pressure. Distillation afforded 4.5 g (77%) of colorless IV, bp 99–100° (3.5–4.0 mm), infrared absorption at 5.80 μ. This product was not purified further but was decarbonylated as described below. The 2,4-dinitrophenylhydrazone of IV, mp 134–135°, was obtained in high yield after two recrystallizations from ethanol–benzene.

Anal. Calcd for $C_{18}H_{20}N_4O_4$: C, 60.7; H, 5.6; N, 15.7. Found: C, 60.7; H, 5.7; N, 16.0.

Neopentylbenzene (I).—In the best of three runs, a mixture of 4.5 g of IV and 0.2 g of 10% palladium-on-charcoal catalyst[5] in a small Claisen flask was heated in a fused salt bath. Gas evolution started at 160° and became rapid at 220°. After 4 hr the theoretical amount of carbon monoxide had been evolved. The crude distillate had almost no infrared absorption at 5.80 μ and weighed 3.6 g. A solution of this material in pentane was stirred with water, then worked up as usual except that the pentane was removed on a column to yield 3.4 g (90%) of I as a colorless liquid:[11] bp 186.0–187.5°; homogeneous by vpc analysis; nmr (CCl_4), δ 0.89 (singlet, 9 H, CCH_3), 2.43 (singlet, 2 H, CH_2), 7.11 (closely spaced multiplet, 5 H, aromatic); infrared absorption at 8.05, 12.95, and 13.90 μ.

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(11) H. Pines and J. T. Arrigo, *J. Am. Chem. Soc.*, **79**, 4966 (1957), give bp 185.6–187.0°.

Reactions of Acetylenic Ketones and an Aldehyde with Phosphorus Pentachloride[1]

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Because of interest in the mechanism of reactions of phosphorus pentachloride with ketones[3] we report on the reactions of three compounds containing the phenylethynyl group: 3-phenylpropynal (I), 4-phenyl-3-butyn-2-one (II), and 1,3-diphenyl-2-propyn-1-one (III).

On treatment of I with phosphorus pentachloride in methylene chloride for 20 hr at room temperature and in carbon tetrachloride for 20 hr at reflux, there was obtained 1,1-dichloro-3-phenyl-2-propyne (IV) in 94 and 85% yields, respectively. As no dichloroallene was formed in this reaction, a chlorocarbonium ion mechanism[3] is probably not involved. Hydrolysis using an aqueous suspension of calcium carbonate[4] yielded the starting I.

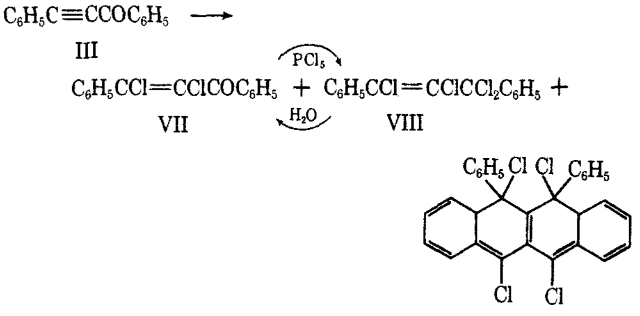
$$\underset{\text{I}}{C_6H_5C{\equiv}CCHO} \longrightarrow \underset{\text{IV}}{C_6H_5C{\equiv}CCCl_2H}$$

The reaction of II with phosphorus pentachloride was carried out only in methylene chloride at room temperature. A mixture of 2-chloro-4-phenyl-1-buten-3-yne (V) and 3,3-dichloro-1-phenyl-1-butyne (VI) in the ratio of about 3 to 1 was formed. The absence of any dichloroallene in the mixture was established by the lack of a band near 5.1 μ in the infrared spectrum. The compounds V and VI were not isolated in the pure state because of decomposition on attempted fractionation. However, analyses and nmr data were sufficient to establish the structures beyond reasonable doubt (see the Experimental Section).

$$\underset{\text{II}}{C_6H_5C{\equiv}C{-}COCH_3} \longrightarrow$$

$$\underset{\text{V}}{C_6H_5C{\equiv}C{-}CCl{=}CH_2} + \underset{\text{VI}}{C_6H_5C{\equiv}CCCl_2CH_3}$$

On reaction of III with phosphorus pentachloride in carbon tetrachloride or in methylene chloride, mixtures of 2,3-dichloro-1,3-diphenylpropenone (VII), 1,3-diphenyl-1,2,3,3-tetrachloropropene (VIII), 5,6,11,12-tetrachloro-11,12-diphenyl-10a,12a-dihydronaphthacene[5] (IX), and III were obtained, the composition of which depended mainly on the ratio of phosphorus pentachloride to III used. We confirm the formation of IX but find it to be a very minor (2–6%) product, the main products in these solvents being VII and VIII, with the latter predominating when 2 equiv of phosphorus pentachloride are used.



$$\underset{\text{III}}{C_6H_5C{\equiv}CCOC_6H_5} \longrightarrow$$

$$\underset{\text{VII}}{C_6H_5CCl{=}CClCOC_6H_5} \underset{H_2O}{\overset{PCl_5}{\rightleftharpoons}} \underset{\text{VIII}}{C_6H_5CCl{=}CClCCl_2C_6H_5} +$$

IX

The structure of VII was confirmed by adding chlorine to III. In addition, treatment of VII with phosphorus pentachloride yielded VIII which, on treatment with methanol, yielded α,β-dichlorochalcone dimethyl ketal (X) and, with dilute acid, VII.

In none of the ethynyl carbonyl compounds studied was there any evidence for the formation of a dichlorinated allene as might have been expected if reactions with phosphorus pentachloride had taken place *via* a chlorocarbonium ion.[3]

Experimental Section[6]

1,1-Dichloro-3-phenyl-2-propyne (IV).—3-Phenylpropynal (I), bp 66–69° (1 mm), was prepared by hydrolysis of its diethyl acetal as described.[7] The diethyl acetal was prepared as described by reaction of phenylethynylmagnesium bromide with ethyl orthoformate.[8] To a suspension of 29.2 g of PCl_5 in 100 ml of methylene chloride was added a solution of 17.0 g of I in 50 ml of CH_2Cl_2 during 2 hr. After 18 hr at room temperature the mixture was poured on ice and the organic layer was separated, washed, and dried over $MgSO_4$. Distillation afforded 22.6 g (94%) of IV, bp 82–83° (1 mm), infrared absorption at 4.50 μ. The nmr spectrum showed a singlet at τ 3.60 (CCl_2H) in addition to an aromatic complex centered near 2.7.

Anal. Calcd for $C_9H_6Cl_2$: C, 58.4; H, 3.3; Cl, 38.3. Found: C, 58.3; H, 3.2; Cl, 38.6.

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(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. AF-AFOSR-569-64.

(2) The material in this paper was taken from the Ph.D. thesis presented by B. C. Ream to The Ohio State University, 1965.

(3) M. S. Newman and L. L. Wood, *J. Am. Chem. Soc.*, **81**, 4300 (1959); M. S. Newman, G. Fraenkel, and W. N. Kirn, *J. Org. Chem.*, **28**, 1851 (1963).

(4) L. J. Andrews and S. L. Linden [*J. Am. Chem. Soc.*, **69**, 2091 (1947)] used this method to hydrolyze 1,1-dichloro-3-phenyl-2-propene.

(5) C. Dufraisse, A. Etienne, and M. Jolly, *Compt. Rend.*, **231**, 5 (1950). No experimental details or yields were cited.

(6) All melting points were determined on a Fisher-Johns apparatus and are uncorrected. All microanalyses by Micro-Analysis Inc., Wilmington, Del.

(7) C. R. H. Allen and C. O. Edens, Jr., "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 731.

(8) B. W. Howk and J. C. Sauer, *J. Am. Chem. Soc.*, **80**, 4607 (1958).

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°.

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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°.

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

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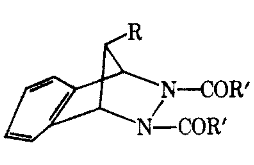
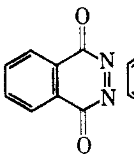
We wish to report the first example of a 1,2-cycloaddition of phthalazine-1,4-dione to an olefin.[1] This process provides a one-step synthesis of a derivative of diazacyclobutane. Phthalazine-1,4-dione has been described earlier as devoid of enophilic character.[2,3]

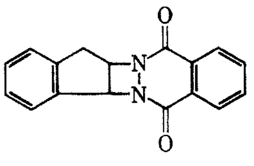
In connection with other work we were interested in preparing a series of compounds of structure I.



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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[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).