N-Methyl-2-(3′,4′,5′-trimethoxyphenyl)maleimide.—To a well stirred suspension of 2.8 g. (0.01 mole) of 2-(3′,4′,5′-trimethoxyphenyl)maleimide in 75 ml. of freshly distilled tetrahydrofuran (from lithium aluminum hydride), was added 0.24 g. (0.01 mole) of sodium hydride (from 0.45 g. of a 54.7% oil dispersion). There was an immediate evolution of hydrogen which continued briskly as the mixture was brought to reflux. A solution of 7 g. (0.05 mole) of methyl iodide in 10 ml. of tetrahydrofuran was then added to the yellow, boiling, mixture over a 45-min. period, and heating was continued for another 1.75 hr. At the end of this time, the reaction mixture was a dark green color and was neutral to indicator paper. The solvent was distilled at reduced pressure and the residue was dissolved in 75 ml. of chloroform. The chloroform solution was washed twice with water, dried ($MgSO_4$), and evaporated to give 3.1 g. of a deep orange solid. Crystallization from a large volume of hot absolute alcohol in which the material was sparingly soluble (or, from a mixture of ethyl acetate and petroleum ether (b.p. 65–90°)) gave 2 g. (71%) of orange, matted needles, m.p. 155–156°. The ultraviolet spectrum showed λ_{max} 235 (ϵ 13,600), 297 (ϵ 700), and 373 mμ (ϵ 3900).

Anal. Calcd. for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.74; H, 5.71; N, 4.86.

N,5-Dimethyl-3-phenyl-1-pyrazoline-3,4-dicarboximide.—To an ice-cold solution of 8.9 g. (0.048 mole) of N-methyl-2-phenylmaleimide in 150 ml. of methylene chloride was added in one lot a cold, dried (over potassium hydroxide pellets) solution of 0.054 mole of diazoethane in ether.[9] The discharge of the orange-red color was immediate and the final solution retained only a pale yellow color. Evaporation of the solvent and the slight excess of diazoethane gave 11.6 g. (100%) of the crystalline pyrazoline, m.p. 78–85° dec. A sample was purified further by recrystallization from a mixture of methylene chloride and petroleum ether (b.p. 30–60°), giving colorless needles, m.p. 106–107° dec.

Anal. Calcd. for $C_{13}H_{13}N_3O_2$: C, 64.18; H, 5.39; N, 17.28. Found: C, 64.74; H, 5.49; N, 17.43.

N-Methyl-2-ethyl-3-phenylmaleimide.—A 5.1-g. (0.02 mole) sample of the crude pyrazoline (m.p. 78–85° dec.) obtained as described was dissolved in 50 ml. of alcohol and heated on a steam bath for 30 min. There ensued an immediate and rapid evolution of nitrogen. The alcohol was removed by distillation *in vacuo* to give 4.4 g. (100%) of a viscous, colorless oil. This material was subjected to partition chromatography in which the system, *n*-heptane–Methyl Cellosolve, was used. This procedure led to the separation of a major and a minor component. The desired N-methyl-2-ethyl-3-phenylmaleimide was the minor and faster moving component. It was obtained by the evaporation of the solvent in the first peak to give 200 mg. (5%) of solid. Two recrystallizations from aqueous alcohol gave large rhombs, m.p. 69–70°. This compound gave positive tests for unsaturation with bromine in carbon tetrachloride and with potassium permanganate in acetone. The ultraviolet spectrum showed λ_{max} 225 (ϵ 13,500), 260 (ϵ 6000), and 331 mμ (ϵ 1500).

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.69; H, 5.74; N, 6.37.

The second and slower moving component, obtained as a colorless, viscous oil, was the main product. This was the expected, N,3-dimethyl-1-phenyl-1,2-cyclopropanedicarboximide. The yield was 4.0 g. (93%).[10] This substance could not be crystallized from solvents, even after an evaporative distillation. It did, however, solidify in part after many days at room temperature. The ultraviolet spectrum showed λ_{max} 255 (ϵ 860) as the only band above 220 mμ. The infrared spectrum showed the characteristic succinimide doublet at 5.62 and 5.82 μ.[2]

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.57; H, 6.42; N, 6.25.

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[9] This was prepared from 11.7 g. (0.10 mole) of moist nitrosoethylurea by a procedure analogous to that used for diazomethane (F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

[10] The details of this and other associated work will appear in a future publication.

A Convenient Synthesis of 1,2,5,6-Dibenzocyclooctatetraene[1]

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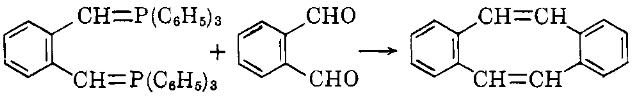
The Wittig reaction has been applied in several instances for the preparation of cyclic olefins containing five to sixteen carbon atoms and offers a number of advantages over conventional synthetic procedures particularly in the case of larger rings[3]; however, in each of the reported examples, the products have either possessed the *trans* stereochemistry favored by Wittig processes[4] or have been flexible ring systems. In order to determine the limits of applicability of this cyclization procedure, it was of interest to examine a case in which the product was a rigid ring system possessing unfavorable stereochemistry. The model compound chosen for this study was the well characterized 1,2,5,6-dibenzocyclooctatetraene (I),[5–8] for which molecular models indicate a highly rigid *cis* structure,[3a] existing in a tub conformation and incapable of equilibration to a *trans* isomer. The projected synthetic scheme is a simple modification of well established methods,[3a,d] and involves the reaction of the bisylide (II) with *o*-phthaldehyde (III) to form the product (I). The bisylide (II) is readily prepared from *o*-xylylenebis-(triphenylphosphonium bromide) (IV) by the action of base.[3d]



II III I

The reaction of III and IV was first attempted under standard Wittig conditions, *i.e.*, in absolute ethanol employing sodium ethoxide as the base for the generation of the ylide (II).[3d] However, in no instance could I be isolated from reactions carried out under these conditions and the presence of only trace amounts was indicated spectrally; only triphenylphospine oxide, III, and polymeric materials were isolated. Since the Wittig reaction under these conditions leads normally to *trans* olefins,[3d,4] it is probably that the reaction of II and III produces initially *trans*-V, which predominantly undergoes intermolecular reaction to form polymer rather than intramolecular ring closure

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[1] Supported in part by a grant (G-11280) from the National Science Foundation.

[2] National Science Foundation Undergraduate Research Participant, Summer, 1962.

[3] (a) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958); (b) K. Dimroth and G. Pohl, *Angew. Chem.*, **73**, 436 (1961); (c) T. I. Bieber and E. H. Eisman, *J. Org. Chem.*, **27**, 678 (1962); (d) C. E. Griffin, K. R. Martin, and B. E. Douglas, *ibid.*, **27**, 1627 (1962); (e) C. E. Griffin and G. Witschard, *ibid.*, **27**, 3334 (1962).

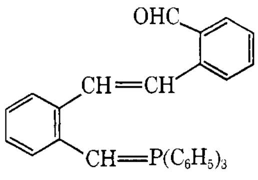
[4] U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

[5] L. F. Fieser and M. M. Pechet, *J. Am. Chem. Soc.*, **68**, 2577 (1946).

[6] A. C. Cope and S. W. Fenton, *ibid.*, **73**, 1668 (1951).

[7] (a) G. Wittig, H. Tenhaeff, W. Schoch, and G. Koenig, *Ann.*, **572**, 1 (1951); (b) G. Wittig, G. Koenig, and K. Clauss, *ibid.*, **593**, 127 (1955).

[8] M. Avram, D. Dinu, G. Matescu, and C. D. Nenitzescu, *Chem. Ber.*, **93**, 1789 (1960).



V

to I; the latter process would require *cis* stereochemistry in V.

Recently Shemyakin has shown that the Wittig reaction can be modified to favor the formation of *cis* isomers by conducting the reaction in the presence of a Lewis base and reported that the best results were obtained with lithium bromide or iodide in dimethylformamide.[9] Partial neutralization of the charge on the ylide phosphorus by interaction with the base is postulated as leading to a lessening of the importance of initial ylide–carbonyl dipolar interaction as a determinant in product stereochemistry. Since both of the double bonds to be formed in I are required to be *cis*, the reaction of III and IV was attempted employing conditions similar to those reported by Shemyakin, *i.e.*, the slow addition of a solution of lithium ethoxide in absolute ethanol to a dilute solution of III and IV in dimethylformamide. In this instance, the desired product (I) was isolated from the reaction mixture in 18% yield; since IV can be prepared in 86–89% yield from *o*-xylylene dibromide, an over-all yield of 15–16% of I can be obtained in a two-step process. This yield is comparable to those obtained in the reported four- to five-step procedures.[5–7a]

The successful formation of I by a Wittig procedure indicates that the only probable limitation to effective Wittig cyclization is ring size; the only failures reported to date are in the attempted syntheses of cyclopropenes[3e] and cyclobutenes.[10]

The infrared spectra of samples of I prepared in this study are identical in all respects to the spectrum reported by Wittig[7b] and totally different from that reported earlier by Cope.[6] One of the most prominent features of the spectrum reported by Cope is an intense band at 11.0 μ which is absent in the spectra obtained by Wittig and the present investigators. The ultraviolet spectrum of I shows a single band without fine structure at 239 mμ (ϵ 28,900); Wittig has reported a band at the same wave length of somewhat higher intensity (ϵ 48,000). McEwen and Longuet-Higgins[11] have carried out an LCAO calculation of the electronic transition energies of I; the observed band for I probably corresponds to the calculated $A_1 \rightarrow B_1$ transition at 230 mμ. Because of its high intensity and lack of fine structure, the observed band probably is not related to the calculated forbidden $A_1 \rightarrow A_2$ transition at 239 mμ.

Experimental[12]

***o*-Xylylenebis-(triphenylphosphonium bromide)** (IV) was prepared in 86.5% yield by the reported method.[3d] In the original preparation, IV was reported to have m.p. >340°; however, in subsequent preparations, material decomposing as low as 295° was obtained. The lower melting material was satisfactory in all respects; examination of the infrared spectra of these preparations indicates the melting point depression to be caused by the presence of a trace amount of the monophosphonium salt.[3d]

1,2,5,6-Dibenzocyclooctatetraene (I).—A mixture of 18.1 g. (0.023 mole) of IV and 3.0 g. (0.022 mole) of *o*-phthaldehyde in 400 ml. of dry dimethylformamide (distilled from calcium hydride) was heated to 90° under an atmosphere of dry nitrogen. A solution of 0.059 mole of lithium ethoxide in 100 ml. of absolute ethanol was added to this reaction mixture with rapid stirring over a period of 5 hr. Addition of the basic solution gave a deep orange solution and this color persisted for 4.5 hr. After the addition was completed, the dark reaction mixture was allowed to cool and was diluted with 500 ml. of water. The precipitated material was extracted with ether and the ethereal extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated to give a dark brown oil. This oil was extracted with boiling petroleum ether (60–70°) to effect separation from triphenylphosphine oxide; evaporation of the petroleum ether extracts gave 5.8 g. of a red oil which was chromatographed on a Florisil column (1.25 × 90 cm.). Elution with 1.4 l. of petroleum ether (30–65°) gave 1.8 g. of a pale yellow crystalline solid which was rechromatographed on Florisil (1.25 × 45 cm. column). Twenty-four 10-ml. fractions were collected by elution with petroleum ether (30–65°). Fraction 1 was an oily mixture which failed to crystallize, but fractions 2–24 gave 1.5 g. of a colorless crystalline product on evaporation of solvent; this product was recrystallized from aqueous ethanol to give 0.8 g. (18%) of I, m.p. 109.2–109.4° (lit. m.p. 108.5–109.2°,[7a] 109°,[8] 106.8–108.1°,[5] 106.2–106.9°[6]).

Anal. Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 94.17, 94.11; H 5.80, 5.93.

The ultraviolet spectrum of I in 95% ethanol showed a maximum at 239 mμ (ϵ 28,900). The infrared spectrum was recorded in carbon tetrachloride and acetonitrile and showed bands at the following wave lengths (μ): 3.27 s, 3.32 s, 6.09 w, 6.73 s, 7.01 m, 7.17 m, 8.68 m, 8.97 w, 9.20 m, 9.65 m, 10.42 w, 10.60 m, 11.52 w, 11.98 s, 12.85 vs, 13.42 s, 14.31 s, 14.45 s, 14.87 w.

Treatment of a methanolic solution of I with saturated aqueous silver nitrate gave a colorless precipitate which was recrystallized from ethanol to give the **silver nitrate complex of I**, m.p. 221–222° (lit. m.p. 222°,[9] 214–215°[3a]).

The reaction of *o*-phthaldehyde and IV in refluxing absolute ethanol for 5 hr. employing sodium ethoxide as base was carried out in a manner analogous to the previous experiment. Careful chromatography of the products led to the isolation of triphenylphosphine oxide and the dialdehyde as the only characterizable materials; examination of the infrared spectra of all fractions showed the presence of only trace amounts of I. When the reaction was carried out for a longer period of time (22 hr.), the major portion of the organic material isolated was polymeric in nature, showing aromatic and both *cis* and *trans* olefinic absorptions in the infrared.

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[9] M. M. Shemyakin, L. D. Bergelson, and V. A. Vaver, IUPAC International Symposium on Organic Chemistry of Natural Products, Brussels, June 12–15, 1962.

[10] G. Witschard and C. E. Griffin, unpublished results; T. I. Bieber, private communication.

[11] K. L. McEwen and H. C. Longuet-Higgins, *J. Chem. Phys.*, **24**, 771 (1956).

[12] Micronalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Synthesis of 7-Methyl- and 7-Phenylnorbornadiene

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The synthesis of norbornadiene is a relatively straightforward procedure involving the Diels–Alder condensation of cyclopentadiene and acetylene.[1] However, 7-substituted norbornadienes generally are not available by this simple route because the corresponding 5-substituted cyclopentadienes are unstable relative to

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[1] J. Hyman, E. Freireich, and R. E. Lidov, U. S. Patent 2,875,256; *Chem. Abstr.*, **53**, 13082 (1959).