by filtration. The filtrate was evaporated to dryness in a Rinco at 30° and 10 mm. The crystalline residue was leached with anhydrous ethanol to extract the reaction product from the inorganic salts; the product was distilled *in vacuo* to isolate quinazoline.

The polymers from the cyclohexene and cyclooctene amozonolysis were insoluble in all solvents except organic and mineral acids from which they could be precipitated by base. These polymers were hydrolyzed by adding a 50% aqueous acetic acid solution to vigorously stirred water at 100° through which superheated steam (120°) was passed. The aldehydes were collected in the steam distillates and either precipitated with semicarbazide or extracted with ether. Cyclopentene-1-carboxaldehyde (15–20%) was identified as its semicarbazone, m.p. 209°, lit.[4] m.p. 208°. Suberic aldehyde (26%) gave the disemicarbazone, m.p. 183°, lit.[5,6] m.p. 183–185°.

The ozonizations of cyclohexene and cyclooctene in *t*-butylamine (500 ml.) were carried out as described with ammonia. The hydrocarbons were soluble in the butylamine and needed no emulsifier. After amozonolysis, about three-fourths of the solvent was distilled off, 200 ml. of water was added, and the reaction products were isolated by extraction with ether. Vacuum distillation gave, in the case of cyclohexene, cyclohexene-3-*t*-butylimine, 30 g. (41%), b.p. 150°. It was identified by infrared and mass spectra (parent peak at 151). As the imine was relatively unstable, it was immediately hydrogenated: 10 g. of distillate were dissolved in 100 ml. of methanol and hydrogenated at atmospheric pressure with platinum oxide catalyst, giving 7 g. of N-cyclohexyl-*t*-butylamine, b.p. 87° (37 mm.), picrate m.p. 187°.

Anal. of picrate. Calcd. for $C_{16}H_{24}N_4O_7$: C, 50.0; H, 6.3; N, 14.6. Found: C, 50.3; H, 6.5; N, 14.7.

Mass and infrared spectra were consistent with the proposed structure.

Cyclooctene gave cyclooctene-3-*t*-butylimine, 3 g. (49%), b.p. 75° (18 mm.), which was identified by the mass spectrum (parent peak at 179) and infrared. Hydrogenation of the flash distillate from the crude reaction product at 15 mm. gave N-cyclooctyl-*t*-butylamine, b.p. 59° (4 mm.), picrate m.p. 198°.

Anal. of picrate. Calcd. for $C_{18}H_{28}N_4O_7$: C, 52.4; H, 6.9; N, 13.6. Found: C, 52.2; H, 7.0; N, 13.7.

A higher boiling fraction (b.p. 102°) solidified and was identified as octamethylene-1,8-di(*t*-butylamine), m.p. 55°, by its mass spectrum (parent peak at 256) and infrared; yield 6%.

Pure *t*-butylamine reacted readily with ozone to yield 2-methyl-2-nitrosopropane. In the presence of olefins, however, oxidation of the amine was a minor reaction, owing to faster ozonolysis of the more reactive carbon–carbon double bonds.

In a competitive reaction of butylamine and ammonia with benzaldehyde, N-butylbenzylidenimine was formed by dropwise addition of 10 g. of distilled benzaldehyde together with 0.1 g. of Pronon 523 as emulsifier to a solution of 7 g. of *n*-butylamine in 100 ml. of 80% aqueous ammonia at −20° with vigorous stirring. After 4 hr. the ammonia was evaporated and the reaction product was isolated by ether extraction and distillation. N-butylbenzylidenimine, b.p. 123°, was obtained in 91–92% yield (14.2 g.). It was identified by mass and infrared spectroscopy.

To determine if hydroperoxide was reduced by ammonia, 10 g. of 2-hydroperoxyoctane[7] was emulsified in 120 ml. of 100% aqueous ammonia at −35° and stirred for 6 hr. After evaporation of ammonia, the reaction product was isolated by ether extraction and dried with anhydrous magnesium sulfate. The content of hydroperoxide in 5 g. of the reaction mixture was iodometrically titrated, showing 2.3 g. of unchanged starting material. The infrared spectrum was identical with a 1:1 mixture of authentic 2-hydroperoxyoctane and octanol-2. No carbonyl band was observed.

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(4) L. Ruzicka and E. Peyer, *Helv. Chim. Acta*, **18**, 676 (1935).

(5) O. Wallach, *Ann.*, **347**, 327 (1906).

(6) K. W. Rosemund and F. Zetzsche, *Chem. Ber.*, **54**, 2889 (1921).

(7) C. Walling and S. A. Buckler, *J. Am. Chem. Soc.*, **77**, 6032 (1955).

A New Synthesis of Diaryl- and Alkylaryl-Substituted Acetylenes from α-Diketones and Triethyl Phosphite

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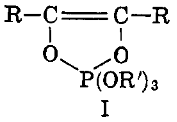
A novel method for the preparation of diaryl- and alkylaryl-substituted acetylenes from α-diketones and triethyl phosphite has been studied. When 1 mole of α-diketones was heated with 2 moles of triethyl phosphite at 215°, corresponding diaryl- and alkylaryl-substituted acetylenes were obtained in the yields ranging from 24 to 60%. Diaryl- and alkylaryl-substituted acetylenes were obtained in good yields by treating 1:1 adducts of triethyl phosphite and α-diketones in the presence of excess triethyl phosphite at 215°.

It has been recently found[1] that diphenylketene reacts with triethyl phosphite to form a 2:1 addition compound which, when pyrolyzed, is converted into diphenylacetylene, a deoxygenated product, and triethyl phosphate in fairly good yields.

$$2(C_6H_5)_2C{=}C{=}O + (C_2H_5O)_3P \longrightarrow [\text{adduct}] \xrightarrow{\Delta} C_6H_5C{\equiv}CC_6H_5 + (C_2H_5O)_3PO + \text{diphenylketene dimer}$$

Further, it has been shown that when the 2:1 adduct was heated in the presence of 1 mole of triethyl phosphite, diphenylacetylene and triethyl phosphate were obtained in good yields along with a small amount of diphenylketene dimer.

On the other hand, Ramirez[2] and Kukhtin[3] reported that tertiary phosphite esters react with α-diketones to form cyclic 1:1 adducts (I).



I

$R{=}R'{=}$ CH_3 or C_6H_5
$R{=}C_6H_5$, $R'{=}CH_3$

In the present experiment, the decomposition of the 1:1 adduct of benzil and triethyl phosphite in the presence of 1 mole of triethyl phosphite was tried first under the assumption that it would yield diphenylacetylene, a deoxygenated product, and 2 moles of triethyl phosphate.

Indeed, when a mixture of 2 moles of triethyl phosphite and 1 mole of benzil was heated at 215° for 2.5 hr. under nitrogen, diphenylacetylene and triethyl phosphate were obtained in 60 and 88% yields, respectively, along with the diphenylketene dimer (24%).

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(1) T. Mukaiyama, H. Nambu, and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962).

(2) (a) F. Ramirez, R. B. Mitra, and N. B. Desai, *J. Am. Chem. Soc.*, **82**, 2651 (1960); (b) F. Ramirez and N. B. Desai, *ibid.*, **82**, 2652 (1960).

(3) (a) V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, **121**, 466 (1958); *Chem. Abstr.*, **53**, 1105*b* (1959); (b) V. A. Kukhtin, K. M. Kirillora, and R. R. Shagidullin, *J. Gen. Chem. USSR*, **32**, 640 (1962).

Similarly, diaryl- and alkylarylacetylenes were obtained in yields ranging from 24 to 48% by the treatment of 4,4'-disubstituted benzils or acetylbenzoyl with triethyl phosphite (see Table I).

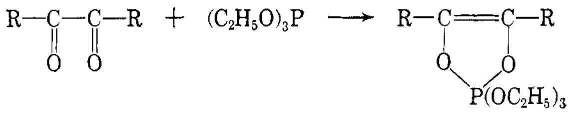
TABLE I

THE REACTION OF BENZIL (1 MOLE) WITH TRIETHYL PHOSPHITE (2 MOLES)

		Disubstituted acetylene			
α-Diketone	Time, hr.	Yield, %	B.p. (mm.), °C.	M.p., °C.	Yield of $(C_2H_5O)_3PO$, %
Benzil	2.5	60	118–121 (3)		88
4,4'-Dimethylbenzil	3	28		134	61
4,4'-Dichlorobenzil	6.5	43		176	64
4,4'-Dimethoxybenzil	6	24		146	72
Acetylbenzoyl	6	41	74–75 (15)		67

However, dialkylacetylenes could not be obtained by this reaction; for example, when biacetyl and triethyl phosphite reacted at 215° for 5.5 hr., butyne-2 could not be obtained, although triethyl phosphate and various unidentified products were obtained.

These reactions could be interpreted as follows.



II

$$\longrightarrow R_2C{=}C{=}O + (C_2H_5O)_3PO \quad (A)$$

$$R_2C{=}C{=}O + (C_2H_5O)_3P \longrightarrow R{-}C{\equiv}C{-}R + (C_2H_5O)_3PO \quad (B)$$

Intramolecular deoxygenation of the adduct II by the trivalent phosphorus occurs concomitant with the migration of the phenyl group on the adjacent carbon atom to yield disubstituted ketene and triethyl phosphate (step A). Disubstituted ketene thus formed is further deoxygenated by triethyl phosphite to form disubstituted acetylene and triethyl phosphate as mentioned in the previous report[1] (step B).

The initial formation of disubstituted ketene (step A) is established by the following experiment. When a mixture of benzil (1 mole) and triethyl phosphite (1 mole) was heated at 215° for 15 min. under nitrogen, diphenylketene (11% yield) and triethyl phosphate (81% yield) were obtained along with the diphenylketene dimer.

There is an alternative pathway for the deoxygenation which involves an attack of triethyl phosphite on the adduct II to yield the products directly without accompanying rearrangement. The use of isotopic carbon should be able to confirm which pathway is correct.

High yields of diphenylacetylene and triethyl phosphate resulted when the 1:1 adduct of benzil and triethyl phosphite initially prepared was heated in the presence of 5 moles of triethyl phosphite in a sealed tube at 215° for 4 hr. under nitrogen.

In similar fashion, the other diaryl- and alkylarylacetylenes were obtained in good yields (see Table II).

TABLE II

THE REACTION OF THE 1:1 ADDUCTS (1 MOLE) WITH TRIETHYL PHOSPHITE (5 MOLES)

		Disubstituted acetylene			
α-Diketone	Time, hr.	Yield, %	B.p. (mm.), °C.	M.p., °C.	Yield of $(C_2H_5O)_3PO$, %
Benzil	4	81	113–115 (2)		78
5,5'-Dimethylbenzil	5	72		134	99
4,4'-Dichlorobenzil	7	59		176	90
4,4'-Dimethoxybenzil	7	58		146	99
Acetylbenzoyl	7	54	74–75 (15)		63

Experimental

Materials.—Triethyl phosphite (b.p. 53–54° at 14 mm.) and acetylbenzoyl (b.p. 114–116° at 20 mm.) were prepared by methods of Ford-Moore[4] and Hartman,[5] respectively. Benzil and substituted benzils were prepared by the usual methods from corresponding aldehydes.

Reaction of Benzil (1 mole) with Triethyl Phosphite (2 moles).—A mixture of benzil (4.20 g., 0.02 mole) and triethyl phosphite (6.64 g., 0.04 mole) was heated at 215° for 2.5 hr. under nitrogen until no more triethyl phosphite distilled. The fractional distillation *in vacuo* gave diphenylacetylene, 2.12 g. (60%), b.p. 118–121° (3 mm.), and triethyl phosphate, 6.36 g. (88%), b.p. 101–102° (18 mm.). A crystalline solid precipitated by the addition of a small amount of ethyl alcohol to the residue. Recrystallization from ethyl alcohol gave diphenylketene dimer, 0.92 g. (24%), m.p. 168–169°.

By a similar procedure, various diaryl- and alkylarylacetylenes were obtained from 2 moles of triethyl phosphite and 1 mole of the corresponding 4,4'-disubstituted benzil. The results are listed in Table I.

Reaction of Benzil (1 mole) with Triethyl Phosphite (1 mole).—When 4.20 g. (0.02 mole) of benzil and 3.32 g. (0.02 mole) of triethyl phosphite were heated directly in a Claisen flask at 215° under nitrogen, the reaction mixture gradually became dark brown. After heating for 15 min., it was distilled immediately giving triethyl phosphate, 2.93 g. (81%), b.p. 58–60° (3 mm.), and diphenylketene, 0.42 g. (11%), b.p. 111–114° (3 mm.). Diphenylketene dimer was obtained from the tarry residue by the method mentioned above, 0.63 g. (16%), m.p. 168–169°.

Reaction of the 1:1 Adduct (1 mole) of Benzil and Triethyl Phosphite with Triethyl Phosphite (5 moles).—The 1:1 adduct was prepared by the addition of triethyl phosphite (1.66 g., 0.01 mole) to benzil (2.10 g., 0.01 mole) with stirring under nitrogen. Benzil dissolved with liberation of heat. Triethyl phosphite (8.30 g., 0.05 mole) was added further to the resulting adduct and the mixture was heated in a sealed tube at 215° for 4 hr. under nitrogen. The reaction mixture was distilled under reduced pressure and gave diphenylacetylene, 1.43 g. (81%), b.p. 113–115° (2 mm.), and triethyl phosphate, 2.58 g. (78%), b.p. 108–110° (24 mm.); triethyl phosphite, 6.34 g., b.p. 56–58° (20 mm.), was recovered.

By a similar procedure, various diaryl- and alkylaryl-substituted acetylenes were obtained in good yields by treating the adducts in the presence of excess triethyl phosphite. The diaryl- and alkylaryl-substituted acetylenes listed in Table II were obtained as crystalline solids from ethanol.

Reaction of the 1:1 Adduct (1 mole) of Triethyl Phosphite and 4,4'-Dimethoxybenzil with Triethyl Phosphite (5 moles).—The benzils, with the exception of 4,4'-dimethoxybenzil, reacted exothermically with triethyl phosphite to form the 1:1 adducts. 4,4'-Dimethoxybenzil (2.70 g., 0.01 mole) was heated at about 60° under nitrogen with triethyl phosphite (1.66 g., 0.01 mole) until the yellowish color had disappeared. After the addition of triethyl phosphite (8.30 g., 0.05 mole) to the adduct, the mixture was heated in a sealed tube at 215° for 7 hr. under nitrogen. The precipitate of 4,4'-dimethoxydiphenylacetylene was filtered from the reaction mixture and recrystallized from ethanol, 1.38 g. (58%), m.p. 146°. The residue was distilled *in vacuo* giving triethyl phosphate, 3.30 g. (99%), b.p. 108–111° (25 mm.); triethyl phosphite, 4.49 g., b.p. 58–60° (27 mm.), was recovered.

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(4) A. H. Ford-Moore and B. J. Perry, *Org. Syn.*, **31**, 111 (1951).

(5) W. W. Hartman and L. J. Roll, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 20.