[Contribution from the Department of Chemistry of Purdue University]

AN ATTEMPTED SYNTHESIS OF A CYCLOÖCTATETRAENE. CIS-TRANS ISOMERISM OF SUBSTITUTED DI- AND TRI-PHENYLBUTADIENES [1]

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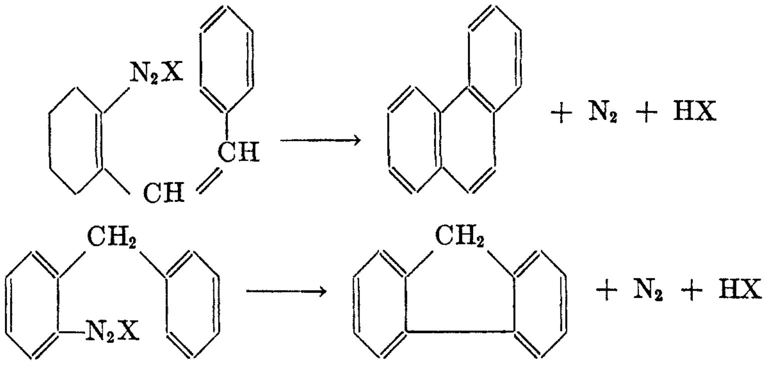
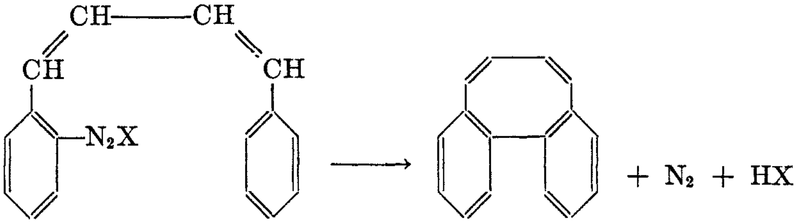
Diazotized aromatic amines will couple under certain circumstances with other aromatic nuclei, eliminating nitrogen and forming a carbon-carbon bond. When the two nuclei are already linked together at some other point a polycyclic structure of a higher order results. This reaction is the basis of the Pschorr phenanthrene synthesis (1), and has recently been applied by one of us to the synthesis of fluorene derivatives (2).



In the first of these applications a six-membered aromatic ring is created, while in the second a five-membered ring of a mixed type is formed. It occurred to us that the same kind of condensation might also be employed in obtaining an eight-membered unsaturated ring of the cycloöctatetraene type.



This synthesis, like others which have been attempted (21, 22), has been found to be inadequate for the proposed purpose. However, certain observations concerning the preparation of geometrical isomers have been made which make it desirable to report our results at this time.

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[1] From the Ph.D. thesis of R. I. Hoaglin. Read before the Organic Section of the American Chemical Society at the Memphis meeting, April 20 to 24, 1942.

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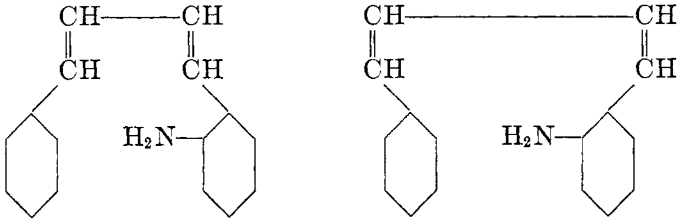
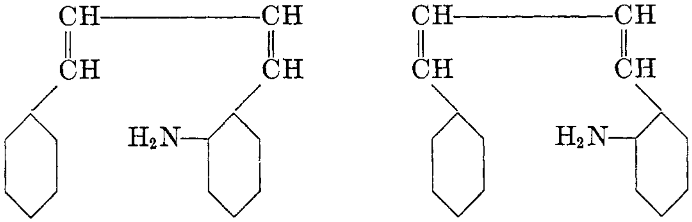
A system of two double bonds separated by a single bond permits of a maximum of four isomers when there are at least two different substituents present on each one of the double bonds. The construction of models of 1-phenyl-4-(*o*-aminophenyl)-1,3-butadiene shows that of the four possible configurations, the cis-cis is the only one in which the two phenyl groups approach each other closely enough to make condensation between them likely. The expected product from the cis-cis isomer, 1,2,3,4-dibenzo-1,3,5,7-cycloöctatetraene, could exist either as a somewhat strained ring or as a puckered ring. The cyclized products from each of the other isomers would be severely strained and almost certainly incapable of existence.

But little is known about the preparation of the various possible geometrical isomers of any substituted butadiene. Actually no single case is known in which all four possible isomers have been synthesized, one case is known in which three isomers have been synthesized and the fourth obtained from natural sources (3), and two cases are known in which the three possible forms (cis-trans and trans-cis forms being identical because of symmetrical substitution) have been synthesized (4, 5).



trans-trans cis-cis



trans-cis cis-trans

FIG. 1[3]

The general problem of synthesis of the four isomers has proved so difficult, especially in so far as the cis forms are concerned, that at one time the opinion

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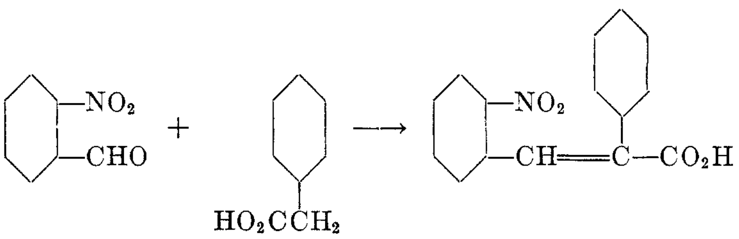
[3] Throughout this paper the configurations of the diphenylbutadienes will be the same as shown in Fig. 1, *i.e.*, on the basis of the relationship of the two phenyl groups to each other. Thus, consistency for purposes of discussion will be maintained. Where four different substituents are present on a given $C{=}C$ nucleus the terms cis and trans obviously have no meaning, unless a general naming system has been adopted. For such purposes it is the usual practice to call the lower-melting or less stable form *allo*, although this is not always done.

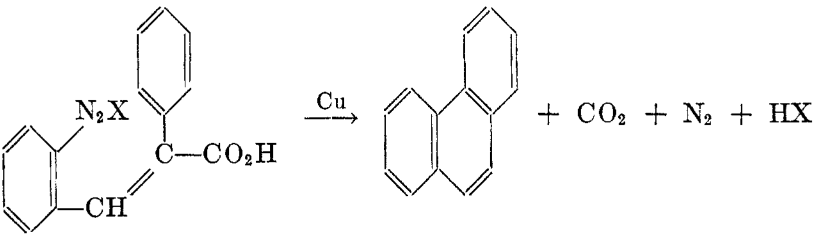
was expressed (6) that such isomers could not exist and even that the electron distribution in such a system precluded the possibility of their existences (7). The latter viewpoint is incorrect and must be abandoned in the light of the data already presented. However, it is true that some factor, probably electron mobility (8), does lead to greater lability in these conjugated systems, and that this same factor prevents the isolation of the unstable or cis forms in many cases where their formations are to be expected. A comprehensive study of the factors involved in the synthesis of cis-trans isomers and in their relative stabilities has not yet been made.

We have approached the synthesis of the desired dienes through the corresponding diene carboxylic acids for the reason that more is known about methods of obtaining the possible geometrical isomers of this class of compounds than of any other class of substituted olefins. The Perkin reaction has been employed in the synthesis of various *o*-nitrostilbene carboxylic acids, the configurations of which have been shown to be of the cis type by conversion to phenanthrene and its derivatives (9, 10).



A cis *o*-nitrostilbene acid
(I)

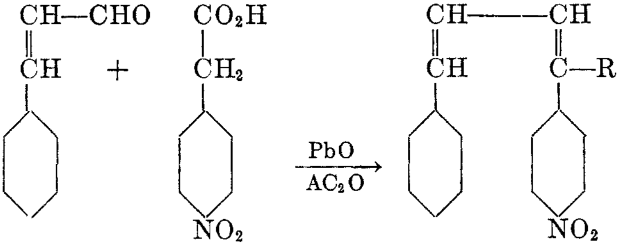
$$\text{(I)} \xrightarrow{H_2} \text{amine} \xrightarrow{HNO_2} \text{diazonium salt.}$$



A literature survey shows that the Perkin reaction usually gives predominantly a product in which the *beta* substituent is trans to the carboxyl group and cis to the *alpha* substituent. This form may or may not be the higher-melting (10). On the other hand if the carboxyl group is eliminated *during the synthesis* the product usually possesses the trans configuration provided an *alpha* substituent other than hydrogen is present to make cis and trans forms possible.

The Kuhn-Winterstein (11) modification of the Perkin synthesis employs the free acid, instead of its sodium salt, and litharge (PbO) as a condensing agent. These workers obtained only a trans-trans hydrocarbon, 1,4-diphenyl-1,3-

butadiene, from cinnamaldehyde and phenylacetic acid. It has been shown however by Bergmann and Weinberg (12), that this method yields not only a hydrocarbon (IIb) but also an equal amount of an acid (IIa) when *p*-nitrophenylacetic acid replaces phenylacetic acid.



(IIa) R = CO_2H
(IIb) R = H

The configuration of neither of these products was demonstrated, although in our opinion IIa was probably trans-cis by analogy with products obtained by similar syntheses in the stilbene series, *e.g.* I. The hydrocarbon IIb would be trans-trans if formed according to the mechanism proposed by Bergmann and Weinberg for the formation of analogous stilbene derivatives. It would probably be trans-cis if formed by decarboxylation of IIa since Ruggli and Staub (13) have shown that such decarboxylations do not usually alter the configuration under ordinary conditions.

Another approach to this group of compounds is made possible by a recently developed synthesis of Meerwein and co-workers (14). Many unsaturated acids react with diazonium salts in the manner shown below for cinnamic acid and benzene diazonium chloride.

$$C_6H_5CH{=}CHCO_2H + C_6H_5N_2Cl \longrightarrow C_6H_5CH{=}CHC_6H_5 + CO_2 + N_2 + HCl \qquad \text{III}$$

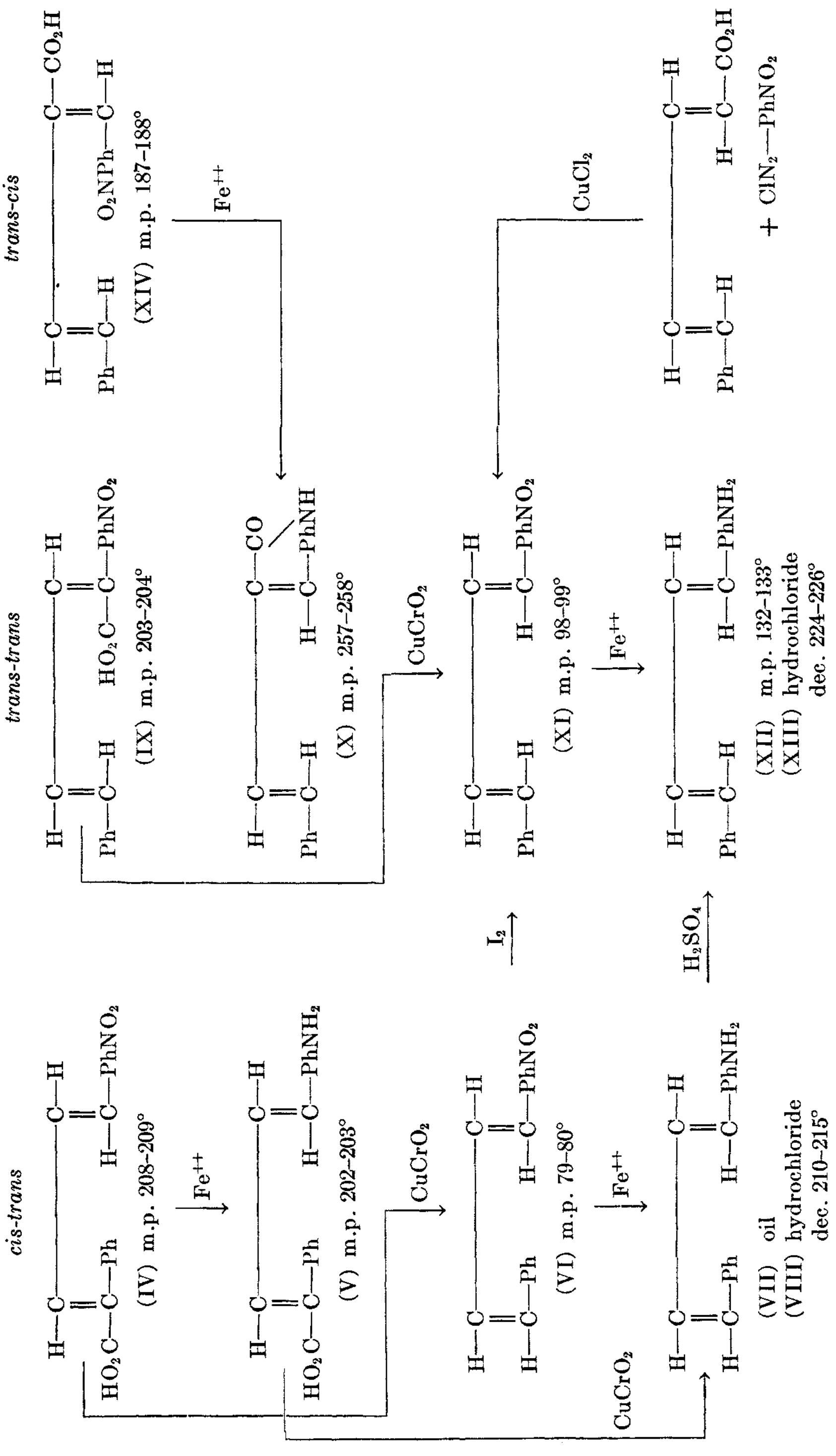
The product in this particular case is trans-stilbene. Bergmann and Weinberg also employed this method in the synthesis of a IIb whose configuration was the same as the IIb obtained by the Kuhn-Winterstein procedure. It is clear that this synthesis tends to yield a trans form. It is probable also that the hydrocarbon IIb is trans-trans and resulted from a direct synthesis as postulated by Bergmann and Weinberg, rather than being trans-cis and arising through a decarboxylation of IIa.

Our results are summarized in Figure 2. We have applied each of the above described syntheses in various ways and have isolated products which are rendered probable on the basis of evidence to be presented. Each of the three series cis-trans, trans-trans, and trans-cis will be discussed in order. For reasons which will appear later, efforts to enter the cis-cis series were abandoned.

Cis-trans series. The first compound in this series, 2-phenyl-5-(*o*-nitrophenyl)-2,4-pentadienoic acid (IV), was made by the condensation of *o*-nitrocinnamaldehyde with phenylacetic acid. The yield by the Perkin procedure using the

FIGURE 2

DERIVATIVES OF 1,4-DIPHENYL-1,3-BUTADIENE

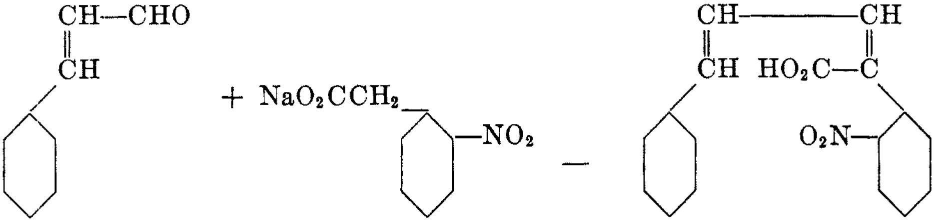


sodium salt of the acid was much better in this case than the yield by the Kuhn-Winterstein modification using a mixture of the free acid and litharge. Both methods gave the same product.

The cis-trans configuration of this acid is probable for the following reasons. The simple cinnamaldehydes (*i.e.*, those with no substituents other than hydrogen on the double bond) are apparently stable only in the trans forms. This trans configuration would be expected to carry over to the product of a condensation reaction. The cis configuration on the other double bond is likely through analogy with the related synthesis of I. Its configuration is made even more probable by the ready isomerization to a higher-melting isomer (XI) of the corresponding nitro hydrocarbon (VI) obtained by decarboxylation of the acid. Such an isomerism would not be expected to occur if both double bonds were initially trans.

Reduction of IV with ferrous sulfate and ammonia yielded the corresponding amino acid (V). Upon decarboxylation this acid yielded an amine (VII) identical with that obtained by reducing the nitro hydrocarbon (VI). The yields were much better when decarboxylation preceded reduction. The amine itself was also readily converted into a higher-melting isomer (XII) indicating that the cis configuration in this case was not disturbed by either decarboxylation or reduction.

Trans-trans series. Trans-trans-1-(*o*-nitrophenyl)-4-phenyl-1,3-butadiene (XI) was made in three different ways: (a) the cis-trans form (VI) was isomerized to XI by heating with a trace of iodine in nitrobenzene; (b) the reaction of 5-phenyl-2,4-pentadienoic acid with *o*-nitrobenzene diazonium chloride yielded XI directly; (c) decarboxylation of 1-(*o*-nitrophenyl)-4-phenyl-1,3-butadiene-1-carboxylic acid (IX) yielded XI. The acid IX resulted unexpectedly from the condensation of cinnamaldehyde with sodium *o*-nitrophenylacetate.

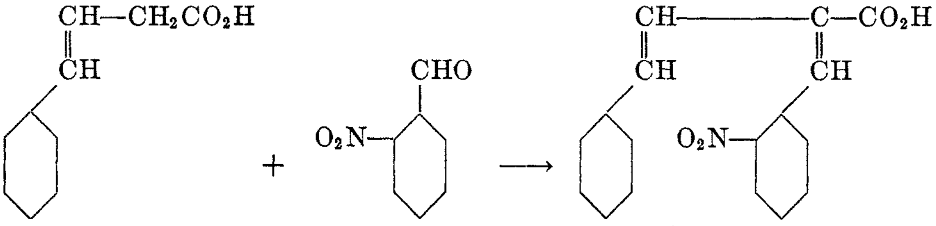


(IX)

By analogy with the syntheses of I and IV a trans-cis configuration was expected. That this configuration was not obtained is probable because of the formation of the stable trans-trans nitrohydrocarbon (XI) from IX by decarboxylation. This explanation is considered more probable than the other possible one, namely that the decarboxylation of IX was accompanied by isomerization. Probably the trans configuration was conditioned by steric hindrance between the carboxyl group and the *o*-nitro group.

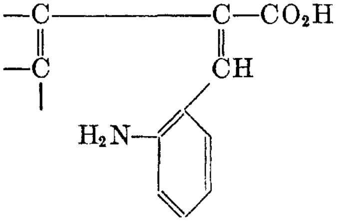
Reduction of the nitro hydrocarbon (XI) gave an amine (XII) which was stable to isomerization and which was identical with the amine obtained by isomerizing the cis-trans amine (VII).

Trans-cis series. By the condensation of *o*-nitrobenzaldehyde with sodium 4-phenyl-3-butenoate an acid (XIV) was obtained whose configuration is presumably trans-cis by analogy with other compounds obtained by similar syntheses (19).



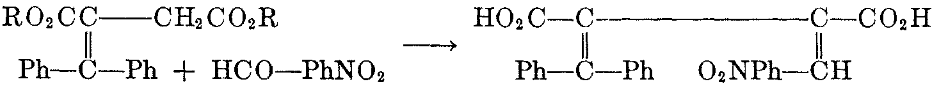
(XIV)

Unfortunately all efforts to isolate a nitro hydrocarbon from decarboxylation experiments with this acid were unsuccessful. Furthermore reduction of XIV yielded an amino acid which immediately lactamized to X. It is clear from models that such a ring closure could only occur readily if the —NH_2 and —CO_2H groups were cis to each other. Although the original acid XIV may have had a trans-trans configuration it is more probable, in our opinion, that the isomerization occurred during reduction to the amino acid. If such be true then the preparation of a diene containing a structure with carboxyl and *o*-aminophenyl



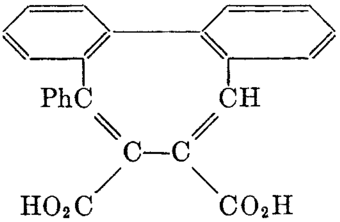
groups trans to each other, may be a practical impossibility in this series because of the apparent lability of this group. Such lability is not strange in view of the presence of a powerful electron donor group (NH_2) at one end and a powerful electron acceptor group (CO_2H) at the other end of a conjugated system. Arrangements of this type permit tautomeric electronic shifts of considerable magnitude and the configuration about the central bond is thereby greatly labilized. On the other hand Stoermer and Oehlert (15) had no trouble with the preparation of similar acids in the stilbene series. Lactams were obtained only in the event that in the original nitro acid the —$C_5H_4NO_2$ and —CO_2H groups were cis to each other. The difference in behavior may be due to the generally greater lability of the diphenylbutadiene system.

Cis-cis series. In view of the practical and theoretical difficulties outlined in the above paragraph, efforts to enter the cis-cis series of compounds of this type were temporarily abandoned. Instead, a 1,1,4-triphenylbutadiene derivative was prepared according to the following reaction.



$$\begin{array}{l}RO_2C\underset{\substack{\|\\ Ph—C—Ph}}{C}——CH_2CO_2R\\ \quad + HCO—PhNO_2\end{array} \longrightarrow HO_2C—\underset{\substack{\|\\ Ph—C—Ph}}{C}——————\underset{\substack{\|\\ O_2NPh—CH}}{C}—CO_2H$$

Hope of success in converting this 1,1-diphenyl-4-(*o*-nitrophenyl)-1,3-butadiene-2,3-dicarboxylic acid (XV) into a cycloöctatetraene by reduction and diazotization was based on three points: (a) The configuration of the double bond on the left is inevitably cis for one of the phenyl groups; (b) the presence of a second carboxyl group on the carbon atom *beta* to the first carboxyl group should diminish the magnitude of the tautomeric electronic shifts in the double bond on the right and hence should stabilize it; and (c) the replacement of the hydrogen atom in the 1-position by a phenyl group prevents a coupling from occurring at that position. Such a coupling would form a six-membered ring and yield a derivative of naphthalene. Finally, this compound presents the further advantage of making it possible, in the event of successful ring closure, to determine whether the cycloöctatetraene ring is merely puckered or whether the bond angles are strained and the ring is planar. In the event of puckering, the two benzene rings would not necessarily occupy the same plane and the system would be optically active.



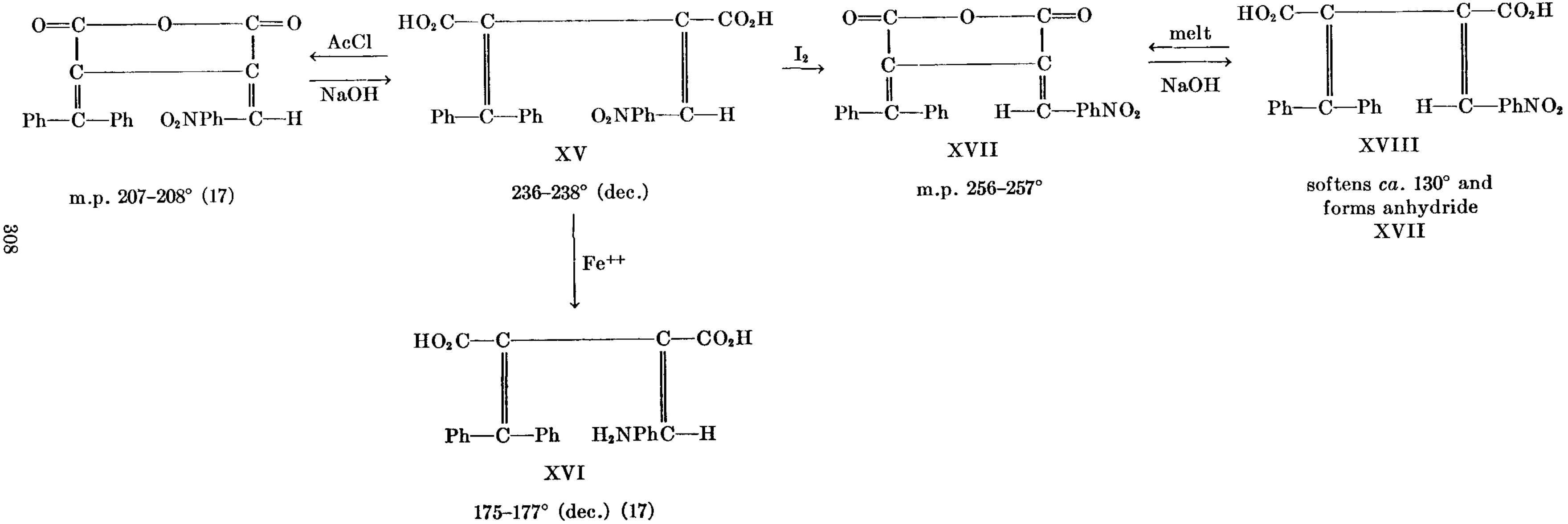
Resolution might be effected through the carboxyl groups, and the relative stability of the isomers would indicate the ease with which one puckered form of the ring is converted to another. This type of optical isomerism in the biphenyl series has been noted before (16), and the isolation of relatively stable optical isomers indicates the ease with which large rings undergo puckering.

The acid XV was obtained readily from succinic ester by condensation first with benzophenone and then with *o*-nitrobenzaldehyde. These compounds and the corresponding amino acid (XVI) (Fig. 3) were originally prepared by Stobbe (17). We were able to improve the yields in the first condensation materially by altering his procedure somewhat. The amino acid finally obtained did not lactamize so that it probably possessed a cis configuration (according to Fig. 1). It was diazotized without difficulty, but all efforts to cause the desired cyclization to occur were unsuccessful—only resinous products could be isolated. The diazotization was carried out in both water and dioxane with similar results. The cyclizations were attempted with copper powder alone and in the presence of sodium hypophosphite. In every case nitrogen was evolved, but acidification of the product gave a dark amorphous precipitate that resisted purification.

Isomerizations. It has already been mentioned that the cis-trans nitrohydrocarbon (VI) and the corresponding amine (VII) were readily isomerized to more stable isomers. This was accomplished with the nitro hydrocarbon by heating its solution in nitrobenzene to boiling for about half an hour in the presence of a trace of iodine. This procedure also caused an isomerization of the acids XIV and XV but failed to change IV and IX. The triphenylbutadiene diacid (XV) was converted into an anhydride (XVII) (m.p. 256–257°) by this treatment.

FIGURE 3

RELATIONSHIPS OF DERIVATIVES OF THE TRIPHENYLBUTADIENE DICARBOXYLIC ACID SERIES



This was different from the anhydride (m.p. 207–208°) obtained by Stobbe (17) on treating XV with acetyl chloride. On hydrolysis the anhydride (XVII) yielded a hydrated acid (XVIII) which was different from the original acid (XV) and which when heated reverted to the anhydride after merely softening but not melting. This ease of anhydride formation indicates a closer approach of the two carboxyl groups in this acid as compared to the original acid. Models show that this behavior would be expected in the trans compound. Steric hindrance between the phenyl and nitrophenyl groups prevents a close approach of the carboxyl groups in the cis isomer. This is a further indication that the diacid (XV) has the postulated cis structure. The anhydride of the isomerized acid was reduced with ferrous ion to an amino dicarboxylic acid whose analysis indicated that it had not lactamized. Insufficient material was available for a more detailed study of the amino derivative. Relationships of these derivatives of the triphenylbutadiene dicarboxylic acid series are shown in Figure 3.

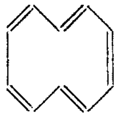
DISCUSSION

The properties of cycloöctatetraene, especially its relative instability and reactivity, are of considerable significance to our theories of the nature of the aromatic nucleus. The continuously conjugated system of double bonds present in benzene may be the cause of the general inertness of that substance. If such conjugation is a sufficient cause of the inactivity then cyclobutadiene and cycloöctatetraene should resemble benzene (cyclohexatriene) very closely in chemical properties. So far all attempts to synthesize cyclobutadiene have been unsuccessful, but this may or may not mean that such a substance, once made, would be unstable and reactive. The burden of proof therefore lies heavily upon cycloöctatetraene. Willstätter's original synthesis of this substance (18) led to a product which was very unstable. This proved so surprising that organic chemists have made sporadic attempts ever since to devise new syntheses for this important compound. Other workers have pointed out the possibility that the compound prepared by Willstätter was not cycloöctatetraene but something else, and many chemists have been reluctant to accept as proven facts the existence and great reactivity of this substance.

As a matter of fact the reactivity of a hydrocarbon having the structure of a cycloöctatetraene may be predicted on the basis of the resonance theory. The resonance energy which stabilizes benzene (39 k cals/mole) would be greatly reduced in cycloöctatetraene in spite of an increase in the number of double bonds and resonance forms in that substance. This is a result of the fact (as shown clearly by models) that the eight-membered fully conjugated ring must exist either in a strained or in a puckered form. If the ring is strained then a considerable portion of the expected resonance energy will be lost in straining the atomic bonds from their normal angles. If the ring is puckered then atomic motions are necessary to alter the pucker in going from one resonance form to another. Resonance is greatly diminished in non-planar rings of this type due to these atomic movements. Probably the actual form taken by cycloöctatetraene would be a partially puckered, partially strained ring with greatly reduced resonance energy. The low resonance energy would lead to reactivity of the type normally associated with double bonds.

Our inability to achieve the synthesis of a cyclooöctatetraene derivative through diazotization and coupling of the amino acid (XVI) may be laid to one or the other of the following causes: (a) The intermediates prepared did not have the expected configurations; (b) the energy and unfavorable steric factors involved in the formation of the cycloöctatraene ring were too great to be overcome by this type of synthesis, and a substitute reaction (perhaps phenol formation) occurred; (c) the expected product formed, but being very labile underwent an immediate further change, such as a polymerization. Of these explanations the second appears to us the most likely. In the first place, the proposed configurations of the amino acids studied, especially that of XVI, seem reasonably probable. In the second place, even the formation of relatively stable rings containing five and six atoms is easily hindered by steric influences in the Pschorr synthesis. Finally there was no evidence of the formation of an unstable intermediate product of the type postulated in (c). The recently reported failure of Rapson and Shuttleworth (21) to obtain 1,2,3,4-dibenzocycloöctatetraene by the action of metallic copper on 1,4-bis-(*o*-iodophenyl)-1,3-butadiene must on the other hand be attributed to the geometrical configuration of their intermediate. This diiodo compound was almost undoubtedly trans-trans since it was obtained directly from a Kuhn-Winterstein modification of the Perkin synthesis.

As a means of verifying the theoretical implications of the resonance theory in its applications to the structure of aromatic compounds a cyclodecapentaene should be prepared. Such a compound may be predicted to be relatively stable because of high resonance energy. Its molecules could take up the configuration



which models show to be nearly planar and but little more strained than naphthalene. Other cyclopolyenes of this type containing 6 + 4n carbon atoms should also be planar molecules and hence stable, in the sense that naphthalene and anthracene are stable. It is our hope to attempt the synthesis of such molecules following the war.

EXPERIMENTAL

*2-Phenyl-5-(*o*-nitrophenyl)-2,4-pentadienoic acid (IV). a. Perkin synthesis.* A mixture of 17.7 g. (0.1 mole) of *o*-nitrocinnamaldehyde, 15.8 g. (0.1 mole) of the sodium salt of phenylacetic acid (dried at 130°), and 100 g. of acetic anhydride was heated with occasional shaking to an oil-bath temperature of 110° for 12 hours. After cooling, the dark semi-solid reaction mixture was hydrolyzed with water and then poured into 1 liter of hydrochloric acid (1:3), whereupon the yellow nitro acid precipitated. Yields of 80–85% were obtained. Crystallization from 95% alcohol gave long yellow needles, m.p. 208–209°.

Anal. Calc'd for $C_{17}H_{13}NO_4$: C, 69.10; H, 4.44.

Found: C, 69.0; H, 4.2.

b. Kuhn-Winterstein reaction. A mixture of 15.9 g. (0.09 mole) of *o*-nitrocinnamaldehyde, 12 g. (0.09 mole) of phenylacetic acid, 10 g. (0.045 mole) of lead oxide (PbO), and 18 g. (0.2 mole) of acetic anhydride was heated under reflux four hours (140–145°, oil-bath temperature). The reaction mixture remained completely liquid even after cooling overnight. It was extracted with several portions of sodium carbonate solution, and the soluble portion was treated with dilute hydrochloric acid to give a yellow amorphous product. After a single purification from 95% alcohol this formed long yellow needles, m.p. 208–209°. A mixture of this material and that obtained by the Perkin reaction in the preceding description gave no depression of the melting point. The yield of nitro acid was 25%.

Anal. Calc'd for $C_{17}H_{13}NO_4$: C, 69.10; H, 4.44.
Found: C, 69.0; H, 4.4.

The neutral or soda-insoluble portion was very gummy and had a resinous appearance. No nitro hydrocarbon could be isolated from this mixture.

*1-(*o*-Nitrophenyl)-4-phenyl-1,3-butadiene-1-carboxylic acid (IX).* This compound was made only by the Perkin condensation of cinnamaldehyde and the sodium salt of *o*-nitrophenylacetic acid. The sodium salt of *o*-nitrophenylacetic acid was prepared by the method of Mayer and Balle (19). The sodium salt,[4] 20.3 g. (0.1 mole), with 13.2 g. (0.1 mole) of cinnamaldehyde and 25 g. of acetic anhydride, was heated ten hours at an oil-bath temperature of 110–120°. The mixture was cooled, warmed with water to hydrolyze the acetic anhydride, and then with dilute ammonia to extract the nitro acid. A considerable quantity of cinnamaldehyde remained unreacted. The ammoniacal solution was filtered, extracted with ether to remove impurities, and the nitro acid precipitated by pouring into dilute hydrochloric acid. After purification it formed canary yellow crystals, m.p. 203–204°, (yield 23.5%).

Anal. Calc'd for $C_{17}H_{13}NO_4$: C, 69.10; H, 4.44.
Found: C, 69.4; H, 4.5.

*1-(*o*-Nitrophenyl)-4-phenyl-1,3-butadiene-2-carboxylic acid (XIV).* This nitro acid was also obtained both by the Perkin synthesis and by the Kuhn-Winterstein modification of it.

a. Perkin reaction. A mixture of 9.2 g. (0.05 mole) of the dry sodium salt of 4-phenyl-3-butenoic acid (15), 7.5 g. (0.05 mole) of *o*-nitrobenzaldehyde, and 12 ml. of acetic anhydride was warmed on a steam-cone under a reflux condenser. A vigorous reaction resulted within three minutes, the mixture became very dark, and heating was discontinued until the reaction subsided. The mixture was heated another 20 minutes on the steam-cone, then allowed to cool and solidify. The product was dissolved in sodium carbonate solution, and the solution extracted with ether to remove non-acid impurities. The nitro acid was precipitated by adding the solution slowly to a cold, dilute solution of hydrochloric acid, with constant stirring to prevent the precipitate from becoming gummy. The acid was an amorphous, yellow product, which after boiling with Norit in 95% alcohol solution, crystallized in beautiful, small, canary-yellow crystals, m.p. 187–188°. The yield was only about 17%.

b. Kuhn-Winterstein. A mixture of 16.2 g. (0.1 mole) of 4-phenyl-3-butenoic acid, 15.1 g. (0.1 mole) of *o*-nitrobenzaldehyde, 11.1 g. (0.05 mole) of litharge (PbO), and 20 g. (0.2 mole) of acetic anhydride was caused to react as in previous condensations. The product was an amorphous, brown material, which after purification with Norit, crystallized from 95% alcohol in small yellow crystals, m.p. 187–188°. The yield of crude material was about 64%, considerably better than that produced by the Perkin synthesis.

Anal. Calc'd for $C_{17}H_{13}NO_4$: C, 69.10; H, 4.44.
Found: C, 69.2; H, 4.5.

*1-(*o*-Nitrophenyl)-4-phenyl-1,3-butadiene (cis-trans) (VI).* One part of the nitro acid, 0.1 part of the Adkins-Connor decarboxylation catalyst (20), and 5 parts of quinoline were heated in a flask equipped with a stirrer, thermometer, and air condenser, to 210–220° for 30–45 minutes. The mixture was cooled, diluted with ether, and filtered to remove the catalyst. The ether solution was shaken with several portions of dilute hydrochloric acid to remove the quinoline, and then with dilute alkali to remove unreacted acid. Evapora-

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[4] The preparation of *o*-nitrophenylacetic acid by the method of Mayer and Balle gave double the yields reported by these authors when the sodium salt of the nitrophenylpyruvic acid was oxidized by H_2O_2 directly instead of isolating and oxidizing the free acid. Yields averaging 55% were obtained.

tion of the ether solution left an oil which solidified on cooling. The residue was taken up in either glacial acetic acid or 95% alcohol, from which solvents the nitro hydrocarbon crystallized in light tan needles, m.p. 79–80°, (yield 75%).

Anal. Calc'd for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22.
Found: C, 76.4; H, 5.56.

1-(o-Nitrophenyl)-4-phenyl-1,3-butadiene (*trans-trans*) (*XI*). *a. By decarboxylation.* Using the same procedure as given in the previous preparation, trans-trans-1-(*o*-nitrophenyl)-4-phenyl-1,3-butadiene was prepared from the corresponding nitro acid, 1-(*o*-nitrophenyl)-4-phenyl-1,3-butadiene-1-carboxylic acid. The nitro hydrocarbon crystallized from 95% alcohol in light tan needles, m.p. 98–99°. A mixture of the cis-trans and trans-trans isomers melted considerably lower than the cis-trans modification.

Anal. Calc'd for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22.
Found: C, 76.7; H, 5.4.

b. By isomerization. One gram of 1-(*o*-nitrophenyl)-4-phenyl-1,3-butadiene (cis-trans) was dissolved in 10 ml. of nitrobenzene, a crystal of iodine added, and the mixture heated to the boiling point for 20–25 minutes. The mixture was concentrated to about 1 ml., taken up in alcohol, and cooled, to yield a dark, rather crude product. Crystallization from glacial acetic acid or 95% alcohol gave light tan needles, m.p. 98–99°. A mixture of this material and that obtained by decarboxylation showed no depression in melting point.

c. By direct synthesis. o-Nitroaniline, 8.6 g (0.0625 mole), was suspended in 25% hydrochloric acid and diazotized at 0° with 4.3 g. (0.0625 mole) of sodium nitrite in 7.5 ml. of water. A small amount of undiazotized amine remained insoluble. The solution was filtered and added dropwise to a solution of 10.9 g. (0.0625 mole) of 5-phenyl-2,4-pentadienoic acid (20) in 175 ml. of acetone. A solution of 2.5 g. of cupric chloride and 13.7 g. of sodium acetate in 12.5 ml. of water was added slowly with stirring to the resulting yellow solution. An immediate and vigorous evolution of nitrogen resulted. The color of the solution changed from yellow to green and the temperature rose to 20°. After stirring 1.5 hours, the mixture was steam-distilled to remove nitrobenzene. On cooling, the residue formed a mixture of a grayish, crystalline material and a black, gummy product. The crystalline material was unreacted 5-phenyl-2,4-pentadienoic acid as evidenced by its melting point. The gummy residue hardened on standing, and after triturating with ammonia solution was powdered and extracted continuously with a hexane fraction (b.p. 60–70°) in a Soxhlet extractor. The extract deposited a yellow, fluffy, crystalline product, which upon recrystallization from 95% alcohol solution gave yellow needles m.p. 98–99°, (yield 10%). No depression in melting point was noted with a mixture of this compound and that obtained by decarboxylation.

Anal. Calc'd for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22.
Found: C, 76.4; H, 5.6.

1-(o-Aminophenyl)-4-phenyl-1,3-butadiene (*cis-trans*) (*VII*). Two grams of the corresponding nitro hydrocarbon was dissolved in 50 ml. of warm 95% alcohol. To this was added with stirring a mixture of 16 g. of $FeSO_4 \cdot 7H_2O$, 80 ml. of concentrated ammonia, and 80 ml. of water. The mixture was heated on the steam-cone and stirred for two hours. After standing overnight the reduction mixture was filtered with suction and the residue dried. This black residue containing the amine was allowed to stand in ether several hours, filtered, and the ether solution of the amine dried over potassium carbonate. Dry hydrogen chloride gas was passed into the ether solution precipitating the amine hydrochloride in gray crystalline form. It began to soften at 195°, and decomposed at 210–215°. The free amine is an oil.

Anal. Calc'd for $C_{16}H_{16}ClN$: C, 74.55; H, 6.26.
Found: C, 74.6; H, 6.7.

1-(o-Aminophenyl)-4-phenyl-1,3-butadiene (*trans-trans*) (*XII*). *a. By isomerization.* An ether solution of the cis-trans amine, obtained as described in the preceding procedure, was evaporated to dryness and the residue boiled with dilute sulfuric acid. The amine sulfate precipitated on cooling. It was filtered, and without drying was washed into dilute alkali. On warming, the amine precipitated as a dark, amorphous material, which separated from alcohol-water solution as orange-yellow, fluffy crystals, m.p. 132–133°. The hydrochloride (XIII) consisted of cream-white flakes, decomposing at 224–226°.

Anal. Calc'd for $C_{16}H_{15}N$: C, 86.84; H, 6.83.
Found: C, 86.3; H, 6.9.

b. By reduction. The trans-trans nitro hydrocarbon was reduced in the same way as described for the cis-trans isomer. The product of this reaction gave no depression of the melting point when mixed with that obtained by isomerization. The amine hydrochloride was made in the usual way and decomposed at 224–226°.

*2-Phenyl-5-(*o*-aminophenyl)-2,4-pentadienoic acid (V).* An ammoniacal suspension of 14.7 g. (0.05 mole) of the nitro acid (IV) was added with constant stirring to a boiling mixture of 100 g. of $FeSO_4 \cdot 7H_2O$, 300 ml. of water, and 250 ml. of concentrated ammonia. The amino acid was recovered from the filtered mixture by neutralization with hydrochloric acid (1:3). The product formed fluffy crystals from alcohol, m.p. 202–203°, yield 85–90%.

Anal. Calc'd for $C_{17}H_{15}NO_2$: C, 76.95; H, 5.70.
Found: C, 76.8; H, 6.0.

*Lactam of 1-(*o*-aminophenyl)-4-phenyl-1,3-butadiene-2-carboxylic acid (X).* Following the same procedure as described for the amino acid (V), 1-(*o*-nitrophenyl)-4-phenyl-1,3-butadiene-2-carboxylic acid was reduced with ferrous sulfate. The product, after crystallization from absolute alcohol, consisted of yellow plates, m.p. 257–258°. It was insoluble in acid and base and did not give a test for the primary amine group by diazotization. The most probable configuration for this compound is a lactam structure.

Anal. Calc'd for $C_{17}H_{13}NO$: C, 82.57; H, 5.30; N, 5.66.
Found: C, 82.6; H, 5.4; N, 5.7.

*1,1-Diphenyl-4-(*o*-aminophenyl)-1,3-butadiene-2,3-dicarboxylic acid (XVI).* This acid (cis form) was prepared from succinic ester by Stobbe's (17) method with similar results in each step except the first. We obtained 90% yields in the condensation of succinic ester with benzophenone to give 1,1-diphenyl-1-propene-2,3-dicarboxylic acid. This greatly improved yield may be attributed to the use of strictly anhydrous sodium ethoxide as the condensing agent and to the maintenance of a temperature of 0° during the early stages of the reaction. Furthermore, our nitro acid XV (solvent-free) showed the m.p. 237–238° (dec.) as compared to the product containing one molecule of ethanol and melting at 223–224° (dec.) obtained by Stobbe. As noted by Stobbe, the final product is an amorphous yellow material which resists crystallization. The hydrochloride decomposes at 276–278°.

*Isomerization of cis-1,1-diphenyl-4-(*o*-nitrophenyl)-1,3-butadiene-2,3-dicarboxylic acid (XV). Formation of the trans anhydride XVII.* The nitro acid (XV) was refluxed with nitrobenzene containing a trace of iodine for 20 minutes. The product was isolated as a light brown amorphous substance, m.p. 256–257°. Analysis and solubility relationships showed it to be an anhydride (XVII).

Anal. Calc'd for $C_{24}H_{15}NO_6$: C, 72.55; H, 3.80.
Found: C, 72.6; H, 3.6.

The anhydride XVII was dissolved in alkali and reprecipitated by addition of dilute hydrochloric acid, giving an acid (XVIII), which was not completely soluble in absolute alcohol. Light tan needles crystallized when the alcohol solution was diluted with about twice its volume of water and cooled. The portion not soluble in absolute alcohol melted at 256–257° and was identical with the original anhydride (XVII). This shows the ease of anhydride formation from the acid. The hydrolyzed product was also recrystallized by dissolving it in benzene and adding hexane until incipient precipitation was reached. When dry it softened at about 130°, resolidified, and finally melted at 256–257°, the melting point of the anhydride. Analysis showed the product to be the dibasic acid, hydrated with one molecule of water.

Anal. Calc'd for $C_{24}H_{17}NO_6 \cdot H_2O$: C, 66.50; H, 4.39.
Found: C, 66.7; H, 4.5.

Diazotization and attempted cyclizations of (XVI). a. In aqueous solution. A fine suspension in water of the amino acid (XV) was prepared by rapidly precipitating with excess dil. sulfuric acid a solution of 1.93 g. (0.005 mole) of the amino acid in dil. sodium hydroxide. The suspension was cooled to 0° and a cold solution of 0.35 g. of sodium nitrite in 25 ml. of water added slowly with stirring. Starch-iodide paper showed the presence of nitrous acid. The yellow diazotized mixture was stirred at 0° for about 4 hours, then treated with 3–4 g. of precipitated copper powder. The mixture was stirred vigorously and heated on the steam-cone at 50–53° for six hours. A test for diazotization with alkaline β-naphthol was positive at this point. The mixture was heated another two hours at 60–70°. No test for the diazonium group was noted after this time. The color of the mixture was dark brown. It was filtered and the residue washed with ammonia to remove the acid product, leaving the copper behind. The ammoniacal solution was cooled and neutralized carefully with dilute acid, giving a dark gelatinous precipitate. No crystalline product could be isolated from this gelatinous material.

b. Diazotization in dioxane. The amino acid, 1.93 g. (0.005 mole), was dissolved in about 75 ml. of dioxane, giving a dull red solution. To this solution was added 1 ml. of concentrated sulfuric acid. After cooling the mixture to room temperature, 0.6 g. of amyl nitrite, diluted with 15 ml. of dioxane, was added slowly with stirring. After stirring at room temperature for 2 hours, the mixture was added slowly to a mixture of 1 g. of copper powder, 10 g. of sodium hypophosphite and 10 g. of water held at 45–55°. After the addition of the diazo solution was complete, the temperature was raised to 80° for 15–20 minutes. This mixture was cooled and poured into 500 ml. of water containing sodium hydroxide. The copper powder was removed by filtration. The alkaline solution was neutralized with dilute sulfuric acid, giving a dark amorphous precipitate, from which no crystalline product could be obtained.

Similar unsuccessful attempts were made to cyclize (V), although this acid probably has a cis-trans structure.

SUMMARY

An unsuccessful attempt has been made to apply the Pschorr phenanthrene synthesis to the preparation of a dibenzocycloöctatetraene. Theoretical implications of the work have been discussed.

A number of cis-trans isomeric derivatives of di- and tri-phenylbutadienes have been prepared and characterized.

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