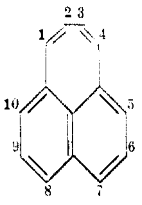
[Contribution from the Department of Chemistry, University of Rochester]

A Study of the Synthesis and Some Properties of Acepleiadiene

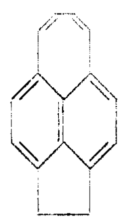
By V. Boekelheide, W. E. Langeland[1] and Chu-Tsin Liu

Acepleiadiene (peributadienoacenaphthene) has been prepared from acenaphthene by the successive steps of condensation with succinic anhydride, reduction and dehydration. From theoretical considerations it would be predicted that the seven-membered peri ring in acepleiadiene should be stabilized to an appreciable extent by resonance. The results of bromination, oxidation, and Diels–Alder reaction studies suggest that the peri ring of acepleiadiene is less reactive than an ordinary cyclic diene but that the molecule is stabilized by resonance to a lesser extent than its phenanthrene or anthracene analogs.

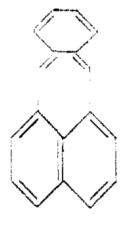
Although a great deal of effort has been expended in studying the chemistry of phenanthrene and anthracene, the isomeric hydrocarbon, I, in which a butadieno chain has been fused to naphthalene at the 1,8-positions, has never been prepared nor have any simple derivatives of this structure been reported. The purpose of this paper is to report the preparation of the closely related hydrocarbon, II. Because of the unwieldiness of the systematic names for I and II, we suggest that they be given the trivial names pleiadiene and acepleiadiene, respectively.[2]



I



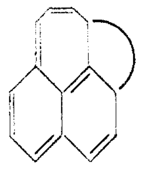
II



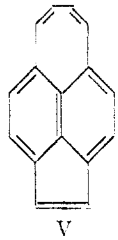
III

Aside from the fact that it would be desirable to increase our knowledge concerning peri hydrocarbons of this type, there is some theoretical interest in obtaining pleiadiene or simple derivatives of it for study. In 1937 Hückel presented a qualitative interpretation of some quantum mechanical calculations of certain unsaturated and aromatic molecules using the molecular orbital (L.C.A.O.) method.[3] This interpretation, which has recently been restated by Rice and Teller,[4] emphasizes the requirement that, for a planar cyclic molecule to be aromatic, it must have available $(2 + 4n)\pi$ electrons, where n may be 1, 2, 3,..., etc. Furthermore, Hückel concluded that the bond angles of planar five- and seven-membered rings were sufficiently close to 120° to allow molecules containing such rings to be stabilized to almost the same extent as the corresponding six-membered ring compounds.[5] Since pleiadiene is a planar molecule having the required number (14) of π electrons, Hückels theory would predict that it should have a fair amount of resonance stabilization, although probably somewhat less than phenanthrene and anthracene.

On the other hand qualitative predictions based on the valence bond approach[6] indicate that pleiadiene should have about the same resonance stabilization as *sym*-diphenylbutadiene-1,3. This disagreement between the two methods is probably only an apparent one and may be due to the fact that, in the qualitative valence bond approach, formal bond structures such as IV are not given sufficient weight. Nevertheless, it seemed that a study of pleiadiene or some simple derivative of it would be worthwhile for evaluating the utility of the two methods when applied to non-benzenoid aromatic molecules.



IV



V

From a consideration of possible routes for the preparation of pleiadiene it became obvious that the corresponding ace-derivative, II, would be a much simpler molecule to prepare. Since acepleiadiene was as well suited for our purpose as pleiadiene, its synthesis was undertaken. Actually, acepleiadiene appeared to offer an additional advantage in that its synthesis might be extended to yield the interesting hydrocarbon, V.

The starting material for the preparation of II was 1,4-acepleiadanedione (VI) which, as Fieser and Peters have shown,[7] can be readily obtained by the Friedel–Crafts condensation of acenaphthene and succinic anhydride. Reduction of VI using lithium aluminum hydride gave two isomeric glycols, which presumably represent the *cis* and *trans* isomers possible for structure VII. Each of the isomeric glycols, on treatment with anhydrous hydrogen chloride, readily underwent dehydration to yield acepleiadiene. This hydrocarbon proved to be a brilliant red solid, m.p. 118–120°. That it had the structure assigned to it was shown by its conversion on catalytic hydrogenation at room temperature to the corresponding tetrahydro

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[1] Aided by a Sherman Clarke Fellowship, 1949–1950.

[2] Fieser and Fieser (This Journal, **55**, 3010 (1933)) have used the name pleiadene to refer to benzo(5,6)cyclohepta(1.2.3-de)naphthalene (III). Their suggestion of the stem *pleiad-* to indicate the presence of the seven-membered ring joined to the naphthalene nucleus is an excellent one. However, in order that the use of this nomenclature may include simpler compounds such as I, it is necessary that III be named as a derivative of I rather than *vice versa*. Therefore, we suggest the above system of nomenclature whereby I becomes pleiadiene and III and its derivatives are renamed as benzopleiadienes.

[3] Hückel, *Z. Elektrochem.*, **43**, 752 (1937).

[4] Rice and Teller, "The Structure of Matter," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 107. For a bibliography of work on the application of quantum mechanics to aromatic compounds and their spectra, see Platt, *J. Chem. Phys.*, **17**, 484 (1949).

[5] One of the interesting, but as yet untested, predictions of this theory is that the carbonium ion derived from cycloheptatriene should be relatively stable whereas the corresponding anion should not.

[6] Wheland, "The Theory of Resonance and Its Application to Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 79; Wheland, *J. Chem. Phys.*, **3**, 356 (1935).

[7] Fieser and Peters, This Journal, **54**, 4347 (1932).

derivative. The identity of the tetrahydro derivative was established by comparing it to a known sample of acepleiadane (VIII) prepared by the Wolff–Kishner reduction of VI.

A preliminary study of the properties of acepleiadiene has yielded the results shown in Fig. 1. Acepleiadiene does not readily react with maleic anhydride in hydrocarbon solvent even on heating to 200°, but addition can be effected by fusion of the two solids. The product obtained after purification corresponded in composition to the diacid shown by structure IX. In support of this structure hydrogenation of the adduct gave a dihydro derivative in good yield.

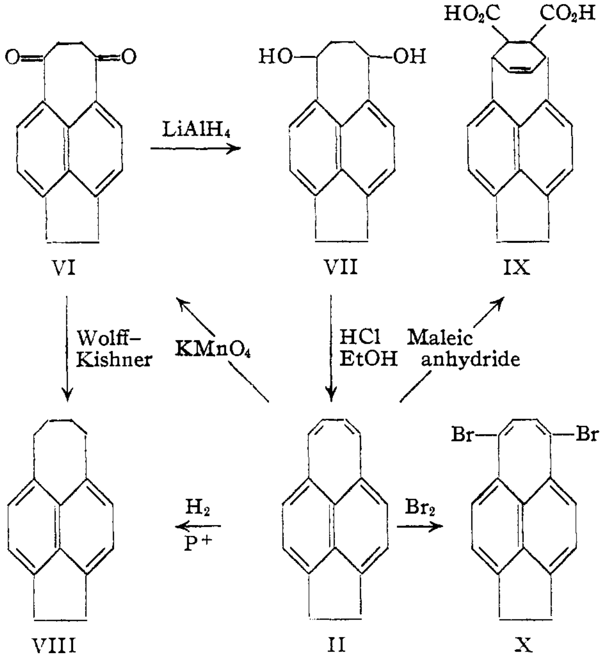
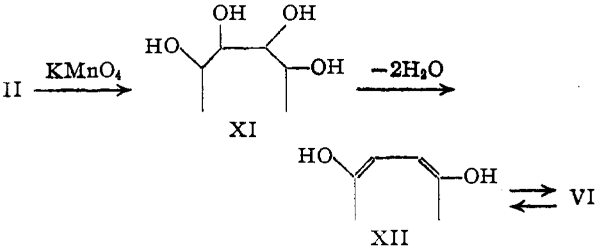


Fig. 1.

When acepleiadiene was titrated with a solution of bromine in ether, an uptake of four equivalents of bromine was noted. Some hydrogen bromide evolution occurred during the titration in every case and attempts to isolate the expected tetrabromide were unsuccessful. The reaction mixture did yield, though, a product having the correct composition for a substituted dibromoacepleiadiene, and this has provisionally been assigned structure X on the assumption that it is formed by dehydrobromination of an intermediate 1,2,3,4-tetrabromoderivative. In addition to X there was also isolated a high-melting black solid which contained bromine and appeared to be the result of some sort of dimerization.

Acepleiadiene caused discoloration of a dilute potassium permanganate solution in a fairly short period of time. Although the gummy solid resulting from this reaction could not be readily purified, evidence that it was 1,2,3,4-tetrahydroxyacepleiadane (XI) was obtained from the fact that it was converted by sublimation to 1,4-acepleiadanedione (VI). The probable course of this conversion is



If the pleiadiene system had sufficient resonance energy, it would be expected, of course, that the equilibrium between XII and VI would be in favor of XII. Although this is probably not the case, as evidenced by the fact that 1,4-acepleiadanedione readily gives a dioxime and does not show color formation with ferric chloride solution, the molecule does enolize much more readily than does an ordinary acetophenone derivative. For example a suspension of the diketone in alcohol dissolves on addition of alkali to give a green solution. Also, the diketone can be recovered unchanged after treatment with methylmagnesium iodide solution, indicating that enolization occurs very readily. This latter behavior was discovered when attempts were made to prepare 1,4-disubstituted acepleiadiene derivatives *via* the Grignard reaction.

The spectrum of acepleiadiene in the ultraviolet and visible is shown in Fig. 2. As would be expected from its red color, it shows a marked absorption in the range from 400 to 600 mμ. To explain why the pleiadiene system absorbs light in the visible region, one can advance a similar argument to that used to explain the occurrence of color in azulene.[8] In terms of structure this requires that ionic or formal bond structures of the type shown by IV make important contributions to the resonance hybrid.

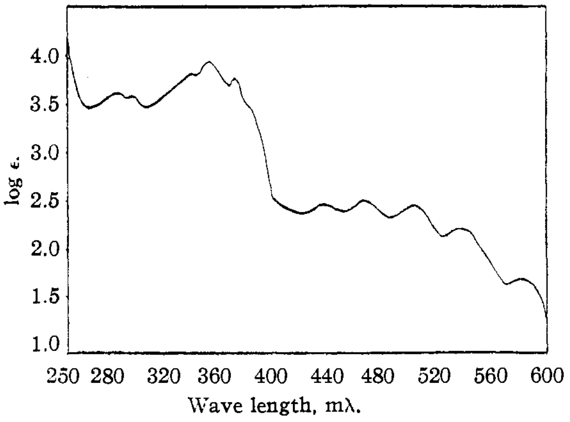


Fig. 2.—Visible and ultraviolet absorption spectrum of acepleiadiene in ethanol.

In summary the above results indicate that the peri diene ring is stabilized by resonance to a greater extent than is true for the diene systems present in ordinary cyclic dienes or in *sym*-diphenylbutadiene-1,3 but that the acepleiadiene molecule is probably closer in aromatic character to azulene than it is to phenanthrene or anthracene.

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(8) Ferguson, *Chem. Revs.*, **43**, 396 (1948).

The thermochemical measurements necessary to assign an accurate value to the resonance energy of acepleiadiene have not yet been done, but it is hoped that a report of this work can be made in the near future.

As mentioned earlier it seemed possible that acepleiadiene might be converted by suitable treatment to V, for which we suggest the name acepleiadylene. All attempts in this direction have thus far been unsuccessful. When acepleiadiene was treated with palladium-on-charcoal catalyst to effect dehydrogenation, there was formed a black, crystalline, high-melting solid whose composition and molecular weight are in accord with the formula $C_{32}H_{28}O_4$. Although we have no good explanation for the peculiar result of this attempted dehydrogenation, the results of subjecting the black solid to catalytic hydrogenation as well as reduction experiments with lithium aluminum hydride suggest that the product may be some sort of dimer in which the two halves of the molecule are joined through peroxide linkages.

Experimental[9]

1,4-Acepleiadanediol (VII).—To a solution of 2.0 g. of 1,4-acepleiadanedione (perisuccinoylacenaphthene)[7] in 40 ml. of benzene there was added 18 ml. of a 1.3 *M* ethereal solution of lithium aluminum hydride. After the mixture had boiled under reflux for four hours, it was decomposed by addition of moist ether. The precipitated alumina was removed and the benzene solution was taken to dryness *in vacuo*. The white residue appeared to be a mixture which after several recrystallizations from alcohol yielded 0.745 g. (46%) of white needles, m.p. 208°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.71; H, 6.28.

When the residue from the above mother liquor was recrystallized from benzene, an isomeric product could be isolated as white crystals, m.p. 149–150°. This product appeared to be favored by shorter reaction times and could be isolated in 31% yield from runs of one hour or less.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.93; H, 6.60.

Acepleiadiene (II).—To a solution of 3.0 g. of 1,4-acepleiadanediol (m.p. 149–150°) in 100 ml. of absolute ethanol there was added 30 ml. of a saturated solution of anhydrous hydrogen chloride in absolute ethanol. The solution turned red immediately and, after the solution had been warmed a few minutes, the ethanol was removed under reduced pressure. There remained a reddish-brown residue which, on sublimation under reduced pressure, gave 1.0 g. (40%) of brilliant red needles, m.p. 118–120°. When the same procedure was applied to the higher melting isomer (m.p. 208°), acepleiadiene was isolated in essentially the same yield.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 93.85; H, 6.24.

The **picrate** of II formed readily in alcohol and was obtained, after crystallization from ether, as black crystals, m.p. 150° dec.

Anal. Calcd. for $C_{22}H_{15}N_3O_7$: C, 60.97, H, 3.49. Found: C, 60.50; H, 3.86.

Hydrogenation of Acepleiadiene.—A mixture of 200 mg. of acepleiadiene, 200 mg. of prereduced Adams catalyst and 30 ml. of alcohol was shaken at room temperature under an atmosphere of hydrogen until no more hydrogen was absorbed. The volume of hydrogen (52 ml.) absorbed corresponded to that calculated for addition of two molar equivalents of hydrogen. After removal of the catalyst and solvent, the residue was crystallized from hexane. There was formed 140 mg. of white needles, m.p. 138°. A sample of acepleiadane prepared by the Wolff–Kishner procedure from 1,4-acepleiadanedione, as described by Fieser and Peters,[7] also melted at 138° and a mixture of the two samples showed no depression of melting point.

Reaction of Acepleiadiene with Maleic Anhydride.—A mixture of 100 mg. of acepleiadiene and 50 mg. of maleic anhydride were fused by heating at 150° under a nitrogen atmosphere for one-half hour. The reaction mixture was taken up in benzene, filtered, and the benzene was removed *in vacuo*. The residue was dissolved in alcoholic sodium hydroxide and, after filtration, the solution was acidified. The precipitate, which separated, was removed, dried and recrystallized from benzene. There was obtained 40 mg. (27%) of light tan crystals, m.p. 248–250°.

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 75.00; H, 5.00. Found: C, 75.23; H, 4.50.

In addition to this primary adduct there was also obtained from the reaction melt a benzene-insoluble, black solid, m.p. >320°. The nature of this product was not investigated but it was found that more of this product could be obtained by prolonged heating of the primary adduct. When the reaction was attempted in hydrocarbon solvent, acepleiadiene was recovered unchanged even when boiling tetralin was employed.

Hydrogenation of the Maleic Anhydride Adduct.—A mixture of 15 mg. of prereduced Adams catalyst, 34 mg. of maleic anhydride adduct (IX) and 25 ml. of absolute ethanol was stirred at room temperature in an atmosphere of hydrogen for 1.5 hours. The hydrogen absorption corresponded to one molar equivalent. The catalyst and solvent were removed and the residue was recrystallized from ethanol. There was obtained 35 mg. (98%) of white crystals, m.p. 220°.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.50; H, 5.63; neut. equiv., 161. Found: C, 74.31; H, 5.52; neut. equiv., 179.

Bromination of Acepleiadiene.—To a solution of 100 mg. of acepleiadiene in dry ether there was added dropwise a solution of 167 mg. of bromine in 10 ml. of ether. Evolution of hydrogen bromide occurred during the addition. The ether was removed *in vacuo*, and the residue was taken up in hexane and filtered to remove an insoluble, black solid. The hexane solution on concentration deposited 20 mg. (10%) of light brown crystals, m.p. 135–136°.

Anal. Calcd. for $C_{16}H_{10}Br_2$: C, 53.00; H, 2.76. Found: C, 52.60; H, 2.53.

In support of structure X assigned to this product it was found that its infrared absorption spectrum had a peak at 6.15 μ just as does acepleiadiene. This peak is most probably due to the ethylene bond of the peri ring. The hexane-insoluble black solid, m.p. 320°, was found to have a molecular weight (Rast) of 502. It was not characterized further.

Permanganate Oxidation of Acepleiadiene.—To a solution of 200 mg. of acepleiadiene in 15 ml. of acetone there was added dropwise 20 ml. of a 2% aqueous potassium permanganate solution. The mixture was allowed to stand at room temperature for three hours before the precipitate of manganese dioxide was removed. Evaporation of the filtrate yielded a gummy orange solid which, on sublimation, gave 20 mg. of a light yellow solid, m.p. 179°. A sample of this solid, when mixed with an authentic sample of 1,4-acepleiadanedione, showed no depression of melting point.

Attempted Dehydrogenations of Acepleiadiene.—A mixture of 500 mg. of acepleiadiene and 300 mg. of 5% palladium-on-charcoal catalyst in 25 ml. of mesitylene was boiled for two hours under reflux in a nitrogen atmosphere, although without rigid exclusion of air. The catalyst was removed by filtration and the mesitylene was evaporated under reduced pressure. The residue was extracted with hexane to remove any unchanged acepleiadiene. The hexane-insoluble residue, after crystallization from benzene, yielded 370 mg. of black crystals, m.p. about 325°. Dehydrogenation in the absence of solvent gave the same product. However, acepleiadiene was recovered unchanged after heating in mesitylene in the absence of catalyst.

Anal. Calcd. for $C_{32}H_{28}O_4$: C, 80.75; H, 5.90; mol. wt., 476. Found: C, 81.29; H, 5.91; mol. wt. (Rast), 432.

A solution of 90 mg. of the black crystals from the above reaction in 15 ml. of dry benzene was treated with 15 ml. of a 0.88 *M* ethereal solution of lithium aluminum hydride. After the reaction appeared to be complete, the excess lithium aluminum hydride was decomposed by addition of

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(9) Analyses by Mrs. G. Sauvage and the Micro-Tech Laboratories.

moist ether. The precipitated alumina was removed and the solvent evaporated under reduced pressure. The residue, on recrystallization from alcohol, yielded 35 mg. of tan crystals, m.p. 168–170°. The composition and molecular weight of this product would indicate that it is the result of hydrogenolysis of peroxide linkages.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71; mol. wt., 240. Found: C, 80.54; H, 6.96; mol. wt. (Rast), 262.

Catalytic hydrogenation of the black crystals gave a similar result. A mixture of 90 mg. of the black crystals, 25 mg. of prereduced Adams catalyst, and 10 ml. of ethyl acetate was shaken at room temperature under an atmosphere of hydrogen until hydrogen absorption was complete. The hydrogen uptake was approximately five molar equivalents. After removal of catalyst and solvent, the residue was recrystallized from alcohol and yielded 45 mg. of yellow crystals, m.p. 125°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.30; H, 7.45. Found: C, 79.40; H, 7.61.

ROCHESTER, N. Y. RECEIVED NOVEMBER 8, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

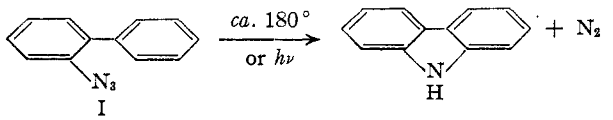
The Synthesis of Heterocyclic Compounds from Aryl Azides. I. Bromo and Nitro Carbazoles[1]

BY PETER A. S. SMITH AND BERNARD BEAU BROWN[2]

A new reaction for the synthesis of carbazoles consists of the cyclization of *o*-azidobiphenyls by heat or ultraviolet light. Six bromo and nitro substituted carbazoles, three of them new, have been made by this reaction. A nitro group ortho to the azide group is shown to react in preference to the phenyl group, resulting in benzfuroxans.

Miscellaneous reports in the literature indicate that aromatic nuclei and unsaturated systems are susceptible to attack by hydrogen azide or organic azides under some conditions. The thermal interaction of hydrogen azide and *p*-xylene to give *p*-xylidine,[3] the photochemical formation of aniline from benzene and hydrogen azide,[4] and the addition of phenyl azide to certain olefinic substances[5] are examples. The adaptation of this type of reaction as a useful method of synthesis appeared to be a reasonable possibility, especially where intramolecular ring-formation could occur, and a search for instances of such reactions was made.

The work reported here is concerned with the behavior of *o*-azidobiphenyl and its derivatives, in which an opportunity is available for the formation of the stable, easily isolated carbazole nucleus. Cyclization was found to occur with *o*-azidobiphenyl (I) itself under the influence of heat or ultraviolet light, preferably in dilute solution, in yields as high as 76%. It may be of interest to note that the cyclization of β-phenylethyl azide (II) to dihydroindole could not be obtained under any conditions, although the skeletal relationship of the azido group with respect to the benzene ring is the same as that of the azido group in *o*-azido biphenyl.



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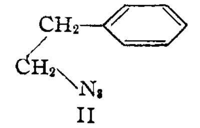
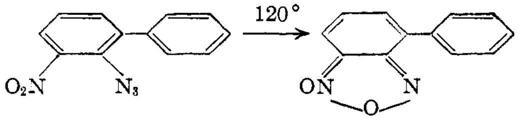


II

The high yields of carbazoles obtained in these reactions and the ease with which the reactions can be carried out suggest that this may have value as a fairly general method for the synthesis of substituted carbazoles.[6] For optimum results, a large ratio of solvent to azide is required; in solutions more concentrated than 1%, lower yields are usually obtained. The method has been applied to the synthesis of six other carbazoles, three of which are new, substituted with nitro and bromo groups, in yields not less than 74%. While nitro groups in most positions did not interfere, a nitro group in the *o*′-position led to dark, amorphous, uncrystallizable material; and a nitro group adjacent to the azido group led to furoxan formation.



In the case of 2-azido-3-nitrobiphenyl, the formation of phenylbenzfuroxan was indicated when the purified product of the reaction was found to melt 100° lower than the known 1-nitrocarbazole, although it gave the same analysis. In addition, the comparison of the ultraviolet and infrared absorption spectra of benzfuroxan, the suspected phenylbenzfuroxans and representative carbazoles supported this identification (Figs. 1 and 2). The sharp peaks in the ultraviolet spectra characteristic of the carbazole nucleus are absent from the spectra of the suspected benzfuroxans. No absorption band assignable to NH was found in the 2.9–3.2 μ region in the infrared spectra of the suspected benzfuroxans, but a band at 3.1 μ, assignable to associated NH, appeared in the spectrum of 3-nitrocarbazole in dioxane solution.

The formation of furoxans has previously been observed in the thermal decomposition of *o*-nitrophenylazides.[7] Although furoxan formation is competitive with cyclization to carbazoles in the

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(1) Presented at the National Meeting, American Chemical Society, San Francisco, California, March, 1949.

(2) From the doctoral thesis of Bernard Beau Brown, 1949.

(3) A. Bertho, *Ber.*, **59**, 589 (1926).

(4) R. N. Keller and P. A. S. Smith, THIS JOURNAL, **66**, 1122 (1944).

(5) K. Alder and G. Stein, *Ann.*, **485**, 211 (1931).

(6) For a summary of other syntheses of carbazoles, see E. C. Horning, M. G. Horning and G. N. Walker, THIS JOURNAL, **70**, 3935 (1948), and N. Campbell and B. M. Barclay, *Chem. Revs.*, **40**, 359 (1947).

(7) E. Noelting and K. Kohn, *Chem. Ztg.*, **18**, 1095 (1894).