19%) of benzyl alcohol, b.p. 82–86° (10 mm.) (identified by v.p.c., enhancement technique), 2.0 g. (30%) of recovered N-methylbenzamide, b.p. 114–118° (0.3 mm.) (m.p. 76–79°, undepressed on mixture with an authentic sample), and 5.1 g. (49%) of 3-phenylphthalide (IX), b.p. 158–164° (0.3 mm.). Recrystallization of this product from hexane–ethanol gave 4.3 g. (42%) of IX, m.p. 114.5–116.5° (lit.[15] m.p. 115°). The infrared spectrum showed a strong peak at 1750 cm.$^{-1}$ indicative of a five-membered lactone.

When the above condensation was effected under the conditions employed with benzophenone (0.5 hr. at reflux), there was obtained only a 26% yield of IX along with a 35% yield of benzyl alcohol.

(B) **With Cyclohexanone.**—The mixture containing II prepared from 8.44 g. (0.0625 mole) of N-methylbenzamide was cooled in a Dry Ice–acetone bath (rapid stream of dry nitrogen) while a solution of 9.8 g. (0.10 mole) of cyclohexanone in 100 ml. of ether was added during 10 min. The mixture was stirred 35 min. at −80°, then 30 min. with the bath removed. After pouring into 90 ml. of 2 *M* hydrochloric acid and 50 g. of ice, the layers were separated and the organic layer was washed with water and combined with an ether extract of the aqueous layers. The solvents were evaporated and a solution of 35 g. (0.625 mole)

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[19] M. S. Newman, *J. Org. Chem.*, **27**, 323 (1962).

[20] A. Drory, *Ber.*, **24**, 2563 (1891).

[21] C. F. Koelsch, *J. Am. Chem. Soc.*, **55**, 3394 (1933).

of potassium hydroxide in 125 ml. of water and 95 ml. of 95% ethanol was added to the residue. The resulting solution was refluxed for 10 hr., and the ethanol was evaporated. The cooled mixture was washed with ether and combined with a 3 *M* sodium hydroxide extract of the ether washing. The aqueous layer was acidified with concentrated hydrochloric acid without cooling. After coming to room temperature, the resulting mixture was taken up in ether. The ether solution was extracted with several portions of saturated sodium bicarbonate solution and dried over sodium sulfate. Removal of the solvent left 5.6 g. of solid residue which was recrystallized from 40 ml. of hexane and a little ethanol. There was obtained 3.4 g. (27%) of spiro[cyclohexane-1,1'-phthalan]-3'-one (X), m.p. 78–81°. Recrystallization from hexane afforded an analytical sample, m.p. 81.5–82.5°.

Anal. Calcd. from $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.02; H, 6.79.

Acidification of the bicarbonate extracts above yielded 2.1 g. (28% based on starting N-methylbenzamide) of benzoic acid, m.p. 120.5–121.5°, undepressed on admixture with an authentic sample.

When the above condensation was effected by refluxing for 0.5 hr., there was obtained an 83% recovery of N-methylbenzamide (isolated by distillation). When the condensation was effected by stirring for 20 min. at 0°, and 45 min. at room temperature, there was obtained 18% of X and 33% of benzoic acid.

(C) With Cyclohexene Oxide.—The mixture containing II was heated at reflux while a solution of 7.84 g. (0.08 mole) of cyclohexene oxide in 80 ml. of ether was added during 12 min. The mixture was refluxed an additional 20 min. and then poured into 65 ml. of 2 *M* hydrochloric acid and 35 g. of ice. From this point the reaction mixture was worked up as described above under B for cyclohexanone. There was obtained 1.4 g. (23%) of benzoic acid and 2.3 g. of crude lactone which was recrystallized from hexane and a little ethanol to give 1.1 g. (11%) of 1,2,3,4,4a,10b-hexahydro-6H-dibenzo[*b*,*d*]pyran-6-one (XI), m.p. 93–94°. A second recrystallization from hexane gave an analytical sample, m.p. 94–94.5°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.92; H, 6.91.

Attempted Metalation of Benzamide.—A mixture of 0.05 mole of benzamide and 0.156 mole of *n*-butyllithium in 100 ml. each of tetrahydrofuran and hexane was refluxed for 15 min., and the resulting mixture was treated with 0.16 mole of benzophenone in 100 ml. of ether essentially as described above for the metalation of N-methylbenzamide and condensation with this ketone. On addition of water to the cooled reaction mixture, no precipitate formed. On working up the organic layer 65% of the benzamide was recovered. No *ortho* product was found. A similar result was obtained when monoglyme was used instead of tetrahydrofuran.

When the mixture of benzamide and butyllithium in tetrahydrofuran and hexane was refluxed for 17 hr. and water then added, a black oily material insoluble in the organic and water layers was produced.

Diazoniapentaphene Salts

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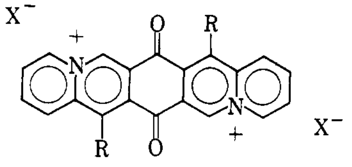
Through use of a recently developed technique, 12a,14a-, 4a,12a-, and 4a,8a-diazoniapentaphene salts have been prepared. These are believed to be the first completely aromatic condensed benzenoid compounds which contain two quaternary nitrogen atoms at bridgehead positions.

In earlier studies it was shown that diaryls could be synthesized with a quinolizinium nucleus in each moiety,[2] and that, as in 4a,11a-diazoniapentacene-6,13-quinone[3] (I), two quinolizinium nuclei may exist in a single fused ring system, separated by a quinone nucleus. The present communciation is concerned with the synthesis of the previously unknown class of compounds in which two quinolizinium nuclei are united through a fused benzenoid ring.



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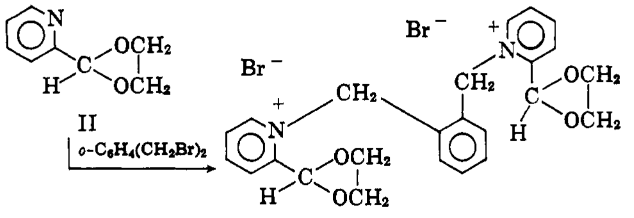

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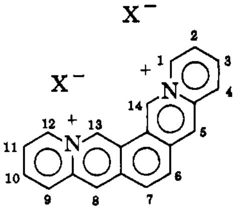
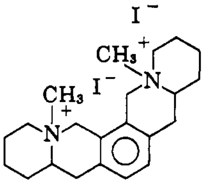


IV



V

The problem involved in the synthesis of such a derivative is that a double cyclization must occur, the second step involving a cyclization into the greatly deactivated acridizinium nucleus. The recently demonstrated[4] ability of salts of 2-(1,3-dioxolan-2-yl)pyridine (II) to undergo cyclization, even in the presence of strongly deactivating groups, recommended the acetal (II) as a starting material.

Reaction of the acetal (II) with α,α'-dibromo-*o*-xylene in dimethylformamide (DMF) or tetramethylene sulfone (TMS) produced the crystalline bisquaternary salt (III) in good yield. Cyclization of the salt in polyphosphoric acid at 145° followed by addition of perchloric acid to the diluted solution afforded what is presumably the perchlorate salt, but which detonated at 350° with such vigor that combustion analysis was out of the question. Anion-exchange resins, the usual recourse in such a situation, proved useless, in that the salt was attacked by the resin with the formation

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[2] C. K. Bradsher and N. L. Yarrington, *J. Org. Chem.*, **28**, 78 (1963).

[3] C. K. Bradsher and M. W. Barker, *ibid.*, **29**, 61 (1964).

[4] C. K. Bradsher and J. C. Parham, *ibid.*, **28**, 83 (1963); J. C. Parham, Ph.D. dissertation, Duke University, 1963.