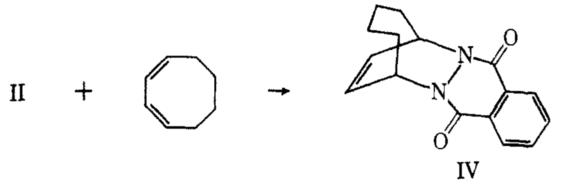
The structure of the adduct III follows directly from the elemental composition, molecular weight (mass spectrometric), and spectroscopic properties. The infrared spectrum shows the amide carbonyl groups as an intense band at 1635 cm^{-1}. The nmr spectrum (Figure 1) shows the expected eight aromatic protons and four others which must comprise a $\overset{|}{C}H\overset{|}{C}HCH_2$ group. This arrangement was confirmed by double-resonance experiments which showed that the methylene protons are coupled to each other (J_{AB} = 18 cps) and to the multiplet at δ 5.78 but not to the doublet at δ 6.32. The nmr spectrum is consistent only with structure III and is not consistent with an isoindene adduct I (R = H; R′, R′ = o-C_6H_4).

Under similar conditions phenanthrene gave in low yield a crystalline 1:1 adduct which we believe is analogous to III. Addition presumably involves the 9,10 bond. Styrene and furan gave amorphous products which were not characterized. Cyclooctatetraene, acenaphthene, and 2-cyclohexenone did not appear to react.

The 1,2-cycloaddition of phthalazine-1,4-dione to indene prompted us to look briefly at other systems where 1,4-cycloaddition is unfavorable. Diels–Alder adducts of 1,3-cyclooctadiene have not been reported to the best of our knowledge. Maleic anhydride and 1,3-cyclooctadiene, for example, give a 1:1 copolymer at room temperature[6] and on refluxing for 1 week in o-dichlorobenzene give an intractable tar.[7] Generation of phthalazine-1,4-dione in the presence of 1,3-cyclooctadiene gives a crystalline 1:1 adduct (60% mp 200–202°). The nmr spectrum of the adduct shows two equivalent olefinic protons as a multiplet at δ 6.22 and two equivalent bridgehead protons as a multiplet at δ 5.82 in addition to the A_2B_2 pattern (δ 8.36 and 7.78) and the eight methylene protons (δ 2.64–1.42). The equivalent bridgehead and olefinic protons are uniquely consistent with the 1,4-adduct structure IV. This is the first reported Diels–Alder adduct of 1,3-cyclooctadiene, and its formation at ice-bath temperatures emphasizes the potent dienophilic character of phthalazine-1,4-dione.



IV

Experimental Section[8]

Phthalazine-1,4-dione Adducts. A. With Indene.—To an ice-cooled, stirred mixture of 1.16 g (0.010 mole) of indene and 1.62 g (0.010 mole) of phthalhydrazide in 50 ml of methylene chloride was added in one portion 4.43 g (0.010 mole) of lead tetracetate. The resulting brown mixture was stirred in an ice bath for 3 hr and then at room temperature for an additional 3 hr. The mixture was filtered, and the solid was washed with methylene chloride. The filtrate and washings were combined and washed successively with 25-ml portions of water, 2% sodium hydroxide, 5% nitric acid, and water and dried over magnesium sulfate. After removal of the solvent on a rotary evaporator, the pale yellow residue was recrystallized from chloroform–hexane to provide 1.60 g (58%) of III as white needles, mp 256–258° dec.

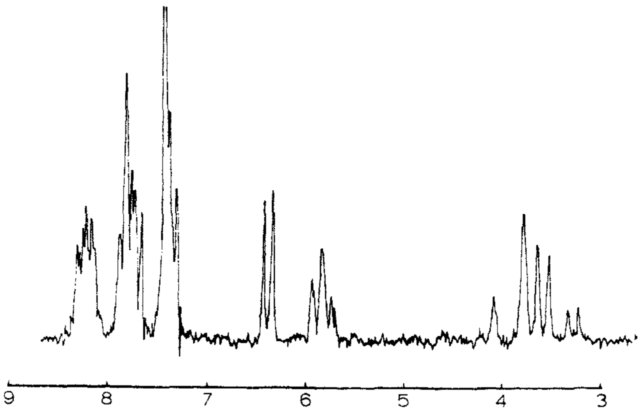


Figure 1.—Nuclear magnetic resonance spectrum of indene phthazine-1,4-dione adduct (III) in deuteriochloroform. The chemical shift scale (δ) is calibrated in parts per million downfield from internal tetramethylsilane.

Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14; mol wt, 276. Found: C, 73.82; H, 4.53; N, 9.90; mol wt, 276 (mass spectrum).

B. With 1,3-Cyclooctadiene.—The procedure described in A above afforded from 1.08 g (0.010 mole) of 1,3-cyclooctadiene, 2.68 g (76%) of crude IV. Recrystallization from a small volume of ethanol provided 1.61 g (60%) of white blocks, mp 200–202°. Repeated recrystallization from ethanol yielded the analytical sample as rhombs, mp 208–210°.

Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44; mol wt, 268. Found: C, 71.53; H, 5.99; N, 10.68; mol wt, 268 (mass spectrum).

C. With Phenanthrene.—Procedure A afforded from 1.78 g (0.010 mole) of purified phenanthrene, 0.18 g (5.3%) of white needles, mp 308–310° after recrystallization from small volumes of toluene. The preparation was repeated several times but without a substantial increase in yield. Several recrystallizations from toluene provided an analytical sample, mp 314–315°.

Anal. Calcd for $C_{22}H_{14}N_2O_2$: C, 78.09; H, 4.17; N, 8.28; mol wt, 338. Found: C, 77.93; H, 4.30; N, 8.19; mol wt, 338 (mass spectrum).

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[6] A. C. Cope and L. L. Estes, Jr., *J. Am. Chem. Soc.*, **72**, 1128 (1959).

[7] S. J. Dominianni, unpublished observation.

[8] Melting points were taken on a micro hot stage and are uncorrected. Elemental analyses were performed by Spang Laboratories, Ann Arbor, Mich.

Dehydration of 1-Methylene-*trans*-2,3-bis-(diphenylhydroxymethyl)cyclopropane[1]

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Received May 9, 1966

Acid-catalyzed dehydrations of cycloalkyldiphenylcarbinols can follow different paths depending upon the structure of the cycloalkane moiety. For example, cyclobutanediphenylcarbinol (1) gives, under a variety of dehydration conditions, diphenylmethylenecyclobutane in good yield.[2] Dehydration of the substituted cyclopropane[3] and cyclopropene[4] alcohols 2 and 3 affords rearranged products rather than the corresponding exocyclic olefins.

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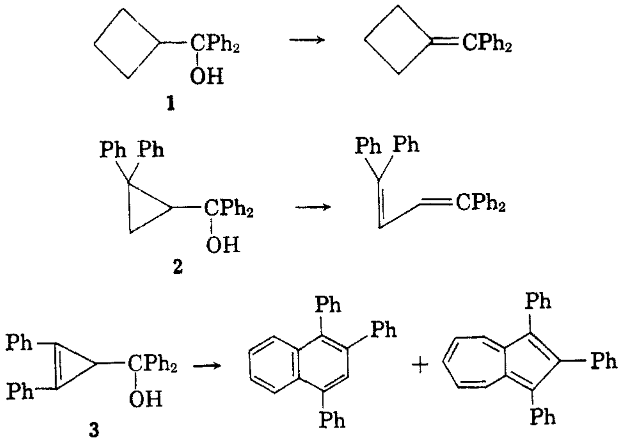
[1] This paper represents part of a thesis submitted by R. R. Doyle to the Rackham School of Graduate Studies, University of Michigan, in partial fulfillment of the requirements for the Ph.D. degree, 1965.

[2] S. H. Graham and A. J. S. Williams, *J. Chem. Soc.*, 4066 (1959).

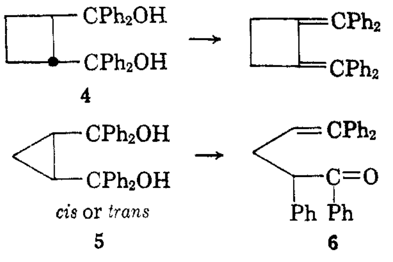
[3] H. M. Walborsky and F. M. Hornyak, *J. Am. Chem. Soc.*, **77**, 6396 (1955).

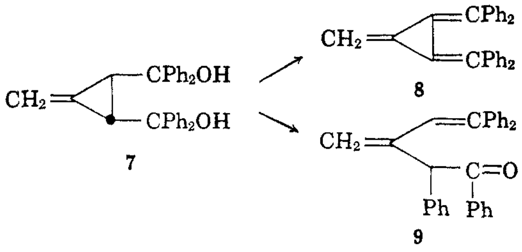
[4] R. Breslow and M. Battiste, *ibid.*, **82**, 3626 (1960).



In the related ditertiary alcohol series, *trans*-1,2-bis(diphenylhydroxymethyl)cyclobutane (**4**) upon dehydration gives 1,2-bis(diphenylmethylene)cyclobutane in 70% yield.[5] In contrast, the corresponding *trans*-[6] and *cis*-cyclopropane[7] ditertiary alcohols **5** undergo pinacol-like rearrangements to give the unsaturated ketone **6**.

In light of the above results it was of interest to examine the effect of the exocyclic double bond on the acid-catalyzed dehydration of the ditertiary alcohol **7**. Dehydration could conceivably occur in a normal fashion to afford the resonance-stabilized[8] trimethylenecyclopropane derivative **8**. Alternatively, should the exocyclic double bond exert no influence on the course of the reaction, the pinacol product **9** would be anticipated.





Accordingly, diol **7**, prepared in 11% yield from the reaction of phenylmagnesium bromide with the diethyl ester of Feist's acid (*trans*-1-methylenecyclopropane-2,3-dicarboxylic acid), was subjected to several dehydration conditions. Treatment of **7** with either iodine in refluxing xylene or iodine in benzene at room temperature gave a brown, tarry residue from which no crystalline material could be obtained. The infrared spectrum of the residue lacked hydroxyl absorption and displayed a carbonyl band at 1690 cm^{-1}. When **7** was treated with hot glacial acetic acid for a short peroid of time a crystalline solid, mp 115–117°, was obtained in high yield. The infrared spectrum of this material shows strong carbonyl absorption at 1685 cm^{-1} and is essentially identical with those of the residues obtained from the iodine-catalyzed dehydrations. Combustion analysis of the product revealed that only 1 equiv of water had been lost in the dehydration. This fact, together with the infrared data, suggested that the reaction **7** → **9** had indeed taken place. Structure **9** for the reaction product was confirmed by ultraviolet and nuclear magnetic resonance characterization and by oxidative degradation.

The ultraviolet spectrum of the product in 95% ethanol has $\lambda_{\max}$ 241 mμ (log ε 4.36) and 273 mμ (log ε 4.20). This compares well with the summation spectrum of a solution equimolar in the model chromophores 1,1-diphenyl-1,3-butadiene[9] and deoxybenzoin, $\lambda_{\max}$ 239 mμ (log ε 4.41) and 284 mμ (log ε 4.36). The proton magnetic resonance spectrum is consistent with structure **9**. The aromatic protons are separated into two distinct groups of peaks centered at τ 2.23 and 2.79 with relative peak areas of 2 to 18, respectively. By comparison with the spectrum of acetophenone,[10] the multiplicity at τ 2.23 is assigned to the *ortho* protons of the benzoyl group and the peaks at τ 2.79 to the remainder of the aromatic protons. In addition, the spectrum displays four broadened singlets, each corresponding to one proton, at τ 3.28, 4.63, 4.79, and 5.11. Finally, chemical evidence consistent with structure **9** was obtained by oxidation of the dehydration product with potassium permanganate in pyridine. Isolation of benzophenone (75%), as its 2,4-dinitrophenylhydrazone, supports the presence of the diphenylmethylene moiety. Benzoic acid, obtained in low yield, indicates phenyl migration in the dehydration reaction.

Under the reaction conditions described, acid-catalyzed dehydration of the dietertiary alcohol **7** affords not the trimethylenecyclopropane[11] **8** but the rearranged product **9**.

Experimental Section[12]

Diethyl 1-Methylenecyclopropane-*trans*-2,3-dicarboxylate (Feist's Ester).—Esterification of 85.3 g (0.601 mole) of Feist's acid[13] by the azeotropic distillation procedure[14] afforded 89.8 g (75.5%) of Feist's ester, mp 38.5–40.0° (lit.[15] mp 38–39°).

1-Methylene-*trans*-2,3-bis(diphenylhydroxymethyl)cyclopropane (7).—A solution of phenylmagnesium bromide was prepared, under nitrogen, from 11 g (0.45 g-atom) of magnesium turnings and 71 g (0.45 mole) of purified bromobenzene in 400 ml of anhydrous ether. The phenylmagnesium bromide solution was added, in the inverse manner, to 19.8 g (0.100 mole) of freshly distilled Feist's ester in 225 ml of ether. The flask containing

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(5) K. B. Alberman and F. B. Kipping, *J. Chem. Soc.*, 779 (1951).

(6) R. A. Darby and R. E. Lutz, *J. Org. Chem.*, **22**, 1353 (1957).

(7) T. Shono, A. Oku, T. Morikawa, M. Kimura, and R. Oda, *J. Chem. Soc. Japan*, **38**, 940 (1965).

(8) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

(9) G. R. Husk, Ph.D. Thesis, University of Michigan, 1964. We are indebted to Dr. Husk for a sample of this compound.

(10) "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962.

(11) For recent syntheses of trimethylenecyclopropanes, see G. Köbrich and H. Heinemann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 594 (1965); E. A. Dorko, *J. Am. Chem. Soc.*, **87**, 5518 (1965); P. A. Waitkus, L. I. Peterson, and G. W. Griffin, *ibid.*, **88**, 181 (1966).

(12) All melting points are uncorrected. The infrared spectra were obtained with a Perkin-Elmer spectrophotometer, Model 21; ultraviolet spectra were measured with a Cary spectrophotometer, Model 11; nmr spectra were obtained with a Varian A-60 instrument and tetramethylsilane as internal reference. We are indebted to Mr. B. E. Wenzel for much of the spectral work.

(13) A. T. Blomquist and D. T. Longone, *J. Am. Chem. Soc.*, **81**, 2012 (1959).

(14) A. H. Blatt, Ed., "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 264.

(15) F. R. Goss, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, **123**, 327 (1923).

the ester solution was cooled with ice during addition of the Grignard solution. During the early stages of the reaction, addition of the Grignard proceeded smoothly with formation of a yellow suspension. Toward the end of the addition the suspended solid coagulated to form a tough, sticky lump which stopped the stirrer. The reaction mixture was hydrolyzed immediately with saturated aqueous ammonium chloride. The ammonium chloride solution was added slowly until the inorganic salts settled out to leave a clear brown ether solution. The sticky lump had dissolved during the hydrolysis. The clear ether solution was decanted through a filter and stored over anhydrous calcium sulfate. The precipitated salts were placed in a Soxhlet thimble and extracted with fresh ether. The combined ether solution and extract was filtered and the ether was displaced by simultaneous distillation of ether and addition of *n*-heptane. Cooling of the heptane solution afforded a white, crystalline precipitate accompanied by a red tar which solidified to a gum. The white solid was separated from the gum by decantation as a slurry. The heptane slurry was chilled overnight and filtered to give 6.9 g of crude product. Recrystallization from ethanol gave 4.7 g (11%) of diol **7**, mp 156–159°. A second recrystallization from *n*-heptane gave 3.9 g of white solid, mp 158–160°.[16]

The nmr spectrum of the diol has a multiplet centered at *ca.* τ 2.8 (aromatic), a triplet at 4.46 (J = 2.2 cps, exomethylene), a triplet at 7.51 (J = 2.2 cps, cyclopropyl), and a singlet at 8.12 (hydroxyl) in the correct ratio of integrated peak areas. The hydroxyl proton assignment was confirmed by deuterium exchange. In addition to the expected aromatic bands the infrared spectrum is characterized by absorptions at 3560 (hydroxyl and 890 cm^{-1} (*exo*-methylene).

Anal. Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 86.30; H, 6.30.

Reaction of Diol 7 with Glacial Acetic Acid.—In a preliminary test, 201 mg (0.480 mmole) of diol **7** was stirred for 50 min with 10 ml of glacial acetic acid at room temperature under a nitrogen atmosphere. The diol dissolved completely in the acetic acid. Quenching the reaction mixture with 30 ml of water caused a white solid to separate. The aqueous mixture was extracted with ether, and the ether extracts were washed with 10% sodium bicarbonate, dried, and evaporated to give a white solid. The infrared spectrum of the white solid is identical with that of the starting diol which indicates that the alcohol is stable under these conditions.

In another experiment, 200 mg (0.478 mmole) of diol **7** was dissolved in 10 ml of glacial acetic acid under a nitrogen atmosphere. The solution was brought rapidly to a boil, using a flame, and refluxed for 2 min. The reaction mixture was cooled and then quenched with 30 ml of water which caused a white, sticky precipitate to settle out. The reaction mixture was neutralized with sodium bicarbonate solution and extracted with ether containing a pinch of phenothiazine as a polymerization inhibitor. The ether extracts were washed with water, dried over sodium sulfate–magnesium sulfate, and evaporated under reduced pressure to give a pale yellow oil. The oil was dissolved in hot heptane and chilled to give white crystals, mp 109–111°. Recrystallization from heptane gave white crystals, mp 115–118°. The infrared spectrum (Nujol) of the product, in addition to the expected aromatic bands, is characterized by peaks at 1685 (PhCO), 1635 (conjugated C═C), and 910 cm^{-1} (CH_2═). The ultraviolet and nmr ($CDCl_3$) spectra are described in the discussion section.

In a larger scale reaction, 4.0 g (9.6 mmoles) of diol **7** was treated as above in 100 ml of acetic acid to give 2.8 g (73%) of the dehydration product, mp 115–117.5°. The structure of the dehydration product was shown, as described in the discussion section, to be 1,1,4,5-tetraphenyl-3-methylene-5-ketopentene-1 (**9**).

Anal. Calcd for $C_{30}H_{24}O$: C, 89.96; H, 6.04. Found: C, 89.99; H, 6.30.

Oxidative Degradation of Dehydration Product 9.—Using the procedure of Bass,[17] 0.5 g of dehydration product **9** was dissolved in 10 ml of pyridine, diluted with 3 ml of water, and heated to reflux. Solid potassium permanganate was added slowly in weighed, 0.2-g portions until the violet color of permanganate persisted. It was necessary to add 1.6 g of permanganate (theoretical, 1.45 g). The condenser sides were washed down periodically with a 10:3 pyridine–water mixture. The reaction mixture was refluxed for 1 hr after addition of permanganate was complete. The reaction mixture was then steam distilled until the distillate came over clear and gave a neutral reaction to litmus. The distillate was acidified with concentrated HCl and steam distilled again until the distillate came over clear. The second distillate was extracted with ether and the ether extracts were dried and evaporated to give 171 mg (75.0%) of impure benzophenone. Treatment with 2,4-dinitrophenylhydrazine reagent in ethanol afforded orange crystals which, after three recrystallizations from ethanol–ethyl acetate, had mp 246.5–249.0° (microhot stage). The melting point was not depressed on admixture with authentic benzophenone-2,4-dinitrophenylhydrazone.

The original reaction mixture, after the first steam distillation, was filtered from MnO_2 and the hot, yellow filtrate was acidified with concentrated HCl. After treatment with Norit, the acidified filtrate was extracted with ether. The ether extract was dried and evaporated to give 9.7 mg (3.2%) of impure benzoic acid. Vacuum sublimation afforded a white solid, mp 117.5–122.0°. The infrared spectrum of the white solid is superimposable upon that of authentic benzoic acid.

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[16] The synthesis of this compound, mp 157–157.5°, was reported during the course of this work: D. J. Connolly, Ph.D. Thesis, Cornell University, 1962. Connolly attempted the dehydration of the diol under a variety of conditions but was unable to characterize products.

[17] R. G. Bass, Ph.D. Thesis, University of Virginia, 1961.

Thermal Rearrangement of 1,1-Dibromo-*cis*-2,3-dimethylcyclopropane

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Received March 22, 1966

Numerous studies on the gas phase rearrangement of cyclopropane to propylene, for which a diradical forming process seems currently favored, show the reaction requires an Arrhenius activation energy of about 65 kcal/mole with an unsurprisingly large frequency factor of 10^{15}.[1] Saturated alkyl groups on the cyclopropane ring appear to have little effect on the activation parameters; *e.g.*, four methyl substituents lower the activation energy by less than 5 kcal/mole and affect the frequency factor negligibly.[2]

That the cyclopropane system is not generally indifferent to substituent effects, however, is apparent from the work of Ellis and Frey[3] on the rearrangement of *cis*-1-methyl-2-vinylcyclopropane to *cis*-1,4-hexadiene. From the product geometry, low activation energy (31.2 kcal/mole) and negative activation entropy (−11.8 eu/mole), these workers suggested a cyclic transition state for this reaction. In addition, DeSelms and Combs,[4] who have shown a large but seemingly erratic solvent dependence of the rate for the kinetically first-order rearrangement of 3,3-dichloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane to 3,4-dichlorobicyclo[3.2.1]oct-2-ene, present data for this reaction in carbon tetrachloride from which we were able to calculate E_a and ΔS^* values of 22 kcal/mole and −7.4 eu/mole.

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[1] D. W. Setser and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **86**, 569 (1964), and references cited therein.

[2] M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.* (London), **A260**, 424 (1961); M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 1157 (1962); H. M. Frey and D. C. Marshall, *ibid.*, 3052 (1962).

[3] R. J. Ellis and H. M. Frey, *Proc. Chem. Soc.*, 221 (1964).

[4] R. C. DeSelms and C. M. Combs, *J. Org. Chem.*, **28**, 2206 (1963).