minutes with the final temperature within the flask being 165°. The crude distillate, 35.2 g. (99%), was dissolved in ether, the ether solution washed with water and dried over anhydrous magnesium sulfate in the refrigerator. After removal of the ether the crude product was distilled under reduced pressure using a 14 × 0.75 in. column packed with 0.75 in. glass helices. There was obtained 25 g. (75%) of pure product; b. p. 68° (50 mm.), $n^{20}$D 1.4403.

*Anal.* Calcd. for $C_5H_9NO_2$: N, 12.17. Found: N, 12.28.

The residue in the pyrolysis was shown to be diethylamine hydrochloride by its m. p. after crystallization from ethyl alcohol (220–224°, lit. 215–223°) and conversion to its benzenesulfonyl derivative, m. p. 59–60°.

**2-Nitropropene** was obtained similarly by pyrolysis at 105–160° of the hydrochloride of N-(2-nitropropyl)-piperidine under 70 mm. pressure in 50% yield. It was identical with the 2-nitropropene prepared by other methods.[3]

**2-Nitro-1-butene** was obtained in 73% yield by pyrolysis of the hydrochloride of N-(2-nitrobutyl)-diethylamine at 100–175° under 100 mm. pressure; b. p. 60.5° (50 mm.), $n^{20}$D 1.4356. It was identical with an authentic sample of 2-nitro-1-butene synthesized by pyrolysis of the benzoate of 2-nitro-1-butanol.[18]

**2-Nitro-1-hexene** was obtained in 70% yield by pyrolysis of N-(2-nitrohexyl)-diethylamine at 105–165° under 50 mm. pressure; b. p. 81–82° (50 mm.), $n^{20}$D 1.4462.

*Anal.* Calcd. for $C_6H_{11}NO_2$: N, 10.86. Found: N, 10.89.

**2-Nitro-1-heptene** was obtained in 70% yield by pyrolysis of N-(2-nitroheptyl)-diethylamine at 110–150° under 50 mm. pressure; b. p. 93–94° (30 mm.), $n^{20}$D 1.4482.

*Anal.* Calcd. for $C_7H_{11}NO_2$: N, 9.76. Found: N, 9.85.

***p*-Toluidine Derivatives of the 2-Nitro-1-alkenes.**—Solid derivatives of the nitroölefins were readily obtained through reaction with *p*-toluidine. The general procedure used in their preparation is described. To 5 g. of the pure 2-nitro-1-alkene, cooled to 0–5°, there was added an equivalent amount of *p*-toluidine. The solution became warm and deep red in color. After maintaining the reaction mixture at 60° for five minutes it was cooled to room temperature and the crude product crystallized. Pure derivatives, as bright yellow solids, were obtained in 80–95% yield after one recrystallization from ethyl alcohol. These compounds are listed in Table I.

TABLE I

N-(2-NITROALKYL)-*p*-TOLUIDINES

| Compound, *p*-toluidine | M. p., °C. | N analyses, % Calcd. | N analyses, % Found |
|---|---|---|---|
| N-(2-Nitropropyl)- | 81.5–82.5 | 14.42 | 14.38 |
| N-(2-Nitrobutyl)- | 67.5–68.5 | 13.45 | 13.37 |
| N-(2-Nitroamyl)- | 72 –72.5 | 12.60 | 12.86 |
| N-(2-Nitrohexyl)- | 68.5–69 | 11.86 | 12.18 |
| N-(2-Nitroheptyl)- | 72.5–73.5 | 11.19 | 11.51 |

The *p*-toluidine derivatives of samples of 2-nitropropene and 2-nitro-1-butene prepared by other methods[3] were identical with those described in Table I.

**N-(2-Nitrobutyl)-*p*-toluidine** (Table I) was also prepared by an independent method. Using the procedure of Johnson,[9] 1-nitropropane, formaldehyde and *p*-toluidine reacted to give a 26% yield of the crude *p*-toluidine derivative, m. p. 60–66°. After recrystallization from methanol its m. p., 67.5–68.5°, was not depressed when mixed with the toluidine derivative prepared from 2-nitro-1-butene.

2-Nitro-2-ethyl-1,3-bis-(*p*-toluino)-propane, a di-substituted *p*-toluidine derivative, was prepared as a check on the mono-substituted derivative described above. To a refluxing mixture of 107 g. (1 mole) of *p*-toluidine, 44.5 g. (0.5 mole) of 1-nitropropane, 1 g. of potassium hydroxide and 300 cc. of ethyl alcohol, 82 g. (1 mole) of 37% formalin solution was added over a period of six hours. After refluxing an additional two hours and standing at room temperature for two days the mixture was cooled in ice and filtered. There was obtained 35 g. (25%) of light tan crystals melting at 101–102° which were recrystallized from ethyl alcohol, m. p. 103–104°.

*Anal.* Calcd. for $C_{19}H_{25}N_3O_2$: N, 12.84. Found: N, 12.73.

## Summary

A series of 2-nitro-1-alkenes has been readily obtained by thermal decomposition of appropriate nitro amine hydrochlorides derived from 1-nitroalkanes.

The 2-nitro-1-alkenes may be characterized by crystalline solid derivatives formed by their reaction with *p*-toluidine.

ITHACA, N. Y.

RECEIVED JULY 28, 1947

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[18] Tapp, Thesis, Cornell University, 1943.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

# Reactions with Tetraphenylcyclopentadienone. II. Condensation with 1-Phenyl-1,3-butadiene[1]

BY OLIVER GRUMMITT AND ERNEST I. BECKER[2]

2,3,4,5-Tetraphenylcyclopentadienone (tetracyclone) is of interest in diene chemistry through its addition reactions with $\alpha,\beta$-unsaturated carbonyl compounds[3] and with conjugated dienes.[4,5] In the case of butadiene the adduct contains two tetracyclone groups as the result of 1,2 and 3,4 addition at the 2,5 positions of the tetracyclone ring.[4] With cyclopentadiene only one tetracyclone reacts, the addition occurring at the 2,3 double bond and at the 2,5 positions of tetracyclone.[5]

These addition reactions are usually considered

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[1] Presented before the Division of Organic Chemistry at the Atlantic City meeting of the American Chemical Society, April 15, 1947.

[2] Sherwin–Williams Research Fellow in Organic Chemistry, 1946. Present address: Polytechnic Institute of Brooklyn, Brooklyn, New York.

[3] For example, with maleic anhydride: *cf.* Dilthey, Schommer, and Trosken, *Ber.*, **66B**, 1627 (1933), and Allen and Sheps, *Can. J. Research*, **11**, 171 (1934).

[4] Dilthey, Schommer, Hoschen and Dierichs, *Ber.*, **68B**, 1159 (1935).

[5] Grummitt, Klopper and Blenkhorn, THIS JOURNAL, **64**, 604 (1942).

to be Diels–Alder reactions.[6] Although tetracyclone has an $\alpha,\beta$-unsaturated carbonyl group, and therefore might behave as a dienophile, it characteristically reacts as a conjugated diene. In the presence of tetracyclone a conjugated diene behaves as a dienophile. In terms of the structures associated with typical Diels–Alder reactions, tetracyclone and the diene show reversed functions.

A survey of the addition reactions of 1-phenyl-1,3-butadiene has shown that most reagents preferentially add 3,4 instead of 1,2 or 1,4.[7] Furthermore, unsymmetrical reagents which add 3,4 usually obey Markownikoff's rule. Since styrene also shows normal addition in most cases, this behavior of phenylbutadiene is in accord with the principle of vinylogy.[8] As a continuation of the study of the mode of addition of both tetracyclone and phenylbutadiene, an investigation of the reaction of these compounds is reported here.

Although 1-phenyl-1,3-butadiene has been made by several different reactions,[7] the synthesis of this hydrocarbon in good yields proved to be quite difficult. The reaction of cinnamaldehyde and methylmagnesium bromide to give methylstyrylcarbinol followed by dehydration of this carbinol was tried first.[9] Although the carbinol can be made in 80–90% yields, dehydration of it gave poor yields because of rapid polymerization of the hydrocarbon during dehydration. The relatively high boiling point of phenylbutadiene aggravates this problem, because it cannot be quickly removed from the reaction mixture, as is possible for lower boiling hydrocarbons.

von der Heide[10] modified this synthesis by hydrolyzing the intermediate Grignard addition compound in acid solution so that phenylbutadiene was formed without isolation of the methylstyrylcarbinol. This reaction also gave low yields until the conditions of hydrolysis were thoroughly explored. By hydrolysis in 30% sulfuric acid solution under carefully controlled conditions of time and temperature, it is now possible to prepare 1-phenyl-1,3-butadiene consistently in 70–80% yields.

In the absence of an inhibitor phenylbutadiene polymerizes more rapidly than 1,3-butadiene.[11] To facilitate work with this compound several inhibitors were tested at a concentration of 1% and at a temperature of 100°. The experiments summarized in Table I were run by noting the time required for samples to flow vertically in 7-mm. reaction tubes. The interval of time elapsed for the flow time to exceed one second was arbitrarily taken as the inhibition period.

TABLE I

POLYMERIZATION INHIBITORS FOR 1-PHENYL-1,3-BUTADIENE[12]

| Inhibitor | Inhibition period, hr. |
|---|---|
| Blank | <9.5 |
| Picric acid | 21 |
| *m*-Dinitrobenzene | 21 |
| Phenyl-$\beta$-naphthylamine | 21 |
| Diphenylamine | 21 |
| Triphenylamine | <9.5 |
| *p*-Phenylenediamine | <9.5 |
| Hydroquinone | <9.5 |
| *t*-Butylcatechol | 5 |
| Benzoquinone | 9.5 |
| Chloranil | 5 |

The aromatic nitro compounds and certain of the amines are considerably more effective than the phenols and quinones. Phenyl-$\beta$-naphthylamine was selected as the most suitable inhibitor. It is interesting to note that this compound is relatively less effective for styrene and 3,4-dichlorostyrene.[13]

Tetracyclone and 1-phenyl-1,3-butadiene were found to react almost quantitatively at 80° in a 1/1 mole ratio, thus resembling the addition to cyclopentadiene.[5] Two structurally isomeric products are possible (chart 1): (A) is the result of 1,2 addition and (B) of 3,4 addition. Since the reaction product was a single compound, it presumably had either the (A) or (B) structure. To establish this structure it was desirable to convert the six-membered ring to a benzenoid ring. As the first step in this process, an effort was made to eliminate the endocarbonyl group by thermal decomposition. However, this characteristic reaction of endocarbonyl compounds[6b] could not be carried out because of a competitive dissociation of the adduct to tetracyclone and phenylbutadiene.[14]

In order to stabilize the adduct it was hydrogenated with the consumption of one equivalent of hydrogen. If the structure of the adduct is assumed to be (B), hydrogenation probably occurred in the styryl side chain (C), since Dilthey[15] has shown the ring double bond to be stable under the conditions employed here. The hydrogenated adduct proved to be sufficiently resistant to decomposition that heating at 180° or above eliminated the endocarbonyl group to give the cyclohexadiene derivative (D). Aromatization of (D) was effected by chloranil at 140° or by palladium on charcoal at 240°. Decarbonylation and aromatization occurred consecutively when (C) was refluxed in *p*-cymene with the palladium catalyst.

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(6) For a review of the chemistry of tetracyclone and related compounds see (a) Norton, *Chem. Rev.*, **31**, 398 (1942), and (b) Allen. *ibid.*, **37**, 209 (1945).

(7) Becker, Ph.D. thesis, Western Reserve University, 1946.

(8) Fuson, *Chem. Rev.*, **16**, 1 (1935).

(9) Klages, *Ber.*, **35**, 2649 (1902); Strauss, *ibid.*, **42**, 2882 (1909).

(10) von der Heide, *ibid.*, **37**, 2101 (1904).

(11) Whitby and Gallay, *Can. J. Research*, **6**, 220 (1932).

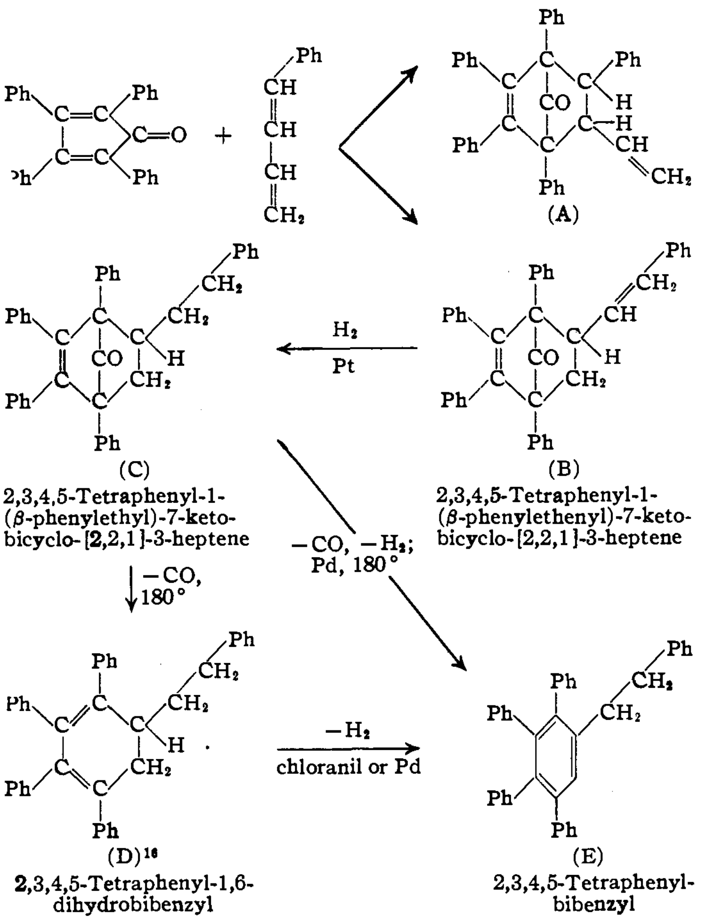
(12) We are indebted to Robert M. Vance of this Laboratory for these experiments.

(13) Frank and Adams, THIS JOURNAL, **68**, 908 (1946).

(14) A similar reverse reaction was noted in the case of cyclopentadiene.[5] This is also typical of many Diels–Alder adducts: *cf.* the work of Bachmann and Kloetzel, THIS JOURNAL, **60**, 481 (1938), on the reactions of maleic anhydride with polycyclic aromatic hydrocarbons.

(15) Dilthey and Quint, *J. prakt. Chem.*, [2] **128**, 143 (1930).

CHART 1

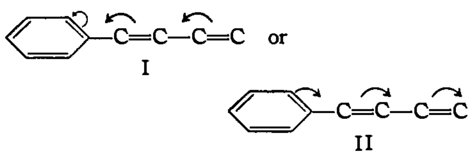


The final product (E) is 2,3,4,5-tetraphenylbibenzyl, or, if adduct (A) had formed, the corresponding product is pentaphenylethylbenzene.

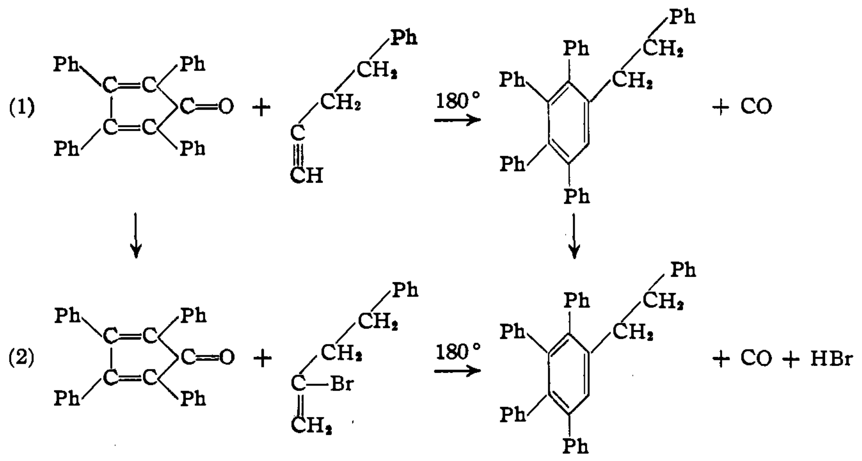
Attempts to establish the structure of the benzene derivative by oxidation to tetraphenyl- or pentaphenylbenzoic acid were unsuccessful. However, the non-crystallizable oxidation products responded to qualitative tests for a benzoin, thus pointing to structure (E). Conclusive evidence for (E) was obtained by an independent synthesis from tetracyclone with 4-phenyl-1-butyne[17] or with 4-phenyl-2-bromo-1-butene.

The authentic 2,3,4,5-tetraphenylbibenzyl from these reactions proved to be identical with the product (E) from the tetracyclone–phenylbutadiene sequence of reactions. Therefore, tetracyclone added 3,4 to 1-phenyl-1,3-butadiene in preference to 1,2 addition. This result is in accord with most addition reactions of this diene.[7]

The explanation for the preferential 3,4 addition is two-fold: first, the steric hindrance from the phenyl group at the 1,2 double bond would favor 3,4 addition, especially in the case of large molecules such as tetracyclone.[18] Possibly of greater importance is the nature of the activated phenylbutadiene molecule. According to the usual electronic interpretations,[19] the butadienyl side chain could be activated in the course of addition of polar reactants by electron displacements toward or away from the ring



Because of the *conjugated* bonds in the side chain this polarization affects *both* double bonds, thus making addition to either double bond theoretically possible, but also creating the greatest relative charge on the terminal carbon atom. There-



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[16] The position of the double bonds in this compound was not established.

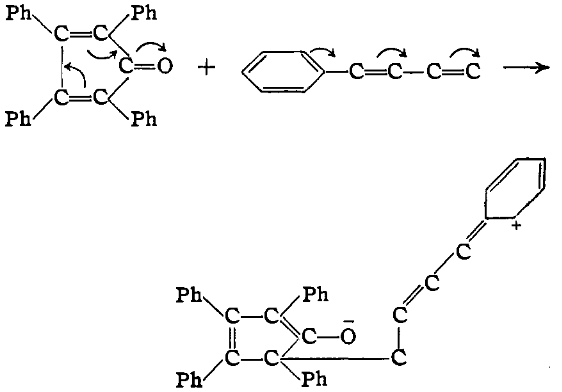
[17] Tetracyclone reacts with acetylene, phenylacetylene and other acetylenic compounds by addition to the triple bond. The resulting endocarbonyl derivatives very readily lose carbon monoxide. See Dilthey, *et al.*, *Ber.*, **66B**, 1627 (1933).

[18] In the addition of maleic anhydride (Robey, Morrell and Weise, THIS JOURNAL, **63**, 627 (1941)) and of sulfur dioxide (Craig, *ibid.*, **65**, 1006 (1943)) to piperylene, it has been shown that the steric hindrance from the methyl group in the *cis* piperylene will retard addition, but the *trans* isomer shows normal reactivity. The phenylbutadiene used in this experiment is very likely a mixture of geometric isomers (Wright, *J. Org. Chem.*, **1**, 457 (1936)). Presumably, the steric factor would be significant only in the case of the *cis* isomer.

[19] Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 245.

fore addition is usually initiated at this point with the result that 3,4 addition occurs more frequently. The direction of the polarization is postulated as in II, *i. e.*, the ring acts as an electron donor, in order to account for the normal addition of unsymmetrical reagents.[20]

The reactivity of tetracyclone in this reaction would result from a polarization in its conjugated system to make carbon atom 5 electrophilic. Thus the first step in the addition



This activated intermediate complex can have various structures. The form in which ring closure occurs to give the adduct (B) would have a nucleophilic number 2 carbon atom in tetracyclone and an electrophilic number 3 carbon atom in phenylbutadiene. This mechanism, which is comparable to that frequently proposed for orthodox Diels–Alder additions,[21] accounts for the behavior of tetracyclone as a conjugated diene rather than as an $\alpha,\beta$-unsaturated carbonyl derivative.[22]

## Experimental

**Preparation of Reactants.**—Tetraphenylcyclopentadienone was made by the condensation of benzil and dibenzyl ketone in alcoholic base.[15,23]

Since adequate directions for preparing 1-phenyl-1,3-butadiene are not in the literature, considerable time and effort were expended in finding the optimum conditions described here. In a 1-liter three-necked flask fitted with a mercury seal stirrer, reflux condenser protected with a calcium chloride tube, a 125-ml. dropping funnel, and a nitrogen inlet tube are placed 0.515 mole of methylmagnesium bromide in 250–350 ml. (1.5–2.0 *N*) of ether. The Grignard reagent is cooled to 0–10° with stirring and under a current of nitrogen, and a solution of 66.1 g. (0.5 mole) of cinnamaldehyde in 60 ml. of absolute ether is added so that the temperature does not exceed 10°. This addition requires about one hour. The cinnamaldehyde should be freshly purified by washing with sodium carbonate solution, then with water, dried over Drierite, and distilled under nitrogen; b. p. 101–102° (2–3 mm.), $n^{20}$D 1.6195.

The contents of the reaction flask are transferred to a 500-ml. dropping funnel. The apparatus is reassembled, omitting the nitrogen inlet tube and drying tube, and 175 ml. of 30% (by weight) sulfuric acid placed in the flask. With vigorous stirring and without cooling, the Grignard addition compound is rapidly added to the acid solution. With an efficient reflux condenser this time of addition is five to seven minutes. The mixture is then heated at gentle reflux on the steam-bath until the *total* time of hydrolysis is twenty minutes. The conditions of this hydrolysis are very important in determining the yield of phenylbutadiene. Vigorous stirring was attained by a Hershberg[24] nichrome-wire stirrer run at 1500–1700 r. p. m. The time of addition and of reflux are critical in avoiding polymerization of the product and contamination by methylstyrylcarbinol.

The contents of the flask are *immediately* transferred to a 1-liter separatory funnel, the lower aqueous layer is discarded, and the ether solution is washed successively with (1) 50 ml. of water, (2) a mixture of 50 ml. of 5% sodium hydroxide solution and 50 ml. of saturated ammonium chloride solution, and (3) 50 ml. of water. Before each washing the air in the funnel is displaced by nitrogen. When the second wash solution is added, 0.3 g. of phenyl-$\beta$-naphthylamine is dissolved in the ether solution. The washed solution is dried with 20 g. of anhydrous sodium sulfate for one-half hour and then overnight with 15 g. of anhydrous potassium carbonate.

The ether solution is distilled to a volume of 80–100 ml. on the steam-bath, cooled, and dried further by shaking with 15 g. of potassium carbonate for five to ten minutes. The solution is filtered into a 125 ml. modified Claisen flask[25] and distilled under nitrogen at reduced pressure into a receiver containing 0.3 g. of phenyl-$\beta$-naphthylamine. The crude phenylbutadiene is collected at 81–85° (10–11 mm.); the yield is 52–54 g., 80–83% of the theoretical. To remove traces of water and methylstyrylcarbinol, this distillate is dried with 5 g. of potassium carbonate, filtered and redistilled. The distillate consists of 47–49 g. (72–75%), b. p. 78–81° (8 mm.), $n^{20}$D 1.6070. The reactions with tetracyclone were run with this product.

A highly purified sample of 1-phenyl-1,3-butadiene was made by distilling the above product through a 12-plate, glass helix packed column of the total reflux variable take-off type and collecting a middle fraction representing about 50% of the sample taken. The following physical constants were noted: b. p. 86° (11 mm.), $n^{25}$D 1.6088 ± 0.0002, $d^{25}_4$ 0.9237 ± 0.0002. A qualitative test for nitrogen by sodium fusion and formation of Prussian blue was negative, showing that phenyl-$\beta$-naphthylamine had not distilled.

*Anal.* Calcd. for $C_{10}H_{10}$: C, 92.25; H, 7.75. Found: C, 92.25; H, 7.81.

**Tetracyclone–Phenylbutadiene Adduct (B).**—In a typical experiment 2.50 g. (0.019 mole) of 1-phenyl-1,3-butadiene, 7.00 g. (0.018 mole) of tetracyclone (m. p. 219–220°), and 0.01 g. of phenyl-$\beta$-naphthylamine in 50 ml. of reagent-grade benzene were refluxed on the steam-bath for four hours. No carbon monoxide, as indicated by tests with palladium chloride solution, was evolved. Benzene and unreacted phenylbutadiene were removed by steam distillation and the residual pink solid dried at 50° to give 9.40 g. (100%), m. p. 170–175° (dec.). Crystallization from 90 ml. of a 1:1 mixture of benzene and petroleum ether (b. p. 60–70°) gave 6.0 g. of almost colorless fine needles, m. p. 178–180° (dec.). A second crop weighed 2.05 g. and melted 177–180° (dec.). The behavior on melting is noteworthy: at 140–145° the colorless crystals began to turn pink. The color deepened with increasing temperature and at 178–181° the solid melts to a deep red liquid.

*Anal.* Calcd. for $C_{39}H_{30}O$: C, 91.02; H, 5.88; mol.

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[20] Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 247.

[21] Price, "Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 49.

[22] It is not suggested that all reactions of tetracyclone proceed by this mechanism. The addition of maleic anhydride and similar molecules probably differ in mechanism because of the electron deficient character of the carbon–carbon double bond in maleic anhydride.

[23] Johnson and Grummitt, "Organic Syntheses," 23, 92 (1943).

[24] Hershberg, *Ind. Eng. Chem., Anal. Ed.*, 8, 313 (1936).

[25] "Organic Syntheses," Coll. Vol. I, 130 (1941); Fig. 9(b).

wt., 515. Found: C, 91.11; H, 5.93; mol. wt., 517 (cryoscopic in benzene).[26]

This product is unsaturated with respect to bromine in bromobenzene and potassium permanganate in acetone. It does not give a positive ketone test with 2,4-dinitrophenylhydrazine reagent.[27] It is very soluble in benzene and acetone, moderately soluble in ethyl acetate, slightly soluble in ethyl alcohol and insoluble in petroleum ether. When a benzene or ethyl acetate solution is boiled, decomposition occurs, as shown by the formation of a pink color.

**Attempted Decarbonylation of (B).**—Experiments were run in refluxing toluene (b. p. 110°), chlorobenzene (b. p. 132°), bromobenzene (b. p. 155°), and *p*-cymene (b. p. 175°). For example, a solution of 1.0 g. of the addition compound (B) in 15 ml. of chlorobenzene was refluxed in a 25-ml. flask fitted with a nitrogen inlet tube. The top of the condenser was attached to a trap and to a gas bubbler containing 2–3 ml. of 0.025% palladium chloride. After two hours of refluxing no more carbon dioxide was evolved. The product, 0.8 g. of dark red solid melting 80–84°, was recovered by steam distillation, filtration, and drying at 50°. Repeated crystallization from benzene–petroleum ether (60–70°) gave only impure products of wide melting range. Examination of the solids under the microscope showed that fine, black crystals, closely resembling tetracyclone, were present. Varying the reaction temperatures by the use of other solvents gave no better results. Apparently the product of decarbonylation and the tetracyclone from dissociation could not be separated.

**Hydrogenation of (B).**—The hydrogenated addition compound (C) was made by low pressure hydrogenation of (B) in ethyl acetate solution with 5% palladium on charcoal as the catalyst. Ten and three-tenths grams (0.020 mole) of (B) in 200 ml. of absolute ethyl acetate plus 0.5 g. of catalyst was hydrogenated at about 30 lb. pressure in a Burgess–Parr apparatus. In three minutes the pressure drop indicated the consumption of 0.023 mole of hydrogen. After filtration of the catalyst, concentration of the filtrate to 120 ml., and cooling to 0°, 6.2 g. of colorless, thick flat crystals, m. p. 207–208.5° (dec.), was obtained. Two successive crops from the mother liquor made the total yield 7.64 g., 74% of the theoretical. Crystallization from 1:1 benzene–petroleum ether (60–70°) did not alter the melting point behavior.

*Anal.* Calcd. for $C_{39}H_{32}O$: C, 90.65; H, 6.25; mol. wt., 517. Found: C, 90.53; H, 6.34; mol. wt., 514 (cryoscopic in benzene).

This product is saturated with respect to bromine in bromobenzene but unsaturated to potassium permanganate in acetone. Unlike compound (B), a boiling benzene or ethyl acetate solution does not decompose it.

**Decarbonylation of (C).**—A solution of 8.0 g. (0.015 mole) of compound (C) in 200 ml. of purified *p*-cymene was refluxed under a current of nitrogen until a positive test for carbon monoxide with palladium chloride solution was no longer obtained. This required about twelve hours. After steam distillation of the product and crystallization from benzene–petroleum ether (60–70°), 6.1 g., 81%, of light orange crystals melting 142–144° were obtained. The decarbonylation can also be run in the absence of a solvent by heating (C) in an oil-bath at 220–225° for one hour under nitrogen, but the yield of product melting 142–144° was only 63%. Repeated crystallizations from benzene–petroleum ether (30–35°) and acetone–ethyl alcohol gave almost colorless crystals melting 145–146°.

*Anal.* Calcd. for $C_{38}H_{32}$: C, 93.39; H, 6.61; mol. wt., 489. Found: C, 93.65; H, 6.70; mol. wt., 488 (cryoscopic in benzene).

Compound (D) was unsaturated to both bromine and potassium permanganate solutions. The position of the double bonds was not established, but the structure shown in Chart 1 is very probable because the double bonds are conjugated with respect to each other and to the aromatic double bonds of the phenyl substituents.

**Dehydrogenation of (D) with Chloranil.**—A solution of 500 mg. (1.02 millimoles) of (D) and 264 mg. (1.07 millimoles) of chloranil (m. p. 298–300°) in 5 ml. of xylene was refluxed for twenty-four hours. After cooling and filtering to remove tetrachlorohydroquinone, the filtrate was washed twice with 10-ml. portions of 4% potassium hydroxide solution, once with water, and steam distilled to remove xylene. The residue was crystallized three times from benzene–petroleum ether (60–70°) to give 247 mg., 49% of the theoretical yield, of solid melting 129–131°.

**Dehydrogenation of (D) with Palladium.**—In the catalytic dehydrogenation apparatus described by Fieser[28] 0.98 g. (2.0 millimoles) of (D) and 0.2 g. of 5% palladium on charcoal were refluxed in 5 ml. of 1-methylnaphthalene (b. p. 238–240°)[29] for six hours. During this time 88% of the calculated amount of hydrogen was evolved. After steam distilling to remove the solvent and crystallization of the residue from benzene–petroleum ether (60–70°), there was obtained 0.81 g., 83% of the theoretical yield, melting 134–138°. A mixed melting point with the impure product from the chloranil dehydrogenation gave 133–137° and with compound (D), 125–142°. Compound (E) is saturated to both bromine and potassium permanganate. For analysis a sample melting 135–137° was made by recrystallization.

*Anal.* Calcd. for $C_{38}H_{30}$: C, 93.79; H, 6.21; mol. wt., 487. Found: C, 93.65; H, 6.27; mol. wt. (Rast camphor), 491.

**Combined Dehydrogenation and Decarbonylation of (D).**—A mixture of 4.0 g. (7.7 millimoles) of (C) and 0.5 g. of 5% palladium on charcoal in 100 ml. of *p*-cymene was refluxed for eight and one-half hours. Carbon monoxide was evolved until the last fifteen minutes of heating. After steam distilling and crystallizing from benzene–petroleum ether, the product consisted of 3.0 g. (80%) melting 136–140°. A mixed melting point with (D) of melting point 135–137° gave 136–140°. Further crystallizations of the 136–140° product did not purify it. It was concluded that the palladium catalyzed dehydrogenation of (D) was the best method of preparation.

**Chromic Acid Oxidation of (E).**—Several attempts were made to oxidize (E) to 2,3,4,5-tetraphenylbenzoic acid, but only oils or impure solids could be obtained. For example, a solution of 2.5 g. of chromium trioxide in 4 ml. of water and 4 ml. of acetic acid was added dropwise to a solution of 1.55 g. (3.2 millimoles) of (E) in 5 ml. of acetic acid. After the exothermic reaction subsided, the product was isolated by pouring the mixture onto ice, filtering, and washing the solid with water. The solid was dissolved in 50 ml. of 1:1 benzene–ether and this solution was extracted with 10 ml. of 5% sodium carbonate solution. Acidification of the alkaline extract gave only 10 mg. of brown solid melting 40–50°, which was not investigated further. The benzene–ether solution yielded an oil which could not be crystallized. When this oil was dissolved in alcoholic potassium hydroxide and heated, a deep red-purple color formed, reminiscent of the behavior of benzoin-benzil mixtures.[30] Attempts to oxidize the oil further with sodium peroxide were unsuccessful. The original aqueous filtrate was extracted with ether in a continuous extractor and the ether extract yielded about 0.1 g. of solid melting 116–120°, which was shown to be benzoic acid by a mixed melting point.

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[26] The molecular depression constant used was 5.49 deg./mole. This value was found experimentally by carefully determining the freezing point depression of several solutions of pure naphthalene in benzene. The constant frequently given in the literature of 5.12 was determined under *equilibrium* conditions (Bury and Jenkins, *J. Chem. Soc.*, 688 (1934). Such conditions do not exist in the usual cryoscopic molecular weight determination.

[27] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 65.

[28] Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Company, New York, N. Y., 1941, p. 462.

[29] Grummitt and Buck, THIS JOURNAL, **65**, 295 (1943).

[30] Michaelis and Fetcher, *ibid.*, **59**, 1246 (1937).

**4-Phenyl-2-bromo-1-butene.**—Although the synthesis of this compound has been reported,[31] the difference in boiling points observed makes it desirable to give the details of this synthesis. Benzylmagnesium chloride, made from 25.3 g. (0.20 mole) of distilled benzyl chloride (b. p. 72–73° (24 mm.)) and 4.9 g. (0.20 atom) of magnesium in 100 ml. of absolute ether, was added to 40 g. (0.20 mole) of 2,3-dibromo-1-propene[32] (b. p. 73–76° (75 mm.)) in 100 ml. of absolute ether so as to maintain a slow reflux. The mixture was then refluxed for two hours, followed by hydrolysis in 80 ml. of saturated ammonium chloride solution and 120 g. of ice. The ether layer was washed, dried, etc., and vacuum distilled; the forerun consisted of 12 g. of 2,3-dibromo-1-propene and the 4-phenyl-2-bromo-1-butene distilled at 85–87° (4–5 mm.). A residue of 11.1 g. was crystallized from methyl alcohol and shown to be bibenzyl by a mixed melting point. After twice redistilling the product, a fraction boiling 90–91° (4–5 mm.) showed $d^{25}_4$ 1.2860 and $n^{25}_D$ 1.5467. Previously reported[31]: b. p. 77–78° (5 mm.), $d^{20}_4$ 1.2901, $n^{20}_D$ 1.5450.

*Anal.* Calcd. for $C_{10}H_{11}Br$: C, 56.89; H, 5.25; Br, 37.86. Found: C, 56.48; H, 5.16; Br, 38.02 (Carius).

**4-Phenyl-1-butyne.**—Sodamide was prepared from 3.1 g. (0.133 atom) of sodium by the method of Murray and Cloke,[33] and the reaction with 10 g. (0.0474 mole) of 4-phenyl-2-bromo-1-butene was carried out according to Johnson and McEwen.[31] The product distilled at 72–78° (11 mm.) and weighed 3.9 g. (64%); $n^{25}_D$ 1.5192. The mercury derivative, bis-(4-phenyl-1-butynyl)-mercury, melted 83.5–84.5°; reported, 83.5–84.5°.[31]

**2,3,4,5-Tetraphenylbibenzyl from Tetracyclone and 4-Phenyl-1-butyne.**—A solution of 1.0 g. (7.68 millimoles) of the acetylenic compound and 2.88 g. (7.50 millimoles) of tetracyclone in 15 ml. of *p*-cymene was refluxed under a slow current of nitrogen until carbon monoxide was no longer evolved (about five and one-half hours). The product was isolated by steam distillation and crystallization from a solution of 10 ml. of benzene and 50 ml. of petroleum ether (60–70°) to give 2.44 g. (67%) of fine, colorless crystals melting 135–137°. A mixed melting point with compound (E) gave 135–137°.

*Anal.* Calcd. for $C_{38}H_{30}$: C, 93.79; H, 6.21; mol. wt., 487. Found: C, 93.57; H, 6.42; mol. wt. (Rast camphor), 476.

With dioxane substituted for *p*-cymene as the solvent, the condensation required 204 hours and the yield of product melting 135–137° was 57%.

**2,3,4,5-Tetraphenylbibenzyl from Tetracyclone and 4-Phenyl-2-bromo-1-butene.**—A solution of 0.78 g. (3.70 millimoles) of the butene derivative and 1.36 g. (3.54 millimoles) of tetracyclone in 15 ml. of cymene was refluxed under a slow current of nitrogen for twenty-nine and one-half hours. During this time carbon monoxide and hydrogen bromide were evolved. The product was isolated as before. The yield was 1.04 g. (60%) melting 135–137°. A mixed melting point with a 2,3,4,5-tetraphenylbibenzyl prepared above showed no depression.

To show that the hydrogen bromide was eliminated from the adduct and not from the 4-phenyl-2-bromo-1-butene, a model experiment was run in which a solution of 0.78 g. of the butene derivative in 15 ml. of *p*-cymene was refluxed for sixteen hours. No hydrogen bromide was evolved during this time. The easy elimination of hydrogen bromide from the addition compound is due to the reactivity of the tertiary bromine atom and is comparable to the behavior of Diels–Alder addition compounds of chloromaleic anhydride.[34]

## Summary

1-Phenyl-1,3-butadiene can be synthesized from cinnamaldehyde and methylmagnesium bromide in 70–80% yields. Phenyl-β-naphthylamine is an effective polymerization inhibitor for this hydrocarbon. 1-Phenyl-1,3-butadiene and 2,3,4,5-tetraphenylcyclopentadienone react in a 1/1 mole ratio to give 2,3,4,5-tetraphenyl-1-(β-phenylethenyl)-7-keto-bicyclo[2,2,1]3-heptene. The structure of the adduct was proven by degradation to 2,3,4,5-tetraphenylbibenzyl. The latter compound was synthesized independently from tetracyclone and 4-phenyl-1-butyne or 4-phenyl-2-bromo-1-butene. This reaction demonstrates further that the preferred mode of addition to 1-phenyl-1,3-butadiene is 3,4. This process is the result of steric hindrance by the phenyl group and of polarization throughout the butadienyl side chain by electron displacements away from the ring.

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[31] Johnson and McEwen, THIS JOURNAL, **48**, 469 (1926).

[32] Lespieau and Bourguel, "Organic Syntheses," Coll. Vol. I, 209 (1941).

[33] Murray and Cloke, THIS JOURNAL, **58**, 2014 (1936).

[34] Synerholm, THIS JOURNAL, **67**, 1229 (1945).

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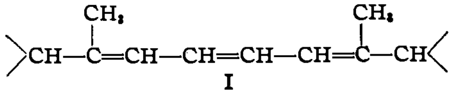
[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF WISCONSIN]

# Acetylenic Glycols Related to Natural Polyenes[1]

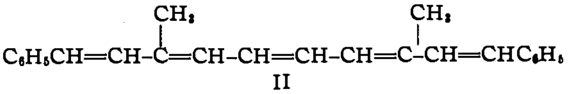
BY LENA F. DEEMER, LEO LUTWAK AND F. M. STRONG

In connection with the general problem of the synthesis of carotenoid pigments and related compounds, it seemed of interest to attempt to prepare substances corresponding in structure to the central ten carbon atoms common to nearly all the natural carotenoids (formula I). Substances of this type bearing terminal substituents which would facilitate further lengthening of the carotenoid chain were desired. As far as the authors are aware the only previously synthesized compound having the carbon skeleton in question is 3,8-dimethyl-1,10-diphenyldeca-1,3,5,7,9-pentaene (II), which was prepared by Kuhn and Wallenfels in 1938.[2]



$$>\!CH-\overset{CH_3}{\overset{|}{C}}=CH-CH=CH-CH=\overset{CH_3}{\overset{|}{C}}-CH\!<$$

I



$$C_6H_5CH=CH-\overset{CH_3}{\overset{|}{C}}=CH-CH=CH-CH=\overset{CH_3}{\overset{|}{C}}-CH=CHC_6H_5$$

II

The recent work of Heilbron and collaborators

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[2] Kuhn and Wallenfels, *Ber.*, **71**, 1891 (1938).