# Homocyclic Ring Closures *via* Benzyne Intermediates. A New Synthesis of 1-Substituted Benzocyclobutenes[1]

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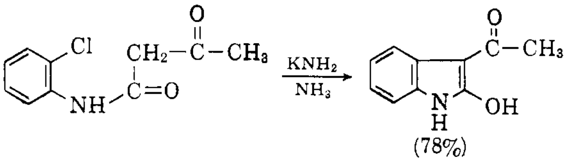
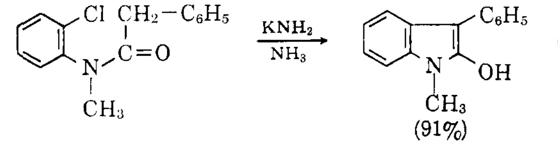
Several aliphatic nitriles, esters, sulfones, and ketones bearing an ω-*o*-chlorophenyl substituent react with potassium amide in liquid ammonia to furnish cyclization products in which a homocyclic ring is fused into the benzene ring. Benzocyclobutene, indane, tetralin, and benzocycloheptene derivatives have been prepared, mostly in yields of 50–80%. Aryne intermediates are thought to be involved; this view is supported by the fact that both *ortho*- and *meta*-4-(chlorophenyl)-butanonitrile undergo cyclization to 1-cyanoindane. For preparation of the benzocyclobutene system, this is a method of choice. However, the potentialities for further application of this principle of synthesis have perhaps greater interest than the specific examples studied.

Strong nucleophiles add readily to arynes.[3-5] If the nucleophile is situated on a side chain of the aryne, intramolecular addition forms a new ring fused to the original aromatic nucleus. This principle of ring closure has been developed and exploited by Huisgen and co-workers[6] and by Bunnett, Hrutfiord, Kato, and Williamson.[7-9]

Examples published to date include intramolecular addition of nucleophiles of the carbanion, nitranion, oxyanion, and sulfur anion types. The products have been heterocyclic compounds, even when a side-chain carbanion was involved, as in equations 1[8] and 2.[9] Attempts to close rings containing only carbon atoms have been unsuccessful.

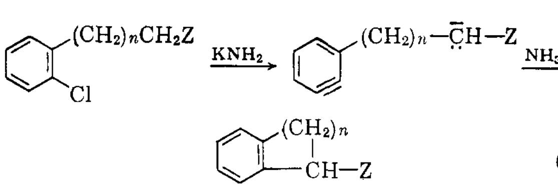


(1)



(2)

We have found that several aliphatic esters, nitriles, sulfones, and ketones bearing an ω-*o*-chlorophenyl group react with potassium amide in liquid ammonia to furnish good yields of homocyclic ring closure products. These reactions and their presumed mechanism are symbolized in a general way by equation 3, where Z is a cyano, sulfonyl, carboethoxy, or acyl group.

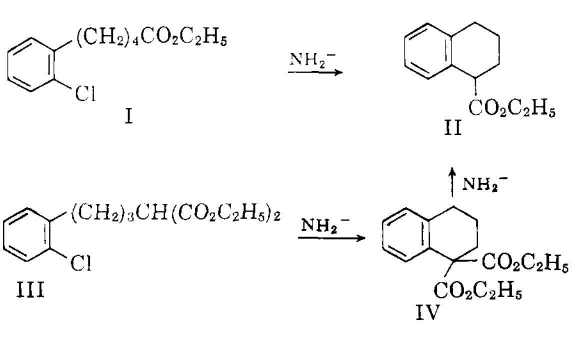


(3)

We have explored the effects of chain length (*n* in equation 3) and of the activating group (Z) on yield of ring closure product. The principal results are summarized in Table I.

Syntheses of all the ω-*o*-chlorophenyl compounds began with commercially available *o*-chlorobenzyl chloride. The chain was lengthened by malonic ester syntheses and by condensation of chlorides with sodium cyanide. Other standard reactions were used to transform the resulting esters or nitriles into structures required for further chain-lengthening or for submission to ring closure conditions. Most of the intermediates and the final products of these syntheses are new compounds. Details are given in the Experimental.

**Successful Ring Closures.**—Treatment of ethyl 5-(*o*-chlorophenyl)pentanoate (I) with potassium amide afforded ethyl 1,2,3,4-tetrahydronaphthalene-1-carboxylate (II) in 54% yield. The same product was obtained from diethyl 3-(*o*-chlorophenyl)-1-propylmalonate (III) in 38% yield. Apparently the expected diester IV was formed first but then underwent a decarbethoxylation involving the



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[1] Presented in part at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962.

[2] Allied Chemical Corp. Fellow, 1960–1961. This paper is based on the Ph.D. thesis of J. A. S., May, 1962. Research supported in part by the Army Research Office (Durham).

[3] R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

[4] J. F. Bunnett, *J. Chem. Ed.*, **38**, 278 (1961).

[5] H. Heaney, *Chem. Rev.*, **62**, 81 (1962).

[6] R. Huisgen and H. König, *Angew. Chem.*, **69**, 268 (1957); *Ber.*, **92**, 203, 429 (1959); R. Huisgen, H. König, and A. R. Lepley, *Ber.*, **93**, 1496 (1960).

[7] J. F. Bunnett and B. F. Hrutfiord, *J. Am. Chem. Soc.*, **80**, 2021 (1958); **83**, 1691 (1961).

[8] J. F. Bunnett, B. F. Hrutfiord, and S. M. Williamson, *Org. Syntheses*, **40**, 1 (1960).

[9] J. F. Bunnett and T. Kato, unpublished results.

TABLE I

RING CLOSURES IN LIQUID AMMONIA

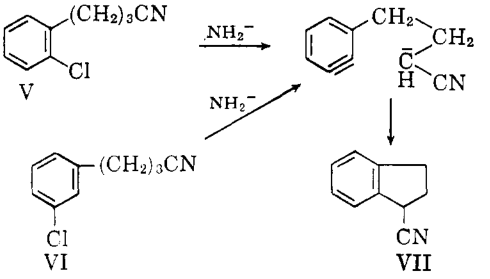
| Reaction | Reactant | Moles $KNH_2$ per mole reactant[a] | Product | Yield, % | Isolable by-products,[b] % |
|---|---|---|---|---|---|
| 1 | Ethyl 5-(*o*-chlorophenyl)pentanoate (I) | 4 | Ethyl 1,2,3,4-tetrahydronaphthalene-1-carboxylate (II) | 54 | 18 |
| 2 | Diethyl 3-(*o*-chlorophenyl)-1-propylmalonate (III) | 4.3 | Ethyl 1,2,3,4-tetrahydronaphthalene-1-carboxylate (II)<br>+ recovered III | 38<br>4 | 10 |
| 3 | 5-(*o*-Chlorophenyl)pentanonitrile | 4 | 1-Cyano-1,2,3,4-tetrahydronaphthalene | 61 | 30 |
| 4 | Ethyl 4-(*o*-chlorophenyl)butanoate | 4 | Ethyl indane-1-carboxylate | 57 | 18 |
| 5 | 4-(*o*-Chlorophenyl)butanonitrile (V) | 4 | 1-Cyanoindane (VII) | 68 | 6 |
| 6 | 4-(*m*-Chlorophenyl)butanonitrile (VI) | 3.5 | 1-Cyanoindane (VII) | 49 | 43 |
| 7 | Phenyl 3-(*o*-chlorophenyl)-1-propyl sulfone | 4 | Phenyl 1-indanyl sulfone | 82 | 10 |
| 8 | Phenyl 3-(*o*-chlorophenyl)-1-propyl ketone | 3[c] | 1-Benzoylindane<br>Indane<br>Benzamide | 46<br>11<br>20 | 10 |
| 9 | Ethyl *o*-chlorohydrocinnamate (VIIIa) | 3 | Ethyl benzocyclobutene-1-carboxylate (IXa) | 10 | 49 |
| 10 | *o*-Chlorohydrocinnamonitrile (VIIIb) | 4[c] | 1-Cyanobenzocyclobutene (IXb) | 61 | 3 |
| 11 | Phenyl 2-(*o*-chlorophenyl)ethyl sulfone (VIIIc) | 4 | Phenyl 1-benzocyclobutenyl sulfone (IXc) | 47 | 27 |
| 12 | 6-(*o*-Chlorophenyl)hexanonitrile (X) | 3.5 | 1-Cyanobenzocycloheptene (XI) | 49 | 44 |
| 13 | 6-(*o*-Chlorophenyl)-2,4-hexanedione (XII) | 4[d] | 1-Acetyl-2-tetralone (XIII)<br>+ recovered XII | 42<br>7 | 3 |

[a] Reaction times were 15 min. except where indicated. [b] Predominantly amine materials. [c] Reaction time of 5 min. [d] Reaction time of 3 hr.

excess amide ion. This is reminiscent of a cleavage recently reported by Cookson and co-workers.[10]

A nitrile corresponding to II, 1-cyanotetrahydronaphthalene, was formed in 61% yield from 5-(*o*-chlorophenyl)pentanonitrile under ring closure conditions.

Five-membered ring closure was realized with several activating groups. Ethyl 4-(*o*-chlorophenyl)butanoate was converted to ethyl indane-1-carboxylate in 57% yield by the action of amide ion in ammonia. Similarly, 4-(*o*-chlorophenyl)butanonitrile (V) gave 1-cyanoindane (VII) in 68% yield.



1-Cyanoindane likewise was obtained from the *meta* isomer, 4-(*m*-chlorophenyl)butanonitrile (VI), in 48% yield. The formation of a common product from both of the positional isomers is significant, for it substantiates the assumed elimination–addition mechanism.

In the best reaction, phenyl 1-indanyl sulfone was formed in 82% yield from phenyl 3-(*o*-chlorophenyl)-1-propyl sulfone. Benzoyl was an inferior activating group, for only 46% of 1-benzoylindane resulted from exposure of phenyl 3-(*o*-chlorophenyl)-1-propyl ketone to potassium amide in ammonia. However, benzamide and indane also were isolated. On the supposition that they were products of cleavage of 1-benzoylindane, they account for an additional 20% of cyclization. These two compounds were shown to be formed from 1-benzoylindane under ring closure conditions.[11]

Four-membered rings could also be closed. Ethyl *o*-chlorohydrocinnamate (VIIIa) gave ethyl benzocyclobutene-1-carboxylate (IXa) in yields ranging from 5 to 13%. Saponification of the ester afforded benzocyclobutene-1-carboxylic acid.[15]

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[10] R. C. Cookson, J. Hudec, and B. Whitear, *Proc. Chem. Soc.*, 117 (1961).

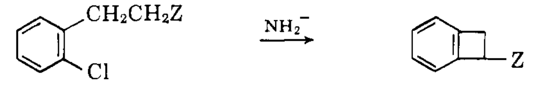
[11] That an appreciable amount of ketone cleavage occurred was rather surprising, for the Haller–Bauer cleavage is usually effected by prolonged boiling of the ketone with sodium amide in benzene, toluene, of xylene.[12] Benzophenone, considered to be rather easily cleaved under typical Haller–Bauer conditions, is virtually unaffected by long standing with potassium amide in ammonia.[13] The few ketones which are cleaved in liquid ammonia medium—*o*-halobenzophenones[13] and phenyl trityl ketone[14]—are apparently those which have groups of considerable potential anionic stability attached to carbonyl carbon. We would not have thought the 1-indanyl group to be outstanding in this respect.

[12] K. E. Hamlin and A. W. Weston, *Org. Reactions*, **IX**, 1 (1957).

[13] J. F. Bunnett and B. F. Hrutfiord, Abstracts from 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 94-O.

[14] W. W. Leake and R. Levine, *J. Am. Chem. Soc.*, **81**, 1169 (1959).

[15] M. P. Cava, R. L. Little, and D. R. Napier, *ibid.*, **80**, 2257 (1958).



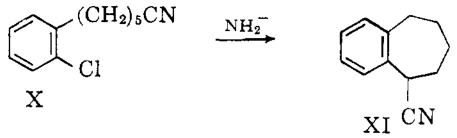
VIIIa. $Z = CO_2C_2H_5$
b. $Z = CN$
c. $Z = SO_2C_6H_5$

IXa. $Z = CO_2C_2H_5$
b. $Z = CN$
c. $Z = SO_2C_6H_5$

This interesting result was surpassed by the behavior of *o*-chlorohydrocinnamonitrile (VIIIb), which gave 1-cyanobenzocyclobutene (IXb) in 61% yield on treatment with potassium amide. The bicyclic nitrile was hydrolyzed to benzocyclobutene-1-carboxamide, which lead to the previously isolated benzocyclobutene-1-carboxylic acid on heating with aqueous alkali. The nitrile, amide, and acid were described originally by Cava, *et al.*[15]

Phenyl 2-(*o*-chlorophenyl)ethyl sulfone (VIIIc) gave phenyl 1-benzocyclobutenyl sulfone (IXc) in moderate (47%) yield. Oxidation of this product to phthalic acid by means of alkaline potassium permanganate was important for proof of structure.

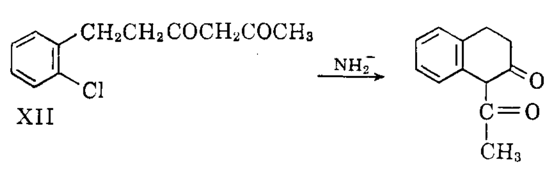
One ring with seven atoms was obtained. 6-(*o*-Chlorophenyl)hexanonitrile (X) afforded 1-cyanobenzocycloheptene (XI) in 49% yield on reaction with amide ion. The product was converted to the respective amide and acid and was oxidized to phthalic acid by alkaline potassium permanganate.



X

XI

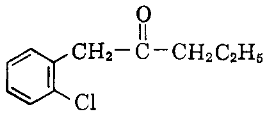
Finally, treatment of 6-(*o*-chlorophenyl)-2,4-hexanedione (XII) with potassium amide ion gave 1-acetyl-2-tetralone (XIII) in 42% yield. The starting diketone (7%) and a large amount of intractable tars likewise were isolated. The tarry material, which displayed monocarbonyl absorption in the infrared and gave no color with alcoholic ferric chloride, apparently resulted from alkaline cleavage of both the starting material and the product.



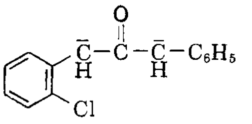
XII

XIII

**Unsuccessful Ring Closure Attempts.**—1-Phenyl-2-indanone was the expected product from the reaction of 1-phenyl-3-(*o*-chlorophenyl)-2-propanone (XIV) and amide ion. However, after a four and a half hour exposure to four equivalents of potassium amide, the only identifiable substance isolated was 71% of unchanged starting material.



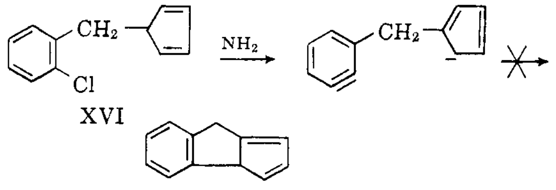
XIV



XV

The 1,3-dianion[16] XV undoubtedly was formed initially in the presence of two or more equivalents of base. Since XV has but one carbonyl group to assist delocalization of two negative charges, the flanking aromatic rings must be called upon to accept, by resonance, considerable negative charge. In the chlorophenyl group, the result is apparently such a reduction in the acidity of the aromatic hydrogens as to prohibit proton abstraction by the amide ion. The operation of this factor in other instances has been noted.[4,7]

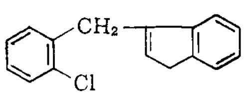
It was hoped to synthesize the unknown dihydrobenzopentalene (XVII) from *o*-chlorobenzylcyclopentadiene (XVI) by way of an aryne intermediate. XVI was easily obtained by condensation of sodium cyclopentadienide with *o*-chlorobenzyl chloride but was difficult to handle because of its proclivity to dimerize. The chlorodiene XVI was allowed to react with approximately four equivalents of potassium amide, in two separate experiments. In both cases only small amounts of dimerized starting material were isolable from the tarry residue. Amination and polymerization apparently predominate.



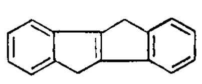
XVI

XVII

The reaction of 3-*o*-chlorobenzylindene (XVIII) with strong base was next investigated. From reaction of XVIII with four equivalents of potassium amide for five and a half hours, a colorless solid, m.p. 222–224°, was obtained in 1% yield together with over 70% of amination products. The analysis of the solid corresponded to the formula $C_{16}H_{12}$. The ultraviolet spectrum was unlike that reported for XIX, one of the conceivable products.[17] Unfortunately the amount of this solid was inadequate for n.m.r. study, and repeated efforts to obtain more were unavailing.



XVIII



XIX

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[16] C. R. Hauser and T. M. Harris, *ibid.*, **81**, 1154 (1959).

[17] C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952).

All of the reactions with potassium amide afforded some amination by-products (Table I), which were separated from the desired products by elution chromatography. An effort was made to identify two amines isolated from the treatment of 3-*o*-chlorobenzylindene (XVIII) with amide ion. These two were obtained in 44 and 22% yields, respectively. Analyses of both materials and of their 1-naphthylurea derivatives indicated they were aminobenzylindenes, undoubtedly the *ortho* and *meta* isomers.

In order to determine which isomer was present in predominate amount, an independent synthesis of the *meta* compound was undertaken. The direct alkylation of indene with *m*-nitrobenzyl chloride and sodium amide as the condensing agent, however, gave only tars. The aryl nitro group apparently could not withstand the strongly basic conditions.[18] Moreover, the reaction of *m*-phthalimidobenzyl chloride with indene and sodium amide afforded only crude intractable oils. The identities of the two amines remain uncertain.

No effort was made to identify amine products from other reactions.

## Discussion

The relationship of cyclization yield to ring size and functional group character is brought into focus in Table II. Phenylsulfonyl and cyano are the preferred activating groups, the former giving the best yield of a five-ring and the latter of a four-ring product. An advantage of sulfonyl groups is that they can be cleaved from the product if desired.[19] On the other hand, synthesis of a nitrile is often easier.

TABLE II

CYCLIZATION YIELDS WITH DIFFERENT PROTON ACTIVATING GROUPS

| Activating group | Yield at ring size, % 4 | 5 | 6 | 7 |
|---|---|---|---|---|
| Carbethoxy | 10 | 57 | 54 | |
| Cyano | 61 | 68 | 61 | 49 |
| Phenylsulfonyl | 47 | 82 | | |
| Benzoyl | | 66 | | |

With a cyano group at the end of the alkyl chain, closure of four-, five-, and six-membered rings occurred to approximately equal extents. Formation of a seven-membered ring was almost as facile; however, the 49% yield was achieved in a more dilute solution than that used for the other three experiments. At a comparable concentration, the yield of 1-cyanobenzocycloheptene was 36%.

Our syntheses of benzocyclobutene derivatives should, we feel, be of considerable value to workers interested in benzocyclobutene chemistry. Both in yield and in the accessibility of precursors, our better four-ring closures compare favorably with other methods employed for the formation of this ring system.[15,20,21] Furthermore, it is probable that these syntheses can be generalized so as to yield directly in the ring closure step benzocyclobutenes substituted with alkyl, aryl, alkoxy, carboxy, dialkylamino, fluoro, and other groups in the benzene and/or the four-membered ring. Also, many of the initial ring closure products would provide reactive sites for further structural elaboration. It is therefore conceivable that ring closure *via* aryne intermediates may become the most useful general method for preparation of benzocyclobutenes.

The indane, tetralin, and benzocycloheptene systems are accessible by other routes, many of them cheaper and more convenient than that with which we are concerned. However, derivatives carrying specified substituents in particular positions are sometimes hard to get by traditional methods. In such cases, cyclization *via* elimination–addition may constitute the best preparative scheme.

In view of evidence for pyridyne, quinolyne, and thiophyne intermediates,[22] it seems likely that this synthetic principle should also be useful for preparation of compounds with four-, five-, six-, seven-membered, and larger homocyclic rings fused to heterocyclic systems. Syntheses of compounds with a four-membered heterocyclic ring fused to a benzene or other aromatic ring can also be visualized.

Finally, we wish to stress the simplicity of the experimental technique which is both quicker and less troublesome than that involved in a typical Grignard synthesis. In nearly every case, a 15-min. reaction time was sufficient to consume completely the starting material, and we suspect that shorter reaction times often would have been adequate. The total elapsed time from start of assembly of glassware (all standard items) to quenching of the reaction mixture with an ammonium salt is about 1.25 hr. The product is then isolated by standard operations that present no unusual difficulty.

## Experimental[23]

In Table III are listed the ethyl esters and nitriles utilized in the ring closure experiments along with the alcohols and chlorides intermediate in their preparation. Two sulfides,

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[18] R. Levine and W. C. Fernelius, *Chem. Rev.*, **54**, 449 (1954).

[19] R. Mozingo, D. E. Wolf, S. A. Harris, and K. Folkers, *J. Am. Chem. Soc.*, **65**, 1013 (1943).

[20] L. Horner, W. Kirmse, and K. Muth, *Ber.*, **91**, 430 (1958).

[21] M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4266 (1959); A. P. ter Borg and A. F. Bickel, *Proc. Chem. Soc.*, 283 (1958); H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961); M. E. Kuehne, *ibid.*, **84**, 837 (1962).

[22] W. W. Leake and R. Levine, *Science*, **121**, 780 (1955); T. Kauffman and F.-P. Boettcher, *Angew. Chem.*, **73**, 65 (1961); T. Kauffmann, F.-P. Boettcher, and J. Hansen, *ibid.*, **73**, 341 (1961); G. Wittig and V. Wahl, *ibid.*, **73**, 492 (1961).

[23] Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill. All melting and boiling points are uncorrected.

TABLE III

RING CLOSURE STARTING MATERIALS AND PREPARATIVE INTERMEDIATES

| $o$-ClC$_6$H$_4$(CH$_2$)$_n$Z | | | Yield, | | | Calcd. | | Found | |
|---|---|---|---|---|---|---|---|---|---|
| $n$ | Z | Method | % | B.p. | Mm. | C | H | C | H |
| 2 | $CO_2C_2H_5$ | A | 90 | 142–143 | 17 | 62.12 | 6.16 | 62.50 | 6.31 |
| 3 | $CO_2C_2H_5$ | B | 74 | 109–110 | 0.8 | 63.58 | 6.67 | 63.77 | 6.55 |
| 4 | $CO_2C_2H_5$ | B | 75 | 111–113 | 0.6 | 64.86 | 7.12 | 65.19 | 7.05 |
| 2 | OH | C | 93 | 84–85 | 0.3 | 61.35 | 5.79 | 61.58 | 6.14 |
| 3 | OH[a] | C | 90 | 150–151 | 12 | 63.35 | 6.50 | 63.54 | 6.50 |
| 3 | OH[b] | C | 89 | 97–98[c] | 0.7 | | | | |
| 4 | OH | C | 91 | 104–105 | 0.7 | 65.04 | 7.10 | 65.74 | 7.19 |
| 5 | OH | C | 95 | 111–112 | 0.6 | 66.49 | 7.61 | 66.41 | 7.49 |
| 2 | Cl | D | 88 | 58–60 | 0.4 | 54.89 | 4.61 | 55.23 | 4.75 |
| 3 | Cl | D | 91 | 131–133 | 11 | 57.17 | 5.33 | 57.54 | 5.37 |
| 3 | Cl[b] | D | 96 | 77–78 | 0.8 | 57.17 | 5.33 | 57.54 | 5.40 |
| 4 | Cl | D | 83 | 97–98 | 1.1 | 59.13 | 5.96 | 59.20 | 5.87 |
| 5 | Cl | D | 88 | 98–99 | 0.7 | 60.84 | 6.50 | 60.88 | 6.56 |
| 2 | CN | E | 31 | 91–93[d] | 0.7 | | | | |
| 3 | CN | E | 79 | 95–97 | 0.2 | 66.86 | 5.61 | 66.61 | 5.80 |
| 3 | CN[b] | E | 71 | 112–113 | 0.8 | 66.86 | 5.61 | 67.13 | 5.80 |
| 4 | CN | E | 82 | 131–132 | 1.1 | 68.22 | 6.25 | 66.38 | 6.24 |
| 5 | CN | E | 71 | 122–124 | 0.7 | 69.39 | 6.79 | 69.34 | 6.59 |
| 2 | $SC_6H_5$ | F | 91 | 143–144 | 0.7 | 67.59 | 5.27 | 67.81 | 5.38 |
| 3 | $SC_6H_5$ | F | 89 | 161–163 | 0.5 | 68.55 | 5.75 | 68.83 | 5.83 |

[a] 1-Naphthylurethane, m.p. 105.5–106.5°. *Anal.* Calcd. for $C_{20}H_{18}ClNO$: C, 70.69; H, 5.34. Found: C, 70.84; H, 5.23. [b] Chlorine *meta* to side chain. [c] H. König and R. Huisgen, *Ber.*, **92**, 429 (1959). [d] A. O. Grebenyuk and I. P. Tsukervanik, *J. Gen. Chem. U.S.S.R.*, **25**, 269 (1955).

intermediates in the synthesis of the phenylsulfonyl substrates, also are included. The preparative methods cited in Table III are now described.

**Method A.**—The ester was prepared from the corresponding acid, in this case $o$-chlorohydrocinnamic acid,[24] by the procedure of Micovic.[25]

**Method B.**—The ester was synthesized by ethanolysis of the corresponding nitrile as described by Goering, Cristol, and Dittmer.[26]

**Method C.**—The carbinol was prepared by reduction of the related ester with lithium aluminum hydride in anhydrous ether.

**Method D.**—The chloride was obtained by treatment of the respective alcohol with thionyl chloride and pyridine.[27a]

**Method E.**—The nitrile was prepared from the corresponding chloride by reaction with sodium cyanide in aqueous ethanol.[27b]

**Method F.**—The related chloride was added dropwise to an absolute ethanol solution of equimolar amounts of thiophenol and sodium ethoxide. After 24 hr. refluxing, the solvent was removed and the remaining sulfide was distilled.

**Diethyl 3-(*o*-Chlorophenyl)-1-propylmalonate (III).**—Diethyl malonate (0.33 mole) was combined with sodium ethoxide (0.27 mole) in absolute ethanol and then with 3-($o$-chlorophenyl)-1-chloropropane (0.26 mole), and the mixture was heated 6 hr. at reflux. Distillation of the crude product gave diester III in 76% yield, b.p. 144–148° (0.4 mm.). A fraction boiling at 147° (0.4 mm.) was redistilled for analysis.

*Anal.* Calcd. for $C_{16}H_{21}ClO_4$: C, 61.44; H, 6.77. Found: C, 61.51; H, 7.00.

**Phenyl ω-(*o*-Chlorophenyl)alkyl Sulfones.**—To the appropriate sulfide in glacial acetic acid (85 ml. per 0.1 mole of the sulfide) at 5° was added slowly a 30% solution of hydrogen peroxide (approximately 27 ml. per 0.1 mole of sulfide). The solution was allowed to warm to room temperature for an hour. When cool, it was poured onto ice, and the solid sulfone which separated was obtained as white needles by crystallization from ethanol.

**Phenyl 2-(*o*-chlorophenyl)ethyl sulfone (VIIIc)**, m.p. 45–47°, was obtained in 80% yield.

*Anal.* Calcd. for $C_{14}H_{13}ClO_2S$: C, 59.89; H, 4.67. Found: C, 60.29; H, 4.88.

**Phenyl 3-(*o*-chlorophenyl)-1-propyl sulfone**, m.p. 73–74°, was prepared in 87% yield.

*Anal.* Calcd. for $C_{15}H_{15}ClO_2S$: C, 61.11; H, 5.13. Found: C, 61.15; H, 5.23.

**Phenyl 3-(*o*-Chlorophenyl)-1-propyl Ketone.**—4-($o$-Chlorophenyl)butanonitrile (V) was allowed to react with a 50% molar excess of phenylmagnesium bromide in anhydrous ether as described by Hauser and Humphlett[28] to give the ketone in 84% yield, b.p. 144–145° (0.3 mm.).

*Anal.* Calcd. for $C_{16}H_{15}ClO$: C, 74.27; H, 5.84. Found: C, 74.22; H, 5.96.

The semicarbazone (white needles from ethanol–water) melted at 151–152°.

*Anal.* Calcd. for $C_{17}H_{18}ClN_3O$: C, 64.65; H, 5.75. Found: C, 64.61; H, 5.81.

**Ethyl 2-*o*-Chlorobenzylacetoacetate.**—A twofold excess of ethyl acetoacetate was used as proposed by Leuchs.[29] It was treated with sodium ethoxide and then was allowed to react with $o$-chlorobenzyl chloride. The product was obtained in 77% yield, b.p. 112–115° (0.7 mm.), (lit.[30] 172–185° at 48 mm.). A sample with b.p. 114.5° (0.7 mm.) was submitted for analysis.

*Anal.* Calcd. for $C_{13}H_{15}ClO_3$: C 61.30; H 5.94. Found: C, 61.06; H, 5.78.

**4-(*o*-Chlorophenyl)-2-butanone.**—Ethyl 2-$o$-chlorobenzylacetoacetate was refluxed with 5% aqueous sodium hydroxide and then with 48% sulfuric acid as described by Johnson and Hager.[31] Distillation of the crude product gave the aryl butanone in good (83%) yield, b.p. 164–168° (25 mm.). A center cut, b.p. 166° (25 mm.), was redistilled for analysis.

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*Anal.* Calcd. for $C_{10}H_{11}ClO$: C 65.72; H, 6.07. Found: C, 65.62; H, 5.95.

The semicarbazone (colorless needles from ethanol-water) melted at 172.5–173.5°.

*Anal.* Calcd. for $C_{11}H_{14}ClN_3O$: C, 55.11; H, 5.89. Found: C, 55.13; H, 6.01.

**6-(*o*-Chlorophenyl)-2,4-hexanedione (XII).**—A procedure similar to that described by Hauser and co-workers[32] was used. To a suspension of commercial sodium amide (0.77 mole) in anhydrous ether was added 4-(*o*-chlorophenyl)-2-butanone (0.385 mole). Several minutes later, ethyl acetate (0.77 mole) was introduced into the yellow solution, which then was refluxed with stirring for 3 hr. Water was added cautiously; and the separated ether solution was dried over anhydrous sodium sulfate, then evaporated. The liquid residue (98 g.) was allowed to react with a hot, aqueous solution of cupric acetate. The resulting copper chelate melted at 205–207.5° after one recrystallization from benzene. Hydrolysis of the chelate with 6 *M* hydrochloric acid and distillation of the crude product gave 40.6 g. (47%) of XII, b.p. 120–123° (2 mm.). A sample of the fraction boiling at 121° (2 mm.) was analyzed. The diketone gave a deep red enol test with ethanolic ferric chloride.

*Anal.* Calcd. for $C_{12}H_{13}ClO_2$: C, 64.15; H, 5.83. Found: C, 64.17; H, 5.81.

A pyrazole derivative prepared according to the method of Hauser and Harris[33] melted at 67–68° after recrystallization from ligroin.

*Anal.* Calcd. for $C_{12}H_{13}ClN_2$: C, 65.30; H, 5.94. Found: C, 65.35; H, 5.96.

A portion of the diketone was reconverted to its blue copper chelate, which melted at 209–210° after several recrystallizations from benzene. Its infrared spectrum displayed bands at 6.33 and 6.53 $\mu$ characteristic of chelates of 1,3-diketones unsubstituted at the intermediate methylene group.[34]

*Anal.* Calcd. for $C_{24}H_{24}Cl_2O_4Cu$: C, 56.42; H, 4.74. Found: C, 56.63; H, 5.04.

**2-(*o*-Chlorophenyl)-4-phenyl-3-oxobutanonitrile.**—A mixture of *o*-chlorophenylacetonitrile (0.33 mole) and ethyl phenylacetate (0.41 mole) was added slowly to a solution of sodium ethoxide (0.66 mole) in ethanol according to the method of Coan and Becker.[35a] After 6 hr. heating at reflux the solvent was removed; the residue was recrystallized from ether–ligroin to give the ketonitrile (73% of theory) as white crystals, m.p. 75–75.5°.

*Anal.* Calcd. for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.48. Found: C, 71.64; H, 4.55.

**1-Phenyl-3-(*o*-chlorophenyl)-2-propanone (XIV).**—2-(*o*-Chloro-phenyl)-4-phenyl-3-oxobutanonitrile (0.122 mole) was refluxed with 60% sulfuric acid (96 ml.) for 24 hr.[35b] An orange oil was isolated and flash distilled twice to give a colorless solid (61%), m.p. 37–38.5° (lit.[36] 38–39.5°) on recrystallization from ether–ligroin. A 2,4-dinitrophenylhydrazone melted at 109–110.5° (lit.[36] 111–112°) after recrystallization from ethanol.

***o*-Chlorobenzylcyclopentadiene (XVI).**—An ethereal solution of cyclopentadiene (0.36 mole) was added rapidly to sodium amide (0.30 mole) in 500 ml. of ammonia. After the introduction of *o*-chlorobenzyl chloride (0.30 mole), the solution was stirred for 2 hr. The brown liquid obtained on evaporation of the ammonia was distilled in a large diameter, direct-path system with an oil bath temperature of 215°.[37] A small amount of forerun was followed by 33 g. (58%) of XVI, b.p. 145–154° (12 mm.).

Freshly distilled XVI (0.6 g., 0.003 mole) was added to a solution of tetracyanoethylene (0.4 g., 0.003 mole) in 50 ml. of benzene. A transient green color appeared and there was appreciable warming. Solvent evaporation yielded an oil which crystallized on trituration with ligroin. Colorless crystals, m.p. 138–139.5°, wt. 0.9 g. (90%), were obtained by recrystallization from benzene–petroleum ether (30–60°). An analytical sample of the adduct melted at 140–141°.

*Anal.* Calcd. for $C_{18}H_{11}N_4Cl$: C, 67.82; H, 3.48. Found: C, 67.70; H, 3.46.

**3-*o*-Chlorobenzylindene[38] (XVII).**—Indene (0.34 mole) was added to sodium amide (0.32 mole) in ammonia (500 ml.) followed by *o*-chlorobenzyl chloride (0.32 mole). The organic residue from ammonia evaporation was taken up in ligroin and distilled to give 35.1 g. (51%) of XVIII as a yellow oil, b.p. 139–141° (0.3 mm.).

*Anal.* Calcd. for $C_{16}H_{13}Cl$: C, 79.83; H, 5.44. Found: C, 79.72; H, 5.41.

**General Ring Closure Procedure.**—A 1-l. three-necked flask was equipped in one neck with a nitrogen inlet, in another with a ball-and-socket–sealed mechanical stirrer, in the third with a Y-tube fitted with an ammonia inlet and a Dry Ice condenser, the outlet of which was protected by a soda lime drying tube. To begin, the reaction vessel was dried by flaming as nitrogen circulated through the system. The condenser was filled with a Dry Ice–isopropyl alcohol mixture; and liquid ammonia from a cylinder was introduced into the flask. Unless specifically stated, the amount of this solvent was 600 ml. for all of the runs. The ammonia inlet tube was replaced by a stopper, and a small piece or two of potassium metal was added so that the blue color persisted for several minutes. Then, a trace of powdered ferric nitrate was added, followed by the calculated weight of potassium metal. When the metal had reacted completely, as indicated by a color change from blue to deep gray, the substrate was introduced quickly. Solids were added directly, whereas liquids were transferred to the flask with the aid of a minimum amount of anhydrous ether. As soon as the reactant came in contact with the basic medium, the entire solution became orange brown in color.

After the chosen reaction time (15 min. unless otherwise specified), the base was quenched with a slight excess of ammonium nitrate, and the ammonia was allowed to evaporate. Water (75 ml.) was added, and the organic material was taken up in chloroform (150 ml.). After drying over sodium sulfate, the solvent was evaporated and the crude residue was put on a column of basic (Merck) alumina (90–110 g.). In elution with the usual chromatographic solvents, the desired cyclic compound appeared first, followed by the more polar by-products. The latter materials were assumed to be amination products on the basis of their infrared spectra and, in the several cases where tested, on their elemental analyses (nitrogen-containing but halogen-free) and their ability as diazonium salts to couple with $\beta$-naphthol.

All of the ring closure products were accompanied by varying amounts of tar which was partially soluble only in acetone. In some cases, a tarry band also remained on the alumina of the chromatography column.

**Ethyl 1,2,3,4-Tetrahydronaphthalene-1-carboxylate (II). A. from Ethyl 5-(*o*-Chlorophenyl)pentanoate (I).**—In reaction 1 (Table I), 5.0 g. of the ester I was allowed to react with the amount of base listed in Table I. The bicyclic ester II boiled at 87–89° (0.04 mm.).

*Anal.* Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C 76.70; H 8.18.

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The ester II was hydrolyzed with methanolic potassium hydroxide to 1 2,3,4-tetrahydronaphthalene-1-carboxylic acid, m.p. 81–83° (lit.[39] 83–84°).

**B. From Diethyl 3-(*o*-Chlorophenyl)-1-propylmalonate (III).**—In reaction 2, 3.6 g. of III in 700 ml. of liquid ammonia was used. The infrared spectrum of the product (0.91 g.) was identical to that of the ester isolated in reaction 1. The mixed m.p. of the acids obtained by alkaline hydrolysis of the two ester samples was 81–83°.

**1-Cyano-1,2,3,4-tetrahydronaphthalene.**—In reaction 3, 5.0 g. of 5-(*o*-chlorophenyl)pentanonitrile was used. Elution with petroleum ether–benzene (1:2) gave 2.5 g. of the bicyclic nitrile, b.p. 109–111° (1.5 mm.). The reported[39] b.p. is 135–140° (2 mm.). Hydrolysis of the product with 30% hydrogen peroxide and 20% aqueous sodium hydroxide gave 1,2,3,4-tetrahydronaphthalene-1-carboxamide (80% yield), m.p. 165–167° (lit.[39] 161–162°) after recrystallization from chloroform. Treatment of the amide with methanolic potassium hydroxide afforded the corresponding acid, m.p. 80–82°. This material did not depress the m.p. of an authentic sample of the acid.

**Ethyl Indane-1-carboxylate.**—In reaction 4, 5.0 g. of ethyl 4-(*o*-chlorophenyl)butanoate was used. Elution with petroleum ether–benzene (2:1) gave 3.9 g. of the indane derivative, b.p. 84–86° (0.8 mm.).

*Anal.* Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.85; H, 7.52.

Indane-1-carboxylic acid, m.p. 55–56° (lit.[40] 55–56°), was obtained on alkaline hydrolysis of the bicyclic ester.

**1-Cyanoindane (VII). A. From 4-(*o*-Chlorophenyl)-butanonitrile (V).**—In reaction 5, 5.0 g. of V was used. Elution with petroleum ether–benzene (1:1) afforded 2.7 g. of VII, b.p. 83–84° (0.8 mm.). The reported[39] b.p. is 108–109° (0.7 mm.). The bicyclic nitrile was hydrolyzed with alkaline hydrogen peroxide to indane-1-carboxamide, m.p. 163–164° (lit.[39] 164–166°). Alkaline hydrolysis of the amide gave indane-1-carboxylic acid. A mixed m.p. with a sample of the acid obtained in reaction 4 was 55–57°, and the infrared spectra were identical

**B. From 4-(*m*-Chlorophenyl)butanonitrile (VI).**—In reaction 6, 5.0 g. of VI was used. The nitrile product (1.97 g.), the corresponding amide, and the acid were identical to the materials encountered in reaction 5.

**Phenyl 1-Indanyl Sulfone.**—In reaction 7, 5.0 g. of phenyl 3-(*o*-chlorophenyl)-1-propyl sulfone was used. Elution with benzene–ether (4:1) gave 3.6 g. of a pale yellow oil which readily solidified. The melting point was 101–103.5° after recrystallization from benzene–ligroin. An analytical sample melted at 103.5–104.5° and did not depress the m.p. of a sample obtained by oxidation of the sulfide from the reaction of 1-chloroindane and sodium thiophenoxide. The infrared spectra of the two sulfone samples were identical.

*Anal.* Calcd. for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46. Found: C, 69.76; H, 5.71.

**1-Benzoylindane.**—In reaction 8, 5.0 g. of phenyl 3-(*o*-chlorophenyl)-1-propyl ketone was used. Petroleum ether–benzene (4:1) elution afforded 0.26 g. (11%) of a colorless liquid with an infrared spectrum identical to that of indane. Elution with benzene–ether (4:1) gave 1.97 g. (46%) of 1-benzoylindane, and chloroform–methanol (2:1) gave 0.47 g. (20%) of benzamide. The ketone, b.p. 142–144° (0.6 mm.), was converted to a semicarbazone, m.p. 208–209° (lit.[41] 210°) after recrystallization from ethanol.

A 2-g. sample of 1-benzoylindane was treated with 5 equivalents of potassium amide in 500 ml. of ammonia for 15 min. Chromatographic separation of the product mixture yielded 0.074 g. (7%) of indane, 1.3 g. (65%) of unchanged ketone, and 0.25 g. (23%) of benzamide. The amide did not depress the m.p. of an authentic sample.

**Ethyl Benzocyclobutene-1-carboxylate (IXa).**—In reaction 9, 5.0 g. of VIIIa was used. Elution with petroleum ether–benzene (1:1) afforded 0.43 g. of IXa, which had an infrared spectrum identical to that of an authentic sample prepared from 1-cyanobenzocyclobutene (see below). Hydrolysis of IXa with 20% aqueous sodium hydroxide gave benzocyclobutene-1-carboxylic acid in 70% yield; after recrystallization from petroleum ether, the m.p. was 73.5–74.5° (lit.[20] 75°).

**1-Cyanobenzocyclobutene (IXb).**—In reaction 10, 5.0 g. of VIIIb was used. Petroleum ether–benzene (1:1) eluted 2.38 g. of IXb, b.p. 78–79° (2 mm.). The reported[15] b.p. is 88° (1.3 mm.). A sample of the nitrile was hydrolyzed by alkaline hydrogen peroxide at 55° to benzocyclobutene-1-carboxamide (36% yield), m.p. 155.5–156° (lit.[15] 158.5–159°) after recrystallization from chloroform–petroleum ether. The amide was converted in 95% yield to the corresponding acid, m.p. 74–75.5°. A mixed m.p. with the acid obtained from IXa was 74.5–75.5°. Their infrared spectra were identical.

Ethanolysis of IXb afforded the ester IXa in 80% of theory, b.p. 68° (0.7 mm.).

*Anal.* Calcd. for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.97; H, 6.90.

**Phenyl 1-Benzocyclobutenyl Sulfone (IXc).**—In reaction 11, 5.0 g. of VIIIc was used. Elution with benzene–ether (3:1) gave 2.04 g. of IXc, m.p. 103.5–104.5° after recrystallization from benzene–ligroin.

*Anal.* Calcd. for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95. Found: C, 68.78; H, 4.93.

Oxidation of IXc with alkaline potassium permanganate gave phthalc acid (71%). A mixed m.p. with an authentic sample was not depressed; and the infrared absorption patterns of the two were identical.

**1-Cyanobenzocycloheptene (XI).**—In reaction 12, 5.0 g. of X was used in 1300 ml. of liquid ammonia. Petroleum ether–benzene (1:2) eluted 2.01 g. of XI, b.p. 107–108° (0.5 mm.).

*Anal.* Calcd. for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C 83.86; H, 7.58.

XI was oxidized to phthalic acid, which did not depress the m.p. of an authentic sample. The bicyclic nitrile was converted with alkaline hydrogen peroxide and a reaction temperature not exceeding 40° to benzocycloheptene-1-carboxamide in 90% yield. The white, crystalline amide melted at 174.5–175.5° after recrystallization from chloroform–petroleum ether.

*Anal.* Calcd. for $C_{12}H_{15}NO$: C, 76.16; H, 7.99. Found: C, 75.76; H, 8.02.

Benzocycloheptene-1-carboxylic acid was obtained in 73% yield from the alkaline hydrolysis of the amide and melted at 116–117.5° after recrystallization from petroleum ether.

*Anal.* Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 76.15; H, 7.39.

**1-Acetyl-2-tetralone (XIII).**—In reaction 13, a 10-g. sample of XII was used in 400 ml. of ammonia. An ether insoluble ammonium salt[33] formed as soon as the diketone came in contact with the ammonia. The product mixture was taken up in ether, and evaporation of the solvent gave 5.1 g. of an oil. A 0.58-g. sample was put on a column of silicic acid–Celite (3:1), and elution with petroleum ether–benzene (4:1) afforded 0.41 g. of XIII. It gave a purple color with alcoholic ferric chloride and a positive iodoform test. Treatment with hydrazine in ethanol converted XIII to a crystalline pyrazole, m.p. 137–138° after recrystallization from ether–ligroin.

*Anal.* Calcd. for $C_{12}H_{12}N_2$: C, 78.23; H 6.57. Found: C, 78.23; H, 6.79.

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A pale green copper chelate, m.p. 229–230.5°, also was prepared from XIII.

*Anal.* Calcd. for $C_{24}H_{22}O_4Cu$: C, 65.82; H, 5.06. Found: C, 65.53; H, 5.14.

**Unsuccessful Ring Closure Attempts. Reaction of 1-Phenyl-3-(*o*-chlorophenyl)-2-propanone (XIV) with Potassium Amide.**—The ketone (7 g., 0.029 mole) was treated with potassium amide (0.114 mole) in ammonia (500 ml.) for 4.5 hr. A brown oil (5.5 g.) was isolated, and a 1-g. sample was chromatographed on alumina. Petroleum ether–benzene (1:1) eluted 0.76 g. (71%) of the starting ketone, m.p. 37–38°. It did not depress the m.p. of an authentic sample and displayed an identical infrared pattern. None of the expected product, 1-phenyl-2-indanone, was found.

**Reaction of *o*-Chlorobenzylcyclopentadiene (XVI) with Potassium Amide.**—The freshly distilled diene (6.5 g., 0.034 mole) as a cold, ethereal solution was added quickly to the base (0.13 mole) in 500 ml. of ammonia, and the solution was stirred for 15 min. The residue from evaporation of the ammonia was taken up in three 100-ml. portions of ether. Solvent evaporation yielded 1.7 g. of a crude oil which was chromatographed on alumina (60 g.). Dimerized starting material (0.64 g., 9.8%) was eluted first, followed by a series of poorly defined, colored, intractable oils.

**Reaction of 3-*o*-Chlorobenzylindene (XVIII) with Potassium Amide.**—A 10-g. (0.042 mole) sample of XVIII was allowed to react with 4 equivalents of potassium amide in 500 ml. of ammonia for 5.5 hr. The product mixture (9.8 g.) was put on a column of alumina (400 g.); elution with petroleum ether–benzene (1:1) afforded 0.12 g. (1.4%) of a white, crystalline material. Benzene–ether (3:1) eluted 2.06 g. (22%) and 4.12 g. (44%) of two primary aromatic amines as brown oils.

The solid melted at 222–224° after recrystallization from ether and displayed $\lambda_{max}$ in chloroform at 267 and 274 $\mu$ ($\epsilon$ of 15,000 for both peaks) with another strong band at the cutoff point, approximately 240 $\mu$.

*Anal.* Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 92.29; H, 5.61.

Several "distillations" of the two amines, assumed to be *o*- and *m*-aminobenzylindene in a vacuum sublimator gave yellow oils which partially solidified on standing. The less abundant compound was obtained as white crystals, m.p. 57.5–58.5° after numerous recrystallizations from ligroin.

*Anal.* Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.82. Found: C, 86.62; H, 6.92.

A 1-naphthylurea derivative prepared from the yellow oil melted at 188–189° after recrystallization from ethyl acetate–acetone.

*Anal.* Calcd. for $C_{27}H_{22}N_2O$: C, 83.05; H, 5.68. Found: C, 82.59; H, 5.63.

The amine eluted in greater amount was obtained as colorless plates, m.p. 54–55° after recrystallization from ligroin. A mixed m.p. with the previously described amine was 39–43°.

*Anal.* Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.83. Found: C, 87.10; H, 6.81.

A 1-naphthylurea derivative prepared from the yellow oil melted at 194–196° after recrystallization from ethyl acetate–acetone.

*Anal.* Calcd. for $C_{27}H_{22}N_2O$: C, 83.05; H, 5.68. Found: C, 82.70; H, 5.70.

**Attempted Synthesis of 3-*m*-Aminobenzylindene. Phthalimide of *m*-Aminobenzyl Alcohol.**—The alcohol (from lithium aluminum hydride reduction of *m*-aminobenzoic acid) and an equivalent amount of phthalic anhydride were allowed to react in dry, refluxing benzene; the water formed was removed by azeotropic distillation. The imido alcohol was isolated on solvent evaporation as pale yellow plates (65%), m.p. 150–152° after recrystallization from aqueous methanol.

*Anal.* Calcd. for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38. Found: C, 71.21; H, 4.61.

**Phthalimide of *m*-Aminobenzyl Chloride.**—The imido alcohol was heated gently with pyridine and an excess of thionyl chloride in chloroform for 30 min. The resulting imido chloride was obtained in 75% yield as colorless crystals, m.p. 159–160° after recrystallization from benzene–ligroin.

*Anal.* Calcd. for $C_{15}H_{16}ClNO_2$: C, 66.31; H, 3.71. Found: C, 66.22; H, 3.71.

**Reaction of *m*-Phthalimidobenzyl Chloride with Sodium Amide and Indene.**—Indene (0.035 mole) and sodium amide (0.022 mole) were allowed to react for 3 hr. in refluxing tetrahydrofuran (40 ml.); then the imido chloride (0.018 mole) was added. The mixture was refluxed for 5 hr. and was stirred overnight at room temperature. The solvent was removed, water added and the organic material was taken up in ether (400 ml.). Evaporation of the ether gave 3.8 g. of a brown oil, which was put on an alumina (125 g.) column. Elution afforded an 18% recovery of indene and a trace of an unidentifiable, orange oil. A dark brown band resistant to even the most polar solvents remained on the column.

The same reaction also was run in liquid ammonia and yielded only intractable oils.