A heterogeneous suspension of 13.7 g of IV in water containing calcium carbonate[9] was refluxed for 2 hr to yield 9.0 g of liquid, bp 75–84° (1.5 mm), after a suitable work-up. Analysis by glpc showed this liquid to consist of about 64% of I and 36% of IV. The 2,4-dinitrophenylhydrazone of I, mp 197–199° dec, was prepared from the mixture and shown to be identical with that formed from pure I.[10]

4-Phenyl-3-butyn-2-one (II).—This compound,[11] bp 66–68° (1 mm), was prepared in 30% yield from phenylethynylmagnesium bromide and acetic anhydride[12] in one experiment at −78°.

2-Chloro-4-phenyl-1-buten-3-yne (V) and 3,3-Dichloro-1-phenyl-1-butyne (VI).—A mixture containing 29.2 g of PCl_5 and 18.7 g of II in 150 ml of CH_2Cl_2 was stirred at room temperature for 20 hr. The mixture was poured on ice and the organic product was rapidly distilled to yield 21.5 g of a colorless liquid, bp 82–92° (1 mm). This liquid had infrared absorption at 4.50, 4.55 (ethynyl groups), and 11.31 μ (terminal methylene). The nmr spectrum had an aromatic multiplet at τ 2.80, a quartet at 4.43 (terminal methylene), and a singlet at 7.64 (methyl). From the relative intensities of the methyl and methylene peaks, the mixture was estimated to be composed of 64% V and 36% VI, whereas glpc indicated 70% V and 30% VI.

Anal. Calcd for 64% $C_{10}H_7Cl$ and 36% $C_{10}H_8Cl_2$: C, 69.0; H, 4.2; Cl, 26.8. Found: C, 69.2; H, 4.3; Cl, 26.6.

The above mixture had to be handled rapidly as after 2 hr much decomposition and darkening had occurred. Because of this all attempts to separate V and VI in quantity failed.

1,3-Diphenyl-2-propyn-1-one (III).—To the Grignard reagent prepared by reaction on 153 g of phenylacetylene in ether with 1 equiv of ethylmagnesium bromide (600 ml of ether in all) was added a solution of 159 g of benzaldehyde (freshly distilled) in 100 ml of ether during 1 hr. After 1 hr more, a conventional work-up afforded 189 g (60%) of pure 1,3-diphenyl-2-propyn-1-ol,[13] bp 167–168° (2 mm). A solution of 81 g of sodium dichromate dihydrate in 400 ml of water containing 60 ml of 96% H_2SO_4 was added during 75 min to an ice-cooled, stirred solution of 110 g of 1,3-diphenyl-2-propyn-1-ol in 250 ml of ether. After the addition, stirring was continued for 2.5 hr at room temperature. After washing the ether layer with alkali and saturated salt solution and drying over magnesium sulfate, distillation afforded 85.5 g of a yellow oil, bp 145–151° (0.15 mm). Crystallization from Skellysolve B (petroleum ether, bp 65–70°) yielded 59.0 g (55%) of III,[14] mp 46.5–48.0°. The 2,4-dinitrophenylhydrazone, mp 226° dec, was prepared.[15]

2,3-Dichloro-1,3-diphenylpropenone (VII) and 1,3-Diphenyl-1,2,3,3-tetrachloropropene (VIII).—To a suspension of 129 g of PCl_5 in 200 ml of CH_2Cl_2 was added a solution of 61.8 g of III in 100 ml of CH_2Cl_2 during 1.5 hr. The mixture was held at reflux for a further 5.5 hr and was then poured on ice. The organic layer was washed with sodium bicarbonate solution and saturated salt solution and was dried over $MgSO_4$. The oil which remained after removal of solvent under vacuum partly crystallized on standing overnight. The solid (19.9 g, 20%) obtained by crystallization from hexane was shown to be VIII, mp 85–85.5°, with infrared absorption at 6.32, 9.35, and 11.38 μ. The nmr spectrum showed only aromatic protons.

Anal. Calcd for $C_{15}H_{10}Cl_4$: C, 54.3; H, 3.0; Cl, 42.7. Found: C, 54.2; H, 3.1; Cl, 42.7.

The mother liquors from the above crystallization were concentrated and the remainder was distilled to yield 47.8 g of a viscous yellow oil, bp 157–160° (1 mm), which glpc showed to be 34% VII and 66% VIII. The residue from distillation was treated as described below (under IX). The quantities of VII and VIII were estimated by glpc analysis and comparison with results obtained from pure VII and VIII. Pure VII was obtained in 86% yield as a viscous yellow liquid, bp 132–135° (1 mm), with infrared bands at 5.98 and 6.00 μ, by adding 3.45 g of chlorine to 10.0 g of III in 75 ml of CCl_4. This product was undoubtedly about a 1:1 mixture of the *cis* and *trans* isomers of VII.

Anal. Calcd for $C_{15}H_{10}Cl_2O$: C, 65.1; H, 3.6; Cl, 25.6. Found: C, 64.9; H, 3.7; Cl, 25.7.

On heating a mixture of 4.17 g of PCl_5, and 2.77 g of VII in 60 ml of CH_2Cl_2 at reflux for 3.5 hr, 2.3 g (70%) of pure VIII, mp 84–85°, was obtained. When a solution of 5.8 g of VIII, 150 ml of 1:1 water-methanol, and 2 ml of H_2SO_4 was refluxed for 1 day, a suitable work-up yielded 4.2 g of yellow oil, bp 140–142° (1 mm), shown by glpc to consist of VII (85%) and VIII (15%).

On attempting to recrystallize VIII from methanol a finely divided solid precipitated from solution in high yield. Recrystallization from methanol afforded the pure dimethyl ketal of VII as colorless plates, mp 98–99°, infrared absorption at 8.80 and 9.51 μ, nmr peaks at τ 2.84 (10 H, aromatic) and 7.05 (6 H, OCH_3).

Anal. Calcd for $C_{17}H_{16}Cl_2O_2$: C, 63.1; H, 5.0; Cl, 2.19. Found: C, 63.0; H, 4.8; Cl, 21.7.

5,6,11,12-Tetrachloro-11,12-diphenyl-10a,12a-dihydronaphthacene (IX).—The above-mentioned distillation residue was triturated with ether to yield 4.8 g (6%) of IX,[5] mp 266° dec. This material gave acceptable analyses for C, H, and Cl. On heating 2.3 g of IX under vacuum at 230–235° for 2 hr, hydrogen chloride was evolved (vigorously during the first 10 min) and the color soon became very dark. The solid black reaction product was powdered and crystallized from ethanol to yield 1.5 g (88%) of 5,6-dichloro-11,12-diphenylnaphthacene[5] as a deep violet solid, mp 240–241°.

1,2-Cycloaddition of an Azo Group to an Olefin

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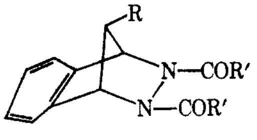
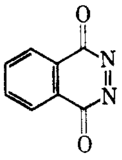
We wish to report the first example of a 1,2-cycloaddition of phthalazine-1,4-dione to an olefin.[1] This process provides a one-step synthesis of a derivative of diazacyclobutane. Phthalazine-1,4-dione has been described earlier as devoid of enophilic character.[2,3]

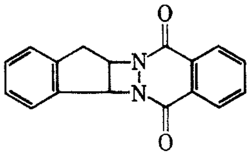
In connection with other work we were interested in preparing a series of compounds of structure I.



I



II



III

Such compounds are formally the Diels–Alder adducts of 2-alkylisoindenes, and, since it has been shown that in the presence of certain active dienophiles adducts of isoindene can be obtained,[4,5] this route seemed worth exploring. As the potential dienophile, phthalazine-1,4-dione (II) appeared promising. Previous work[2,3] has shown that II is a potent dienophile and suggested that it was devoid of enophilic character.

Treatment of indene with II, generated *in situ* by lead tetraacetate oxidation of phthalhydrazide, gave a crystalline 1:1 adduct (58%, mp 256–258° dec).

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[9] L. J. Andrews and S. L. Linden, *J. Am. Chem. Soc.*, **69**, 2091 (1947).

[10] F. Wille and F. Knorr [*Ber.*, **85**, 841 (1952)] report mp 153°.

[11] J. W. Kroeger and J. A. Nieuwland [*J. Am. Chem. Soc.*, **58**, 1861 (1936)] report bp 101–102° (3 mm).

[12] Compare M. S. Newman and W. T. Booth, Jr., *ibid.*, **67**, 154 (1945).

[13] E. D. Venus-Danilova and L. A. Pavlova [*Zh. Obshch. Khim.*, **19**, 951 (1949)] report bp 181–183° (4 mm).

[14] T. Agawa and S. I. Miller [*J. Am. Chem. Soc.*, **83**, 449 (1961)] report mp 48–49°.

[15] I. Iwai and Y. Okajima [*Yakugaku Zasshi*, **78**, 1252 (1958)] report mp 224°.

[1] For a recent review of the chemistry of α-carbonyl azo compounds which summarizes related reactions, see E. Fahr and H. Lind, *Angew. Chem.*, **78**, 376 (1966).

[2] R. A. Clement, *J. Org. Chem.*, **25**, 1724 (1960); **27**, 1115 (1962).

[3] T. J. Kealy, *J. Am. Chem. Soc.*, **84**, 966 (1962).

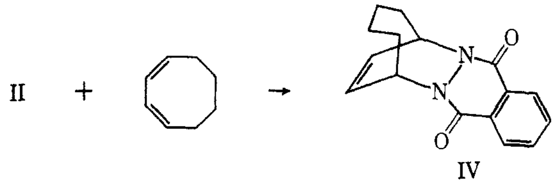
[4] K. Alder, F. Pascher, and H. Vagt, *Ber.*, **75B**, 1501 (1942).

[5] K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).

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.

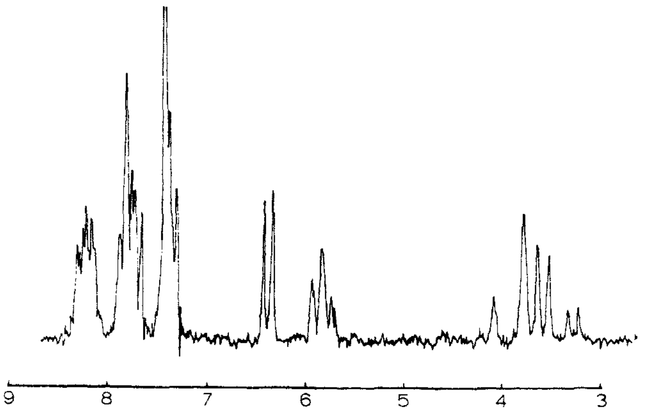


Figure 1.—Nuclear magnetic resonance spectrum of indene phthazine-1,4-dione adduct (III) in deuteriochloroform. The chemical shift scale (δ) is calibrated in parts per million downfield from internal tetramethylsilane.

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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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).