[CONTRIBUTION FROM THE EVANS CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Evidence Favoring a Two-step Mechanism for the Diels-Alder Reaction

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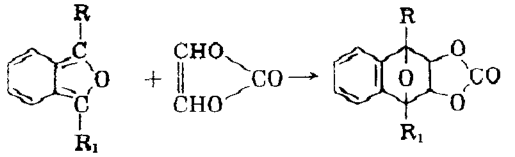
The fact that 1-phenyl-4-mesityl-2,3-benzofuran, II, reacts readily with vinylene carbonate in the Diels-Alder reaction whereas 1,4-dimesityl-2,3-benzofuran, III, fails to do so is interpreted as evidence showing that the Diels-Alder reaction can proceed by a stepwise mechanism.

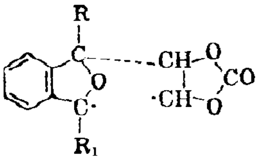
Improved syntheses for 1,4-diaryl-2,3-benzofurans are described. Oxidation of 1,4-diaryl-2,3-benzofurans with lead tetraacetate affords *o*-diaroylbenzenes in high yield. 1,4-Dimesityl-2,3-benzofuran, III, 3-mesitylphthalide, VIII, and *o*-(2-isopropoxy-2-mesityl)toluic acid, XI, are produced on reaction of mesitylmagnesium bromide with the pseudo *i*-propyl ester of *o*-phthalaldehydic acid. This reaction is sensitive to order of addition of reagents, solvent, and mole ratio of reactants. Under certain conditions a 58% yield of XI is obtained.

In connection with another problem, an observation has been made which indicates strongly that the Diels-Alder type can proceed by a two-stage mechanism.[2] 1,4-Diphenyl-2,3-benzofuran, I, and 1-mesityl-4-phenyl-2,3-benzofuran, II, react readily with vinylene carbonate[3] to yield the cyclic carbonates IV and V, respectively. In contrast, no adduct formation between 1,4-dimesityl-2,3-benzofuran, III, with vinylene carbonate, maleic anhydride, or *N*-phenylmaleimide occurs even under more vigorous conditions.



I. $R = R_1 = C_6H_5$ IV. $R = R_1 = C_6H_5$
II. $R = C_6H_5, R_1 = C_9H_{11}$ V. $R = C_6H_5, R_1 = C_9H_{11}$
III. $R = R_1 = C_9H_{11}$

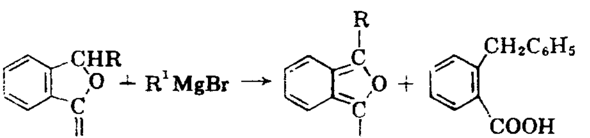
The reason for the unreactivity of III is surely steric hindrance as molecular models show that the mesityl groups must lie almost perpendicular to the plane of the benzofuran nucleus. In this position the methyl groups prevent approach of a dienophile to the 1,4-carbons of the furan ring and hence sterically hinder bond formation. In the case of II, however, the dienophile can approach the carbon containing the phenyl group to form the hypothetical intermediate, VI (shown as a diradical, but dipolar ionic structures might also be written). This intermediate, VI, now can cyclize to yield the adduct, V. The cyclization of VI to V takes place because steric hindrance is much less effective in preventing an intramolecular, than an intermolecular, reaction from occurring. Furthermore, after bond formation (shown by a dotted line in VI to indicate bond formation at the rear) at the carbon attached to the phenyl group the geometry for formation of a bond at the carbon attached to the mesityl group should be more favorable than in any complex between II and vinylene carbonate in which no bond has been formed.



VI

The above argument need not apply to the reaction between I and vinylene carbonate for here a complex might be formed which might collapse to product in a one-stage mechanism.

Several observations with regard to the synthesis of the benzofurans I, II, and III are of interest. The yield of I by the reaction of 3-phenylphthalide, VII with phenylmagnesium bromide is sensitive to solvent and to order of addition of reagents,[4] the best yield (87% pure) being obtained when ethereal Grignard reagent was added to a solution of VII in ether-tetrahydrofuran. Similarly, when excess ethereal phenylmagnesium bromide was added to 3-mesitylphthalide, VIII, a 97% yield of II was obtained. However, when mesitylmagnesium bromide in tetrahydrofuran was added to 3-phenyl-



IX

VII. $R = C_6H_5$ I. $R = R = C_6H_5$
VIII. $R = C_9H_{11}$ II. $R = C_6H_5, R^1 = C_9H_{11}$

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[1] The author is indebted to the Petroleum Research Fund of the American Chemical Society for a grant (356-A) in support of this work and to Mrs. E. H. Wiseman for taking numerous infrared absorption spectra and melting points.

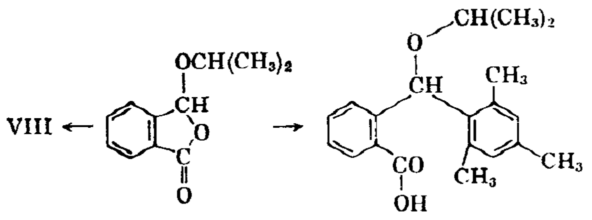
[2] For references concerning mechanism see C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958). See also R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959), and J. A. Berson, A. Remanick, and W. A. Mueller, *J. Am. Chem. Soc.*, 32, 5501 (1960).

[3] M. S. Newman and R. Addor, *J. Am. Chem. Soc.*, **77**, 3789 (1955).

[4] (a) Compare A. Guyot and J. Catel, *Bull. soc. chim. France*, (3) **35**, 1124 (1906). (b) See also E. Clar *et al.*, *Ber.*, **62**, 940 (1929) for analogous reactions.

phthalide, VII, only a 61% yield of II was obtained. In addition, a 16% yield of *o*-benzylbenzoic acid, IX, was obtained. To our knowledge, this is the first example of reductive cleavage of a lactone ring by a Grignard reagent.

Another more surprising cleavage of a lactone ring was discovered when an ethereal solution of the pseudo isopropyl ester of phthalaldehydic acid, X, was added to two equivalents of mesitylmagnesium bromide in ether. The main product (about 58% yield) was *o*-(2-isopropoxy-2-mesityl) toluic acid, XI. About 10% of III was also obtained. If the ratio of ester, X, to Grignard reagent were about 1.5 to 2, the yield of XI fell to 42% and the amount of III formed was unchanged (near 10%).



X XI

When one equivalent of ethereal mesitylmagnesium bromide was added to one equivalent of X in ether-tetrahydrofuran the main crystalline product isolated from the neutral portion of the reaction products was VIII (21% yield) and a negligible quantity of acid (not XI) was produced. This replacement of the isopropoxy group by mesityl represents a new ether cleavage reaction.[5] In this reaction not more than a trace of 1,4-dimesityl-2,3-benzofuran, III, was formed. However, in a similar reaction, except that the mesityl magnesium bromide was in tetrahydrofuran, about 17% of III was formed together with 28% of VIII. When one equivalent of X in tetrahydrofuran was added to two equivalents of mesitylmagnesium bromide in the same solvent, a 61% yield of III resulted. Although not a great many experiments in this field have been carried out, obviously the products formed are extremely sensitive to solvent, mole ratio of reactants, and order of addition.

The reactions described in the above paragraph were originally attempted in order to devise a route to 1,4-dimesityl-2,3-benzofuran, III, because the sodium borohydride reduction of *o*-mesitoylbenzoic acid to 3-mesitylphthalide, VIII, failed, and consequently, the synthesis of III by a route parallel to that of I, was not possible. However, since XI is readily converted into VIII by treatment with hydrobromic acid in acetic acid, such a synthesis of III is readily effected.

Each of the benzofurans, I, II, and III, was easily oxidized by lead tetraacetate to the corresponding *o*-diaroylbenzene.[6]

EXPERIMENTAL[7]

3-Phenylphthalide. To a stirred solution prepared from 226 g. of *o*-benzoylbenzoic acid, sodium hydroxide, and 1 l. of water was added 15 g. of sodium borohydride in portions during 20 min. After stirring for 16 hr. the solution was nearly neutralized with hydrochloric acid and 10 g. of sodium borohydride added in portions (considerable hydrogen evolution). During the next day 5 g. of sodium borohydride was added in portions and stirring of the reaction mixture with warming was continued until about 60 hr. had elapsed in all. After suitable workup 182 g. (87%) of 3-phenylphthalide, m.p. 114–115°, was obtained.[8] When a similar experiment was carried out with *o*-mesitoylbenzoic acid, only a trace of 3-mesitylphthalide, VIII, (see below) was obtained. The starting acid was recovered almost quantitatively.

1,4-Diphenyl-2,3-benzofuran, I. A Grignard reagent prepared from 80 g. of bromobenzene in 250 ml. of ether was added to a solution of 84 g. of 3-phenylphthalide in 500 ml. of tetrahydrofuran (THF) and 100 ml. of ether during the 40 min. at the end a clear dark-colored solution was at hand. After decomposition with dilute hydrochloric acid the mixture was worked up as usual. During the work-up the separatory funnel was warmed to prevent crystallization of product. After concentration of solvent there was obtained 99.1 g. of crude I, m.p. 128–131°, in two crops. Recrystallization from benzene-alcohol yielded 93.6 g. (87%) of pure I, m.p. 130–131°, as bright yellow needles. When solutions of 3-phenylphthalide were added to phenylmagnesium bromide insoluble precipitates were formed and the yields of I were less.

1-Mesityl-4-phenyl-2,3-benzofuran, II. A Grignard reagent from 32 g. of bromobenzene in 150 ml. of ether was added to a solution of 31.8 g. of 3-mesitylphthalide, VIII, (see below) in 300 ml. of tetrahydrofuran and 100 ml. of ether with cooling (15–20°). The reaction mixture turned deep purple and a colorless granular precipitate formed. After all had been added the mixture was heated to reflux for 10 min. and left to stand for 2 hr., after which the purple color had turned to yellow-orange. Decomposition with dilute acid and the usual work-up afforded a neutral fraction which yielded 37.0 g. (97%) of II, b.p. 195–200° at 0.5–1.0 mm., as a yellow-orange glass. To date no crystals have been obtained from this glass which was analytically pure.

Anal. Calcd. for $C_{23}H_{20}O$: C, 88.4; H, 6.4. Found[9a]: C, 88.0; H, 6.5.

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(5) See P. R. Jones and A. A. Lavigne, *J. Org. Chem.*, 25, 2020 (1960) for analogous cleavages in the 1,8-naphthalic acid series involving methylcadmium.

(6) See R. C. Fuson, S. B. Speck, and W. R. Hatchard, *J. Org. Chem.*, 10, 55 (1945), for a route to hindered *o*-diaroylbenzenes. Also Ref. 4(a).

(7) All melting points are uncorrected. The term "worked up in the usual manner" means that an ether-benzene solution (with or without tetrahydrofuran) of the reaction products was washed with dilute hydrochloric acid and then separated into acid and neutral fractions by extraction with dilute potassium carbonate solution. Ether-benzene solutions of the neutral and acid portions were then washed with saturated sodium chloride solution and filtered through a funnel containing anhydrous magnesium sulfate. Solvents were removed by distillation and the products treated as indicated.

(8) See. C. R. Hauser, M. T. Tetenbaum, and D. S. Hoffenberg, *J. Org. Chem.*, 23, 861 (1958). In our experience the yield of 3-phenylphthalide was variable under the conditions described. Possibly variations in the zinc used, both as to size of particles and impurities, might be responsible.

(9) Analyses marked [a] by Schwartzkopf, Microanalytical Laboratory, Woodside 77, N. Y.; marked [b] by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

When a Grignard reagent made from 20.5 g. of bromomesitylene in 90 ml. of tetrahydrofuran was treated with a solution of 21.0 g. of 3-phenylphthalide in 90 ml. of tetrahydrofuran an exothermic reaction occurred and a deep red color was produced. After being refluxed for 10 min., the mixture was cooled, treated with dilute hydrochloric acid, and worked up as usual. From the neutral fraction 19.1 g. (61%) of II was obtained as a clear yellow glass (see above). From the acid fraction 4.6 g. of acid was obtained which, after several recrystallizations from benzene–petroleum ether, afforded 3.3 g. (16%) of *o*-benzylbenzoic acid, m.p. 113.5–115.0°. There was no depression of melting point on mixing with an authentic sample.

3-Mesitylphthalide, VIII. A solution of 18.1 g. of *o*-(2-isopropoxy-2-mesityl)toluic acid, XI, m.p. 172–185° (crude acid, not recrystallized—see below), in 65 ml. of acetic acid containing 15 ml. of 48% hydrobromic acid was refluxed for 2 hr. cooled and diluted with 20 ml. of water. The main crop of crystals of VIII, m.p. 161–163.5°, weighed 13.6 g. (93%). Recrystallization from benzene-alcohol gave a pure sample of VIII, m.p. 164–165°, with little loss.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4. Found[9]: C, 81.0; H, 6.6.

3-Mesitylphthalide, VIII, was also formed in low yield (about 15–20%) when one equivalent of mesitylmagnesium bromide in tetrahydrofuran was added to a solution of one equivalent of either the pseudo isopropyl[10] or pseudo ethyl[10] ester of phthaldehydic acid in ether-tetrahydrofuran (compare below with other reactions of pseudo ester to yield III and XI).

1,4-Dimesityl-2,3-benzofuran, III. A solution of 19.2 g. of ψ-isopropyl phthaldehydate[10] in 60 ml. of tetrahydrofuran was added to the Grignard reagent from 42 g. of bromomesitylene in 150 ml. of tetrahydrofuran. Heat was evolved and the color became deep red-brown. After 1 hr. at reflux the cooled reaction mixture was treated with dilute hydrochloric acid and worked up as usual. *The acid fraction was negligible.* From the neutral fraction 21.5 g. (61%) of III, m.p. 184–187°, was obtained by recrystallization from benzene-alcohol mixtures. The analytical sample, m.p. 186.0–187.0°, formed dense almost colorless prisms with a yellow tinge. In dilute solution an intense blue-violet fluorescence was noted. A similar intense fluorescence was also noted with dilute solutions of I and II, both of which have intense yellow colors in all but dilute solutions.

Anal. Calcd. for $C_{26}H_{26}O$: C, 88.1; H, 7.4. Found[9]: C, 87.7; H, 7.5.

Cyclic carbonate of 2,3-dihydroxy-1,4-diphenyl-1,4-epoxy-1,2,3,4-tetrahydronaphthalene, IV. A solution of 27.3 g. of 1,4-diphenyl-2,3-benzofuran, I, and 10.6 g. of vinylene carbonate[8] in 25 ml. of xylene was refluxed for 20 min. (most reaction complete after 5 min. as judged by disappearance of color). On cooling 34.7 g. of IV, m.p. 256–260° w. dec., was obtained. An additional amount was obtained from the filtrate so that the yield of IV was almost quantitative. Recrystallization from dimethylacetamide[11] afforded fine colorless needles, m.p. 259–261° w. dec. (fast rate of heating) of IV.

Anal. Calcd. for $C_{23}H_{16}O_4$: C, 77.5; H, 4.5. Found[9]: C, 77.7; H, 4.7.

When an equimolar mixture (small scale) of I and vinylene carbonate was heated at the m.p. of I (130–131°) for 1 min. complete decolorization took place and formation of IV was essentially quantitative. When a solution of 2.92 g. of I, and 1.12 g. of vinylene carbonate in 15 ml. of toluene was heated at reflux for 1 hour, an 87% yield of almost pure IV was obtained. In a similar experiment, except that 3.37 g. of II was substituted for I and the time of reflux was 5 hr., there was formed only a small amount of V (see below).

Cyclic carbonate of 2,3-dihydroxy-1-phenyl-4-mesityl-1,4-epoxy-1,2,3,4-tetrahydronaphthalene, V. A solution of 22.8 g. of 1-mesityl-4-phenyl-2,3-benzofuran, II, and 10.5 g. of vinylene carbonate[8] in 50 ml. of xylene was held at reflux for 19 hr. On cooling and diluting with benzene and petroleum ether (b.p. 00–00°) 23.3 g. (80%) of V was obtained as colorless prisms, m.p. 205–215° w. decomp. (slow heating). Recrystallization from benzene yielded an analytical sample, m.p. 219–220° w. dec. (fast heating) with little loss.

Anal. Calcd. for $C_{26}H_{22}O_4$: C, 78.4; H, 5.6. Found[9]: C, 78.5; H, 5.7.

Attempts to effect Diels-Alder reaction with 1,4-dimesityl-2,3-benzofuran, III. A solution of 1.67 g. of III and 1.36 g. of maleic anhydride in 10 ml. of dimethylacetamide, b.p. 161°, was held at reflux for 18 hr. The solution was dark at the end. In all 1.50 g. of pure III, m.p. 186–187°, was recovered from this mixture and no other crystalline product. Similarly, a solution of 1.77 g. of III and 1.2 g. of *N*-phenylmaleimide in 10 ml. of benzonitrile, b.p. 191°, was held at reflux for 21 hr. The mixture became dark but the only crystalline product isolated was 1.53 g. of pure III. In several similar attempts using vinylene carbonate, a less powerful dieneophile than maleic anhydride,[8] and several solvents (also without solvent) no trace of crystalline adduct was obtained and III was recovered in high yields.

o-(2-Isopropoxy-2-mesityl)toluic acid, XI. A solution of 19.2 g. of pseudo isopropyl phthaldehydate,[10] X, in 100 ml. of ether was added during 40 min. at 15–30° to the Grignard reagent prepared from 41.0 g. of bromomesitylene and 5.2 g. of magnesium[12] in 200 ml. of ether, using 1 g. of ethylene dibromide to start the reaction.[13] After the addition, the clear deep red-brown solution was held at reflux for 15 min., cooled, and treated with dilute hydrochloric acid. The products were separated into acid and neutral fractions as usual. By crystallization from benzene–petroleum ether there was isolated 17.7 g. (57%) of colorless XI, m.p. 184–186°, from the acid fraction. Recrystallization from benzene yielded pure XI, m.p. 186–187°, with little loss.

Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.9; H, 7.7. Found[9]: C, 77.1; H, 7.9.

The conversion of XI to VIII in almost quantitative yield by treatment with hydrobromic acid (see above under VIII) is evidence for the structure of XI. In addition, when a solution of 5.3 g. of XI and 1.0 g. of powdered copper (Venus-44) in 20 ml. of quinoline (Eastman-synthetic) was held at reflux for 20 min, there was isolated 3.75 g. of an almost colorless oil. Redistillation yielded 3.4 g. (75%) of a colorless oil, b.p. 169–170° at 7 mm., which was undoubtedly α-isopropoxy-α-mesityltoluene.

Anal. Calcd. for $C_{19}H_{24}O$: C, 85.0; H, 9.0. Found[9]; C, 84.8; H, 8.9.

When a Grignard reagent from 32. g. of bromomesitylene in 100 ml. of tetrahydrofuran was added to a solution of 30 g. of X in 100 ml. of tetrahydrofuran during 15 min. with cooling at 20–30° the color of the resulting clear solution was orange-yellow. After holding at reflux for 30 min. the mixture was worked up as usual. Only a small amount of acid fraction was obtained and this was not studied. By hydrolysis (aqueous-alcoholic sodium hydroxide) the neutral fraction was separated into 3-mesitylphthalide, VIII, (total yield, 28% pure) and 1,4-dimesityl-2,3-benzofuran, IIII, (total yield, 17% pure).

When solutions of the pseudo ester, X, in ether were added to solutions of mesitylmagnesium bromide in ether containing

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(10) D. D. Wheeler, D. C. Young, and D. S. Erley, *J. Org. Chem.*, **22**, 547 (1957).

(11) We thank the Du Pont Company for a generous gift of dimethylacetamide.

(12) We thank the Dow Chemical Company, Midland, Mich., for a generous gift of pure sublimed magnesium. In our experience Grignard reagents made with this magnesium are always lighter in color than those made with ordinary commercial magnesium turnings.

(13) D. E. Pearson, D. Cowan, and J. D. Beckler, *J. Org. Chem.*, **24**, 504 (1959).

only one equivalent of Grignard reagent or one equivalent and an extra equivalent of magnesium bromide (generated by addition of extra magnesium and ethylene dibromide in original Grignard preparation) the yields of pure XI were considerably less and more than one acid was produced. The nature of the other acid, or acids, has not been studied.

o-(α-Isopropoxy-α-phenyl)toluic acid. When the Grignard reagent from 32 g. of bromobenzene in 110 ml. of ether was added to a stirred solution of 19.2 g. of X in 100 ml. of benzene and 50 ml. of ether, a complex separated at first which later dissolved to yield a deep red-brown solution. After refluxing for 15 min. the reaction mixture was treated as usual. A mixture of products was obtained no one of which was isolated in good yield. From the acid fraction 3.0 g. of colorless crystals, of *o*-(α-isopropoxy-α-phenyl)toluic acid, m.p. 83.5–85.0°, was obtained. The structure was established by analysis, infrared spectrum, and the fact that on heating in acetic acid–hydrobromic acid for 2 hr. an 84% yield of 3-phenylphthalide, m.p. and mixed m.p. 115–116°, was obtained.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.5; H, 6.7. Found[8]: C, 75.8; H, 6.6.

Oxidation of benzofurans, I, II *and* III. When a mixture of equivalent weights of each of the furans I, II, and III and of pure lead tetraacetate in tetrahydrofuran was shaken, the furans went into solution. By suitable work-up of the reaction mixtures the pure *o*-diaroylbenzenes were obtained in over 80% yields. 1,2-Dibenzoylbenzene,[4] m.p. 146–147°, and 1,2-dimesitoylbenzene;[6] m.p. 232.5–234.0°, had the reported properties. 1-Benzoyl-2-mesitoylbenzene, m.p. 157.5–158.5°, a new compound, recrystallized as colorless prisms from benzene-ethanol.

Anal. Calcd. for $C_{23}H_{24}O_2$: C, 84.1; H, 6.1. Found[8]: C, 84.2; H, 6.0.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ISRAEL INSTITUTE OF TECHNOLOGY]

Polycyclic Studies. I. Synthesis of Triphenylenes Through Diels-Alder Adducts[1]

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The adducts obtained from the Diels-Alder addition of *p*-benzoquinones to bi(1-cyclohexen-1-yls) have been dehydrogenated over palladium-charcoal (30%) catalyst to form triphenylenes in satisfactory yields.

The interest in triphenylene (I) and its derivatives has been growing recently but few systematic studies of this type of compounds are available largely owing to difficulties in synthesis.[3] Recent work in these laboratories[4] suggested that the Diels-Alder addition of *p*-benzoquinone to bi(1-cyclohexen-1-yl) (II) might provide a simple method for building up the triphenylene nucleus. The addition of *p*-benzoquinone to II has been reported[5] to yield the adduct 1,4,5,6,7,8,9,10,11,12,13,16,17,18-tetradecahydrotriphenylene - 1,4 - dione[6] (IIIa) in low yields and it has been claimed[7] that four forms of a bis-adduct have been separated. There have been no reports, however, of the attempted transformation of adduct III into triphenylene. The successful results of this latter transformation form the subject of this paper and are summarized in chart 1.

The pinacols (IV) were obtained by slightly modifying the method reported[5] for the synthesis of IVa. Dehydration of the pinacols was carried out with phosphorus oxychloride in pyridine.[4a] These reaction conditions afforded reasonably high yields (> 75%) of the desired bicyclohexenyls II. Tables I and II summarize the data for the pinacols and bicyclohexenyls which have been prepared.

All our attempts failed to repeat the reported[5] preparation of adduct IIIa by treating *p*-benzoquinone and bi(1-cyclohexen-1-yl) in ethanol solution. Instead of IIIa we isolated in 17% yield the oxidized adduct Va. On the reasonable assumption that part of the quinone was used up in oxidizing the initially formed adduct IIIa, excess quinone was introduced in the above reaction with the result that the yield of the oxidized product Va was nearly doubled. Similar results were obtained in the reaction between *p*-toluquinone and bicyclohexenyls except in the case of bi(3,5-dimethyl-1-cyclohexen-1-yl) (IIe) which formed the normal adduct IIIe even when excess quinone was used. It seems reasonable to infer that the steric hindrance of the methyl groups in positions 5 and 12 prevents the removal of the hydrogens at positions 17 and 18.

By eliminating the use of solvent in the Diels-Alder reaction and using equimolar quantities of *p*-benzoquinone and bi(1-cyclohexen-1-yl) the normal adduct IIIa was obtained in 62% yield.

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(1) Taken from the Thesis submitted by A. Mandelbaum to the Senate of the Technion-Israel Institute of Technology, in partial fulfillment of the Degree of Master of Science, July 1960.

(2) American Chemical Society-Petroleum Research Fund Fellow, 1959–1960.

(3) For an excellent review of triphenylenes see C. M. Buess and D. D. Lawson, *Chem. Revs.*, **60**, 313 (1960).

(4) (a) D. S. Greidinger and D. Ginsburg, *J. Org. Chem.*, **22**, 1406 (1957); (b) Y. Strumza and D. Ginsburg, Abstracts Colloque International de Chimie Organique, Montpellier, September 1959; (c) Y. Altman and D. Ginsburg, *J. Chem. Soc.*, 466 (1959).

(5) E. B. Barnett and C. A. Lawrence, *J. Chem. Soc.*, 1104 (1935).

(6) The numbering of the triphenylene ring used in this article is the same as the one used in the recent review (ref. 3).

(7) H. J. Backer, J. Strating, and L. H. H. Huisman, *Rec. Trav. Chim.*, **58**, 761 (1939).