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The Reactions of the Benzil-Triethyl Phosphite Adduct

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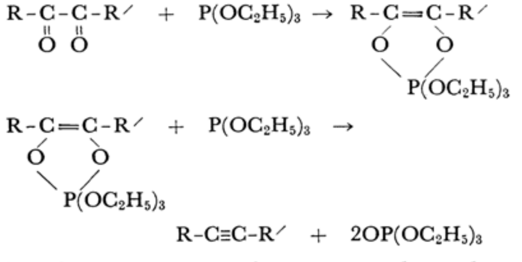
The decomposition of benzil - triethyl phosphite adduct in the presence of copper powder or cupric sulfate has been studied. When benzil, triethyl phosphite and cupric sulfate were treated in boiling toluene, *cis*-dibenzoylstilbene and triethyl phosphate were obtained. When the reaction was carried out in the presence of active hydrogen compounds, such as alcohol, carboxylic acid and amine, the corresponding benzoin derivatives were obtained. Further, when the adduct was decomposed in the presence of phenyl isocyanate or dicyclohexylcarbodiimide, 3, 4, 5-triphenyl-4-oxazoline-2-one or 2-cyclohexylimino-3-cyclohexyl-4, 5-diphenyl-4-oxazoline was obtained, along with triethyl phosphate.

It has recently been found that the decomposition of the adducts of α-diketones and triethyl phosphite[2] gives disubstituted acetylenes and triethyl phosphate in good yields.[1] The reactions take place at a comparatively high temperature, that is, above 215°C.



In the present experiment, several catalysts, such as copper powder and cupric sulfate, were

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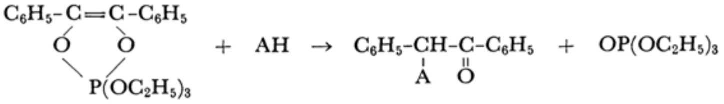
[1] T. Mukaiyama, H. Nambu and T. Kumamoto, *J. Org. Chem.*, **29**, 2243 (1964).

[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., **85**, 3252 (1963). c) V. A. Kukhtin, K. M. Kirillora and R. R. Shagidulline, *J. Gen. Chem. USSR*, **32**, 640 (1962).

TABLE I. THE DECOMPOSITION OF BENZIL-TRIETHYL PHOSPHITE ADDUCT IN THE PRESENCE OF ACTIVE HYDROGEN COMPOUNDS

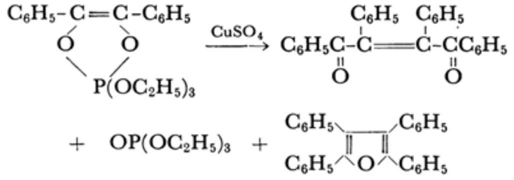


AH	Catalyst	$C_6H_5\text{-}\underset{A}{CH}\text{-}\underset{O}{\overset{\Vert}{C}}\text{-}C_6H_5$		M. p. °C	$OP(OC_2H_5)_3$ Yield, %
		Yield, %	B. p., °C (mmHg)		
CH_3OH	$CuSO_4$	11*	118—121 (0.1)	49—51	70
C_2H_5OH	$CuSO_4$	30*	141—144 (0.4)	60—61	69
$n\text{-}C_3H_7OH$	$CuSO_4$	24*	114—118 (0.03)	53	80
$iso\text{-}C_3H_7OH$	$CuSO_4$	40*	130—134 (0.2)	58	80
C_6H_5OH	$CuSO_4$	47*	160—166 (0.2)	85	96
C_6H_5COOH	$CuSO_4$	29		124—125	85
$C_6H_5NH_2$	Cu	63		97—98	71

* As the isolation of ethers of benzoin from reaction mixture was difficult, the yields of the ethers were comparatively low.

examined in order to carry out the decomposition of the adduct of benzil and triethyl phosphite at a lower temperature.

When a mixture of benzil and triethyl phosphite was refluxed in anhydrous toluene for five hours under nitrogen in the presence of anhydrous cupric sulfate, disubstituted acetylene could not be obtained, contrary to the case of the decomposition of the adduct in the absence of a catalyst. Instead, *cis*-dibenzoylstilbene and triethyl phosphate were obtained in 41% and 81% yields respectively, along with a small amount of tetraphenyl furan (18% yield).



Similarly, when copper powder or mercuric chloride was used as a catalyst, *cis*-dibenzoylstilbene was obtained in a 32% or a 14% yield respectively.

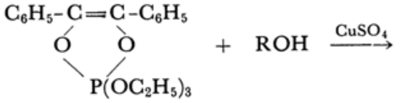
These results may be explained by considering an initial formation of triethyl phosphate and phenyl benzoyl carbene[3)] by the decomposition of the adduct. The carbene thus formed may in turn dimerize to form dibenzoylstilbene.

Usually, α-ketocarbene[4)] is known to be unstable and to yield disubstituted ketene by a Wolff rearrangement. On the other hand, Yater[5)] reported that α-ethoxy acetophenone was produced when α-diazoacetophenone was decomposed in the presence of alcohol and copper powder, but the rearranged product, the ester of phenylacetic acid, could not be obtained.

The intermediate of the decomposition of the adduct, carbene, may be demonstrated by the formation of benzoin derivatives when the adduct is decomposed in the presence of active hydrogen compounds.

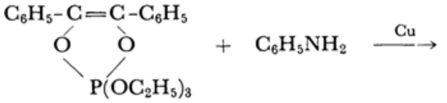
Indeed, when a mixture of benzil, triethyl phosphite and ethanol was refluxed in toluene for five hours under nitrogen in the presence of anhydrous cupric sulfate, benzoin ethyl ether (30% yield) and triethyl phosphate (69% yield) were obtained, along with a small amount of *cis*-dibenzoylstilbene (5% yield) and dibenzoyldiphenyl ethane (3% yield).

Similar reactions were observed in the cases of the other alcohols and phenol (see Table I).

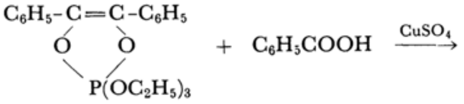


$$C_6H_5CH(OR)COC_6H_5 \quad + \quad OP(OC_2H_5)_3$$

By the same method, anilino desoxybenzoin (63% yield) and benzoin benzoate (29% yield) were obtained when the adduct was treated with aniline and benzoic acid respectively.



$$C_6H_5CH(NHC_6H_5)COC_6H_5 \quad + \quad OP(OC_2H_5)_3$$



$$C_6H_5CH(OCOC_6H_5)COC_6H_5 \quad + \quad OP(OC_2H_5)_3$$

In connection with the reaction of the α-diketone - tertiary phosphite adduct with active hydrogen compounds, Ramirez et al. have

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3) a) F. Ramirez, H. Yamanaka and O. H. Basedow, *J. Am. Chem. Soc.*, **83**, 173 (1961). b) P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, **1963**, 42.

4) F. Weygand and H. J. Bestmann, *Angew. Chem.*, **72**, 535 (1960).

5) P. Yater, *J. Am. Chem. Soc.*, **74**, 5376 (1952).

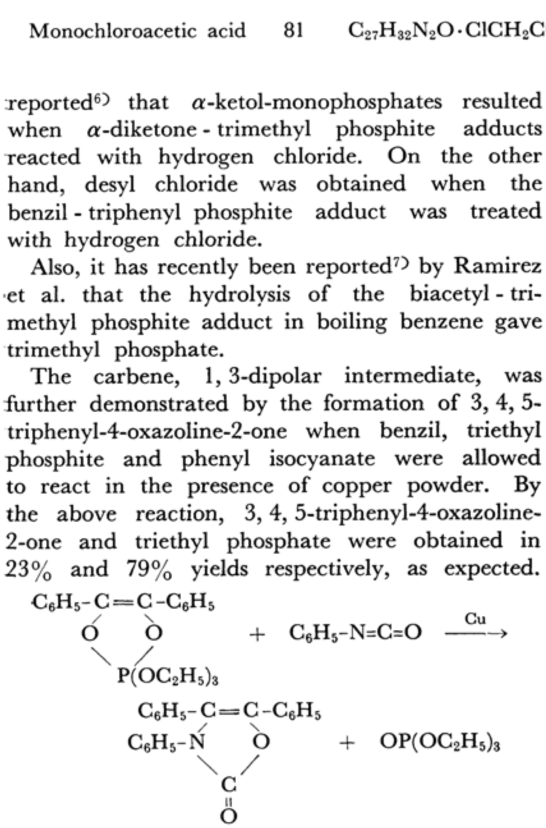
TABLE II. REACTIONS OF 2-CYCLOHEXYLIMINO-3-CYCLOHEXYL-4, 5-DIPHENYL-4-OXAZOLINE AND PROTONIC ACID

Acid	Yield, %	Salt of oxazoline Formula of salt	Analysis Found (Calcd.) C	H	N	M. p., °C (Decomp. p.)
Hydrogen chloride	100	$C_{27}H_{32}N_2O \cdot HCl$	73.66 (74.11	7.82 7.56	6.26 6.41)	(234—236)
Phenylphosphonic acid	86	$C_{27}H_{32}N_2O \cdot C_6H_5PO(OH)_2$			4.90 (5.02)	191—192
p-Toluenesulfonic acid	89	$C_{27}H_{32}N_2O \cdot C_7H_7SO_3H$	70.84 (71.30	7.30 6.99	5.01 4.89)	178—180
Monochloroacetic acid	81	$C_{27}H_{32}N_2O \cdot ClCH_2CO_2H \cdot H_2O$	67.24 (67.85	7.45 7.22	5.68 5.47)	(115—120)

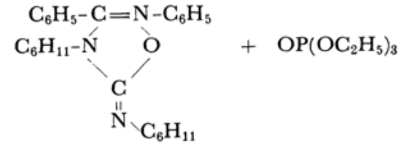
reported[6] that α-ketol-monophosphates resulted when α-diketone - trimethyl phosphite adducts reacted with hydrogen chloride. On the other hand, desyl chloride was obtained when the benzil - triphenyl phosphite adduct was treated with hydrogen chloride.

Also, it has recently been reported[7] by Ramirez et al. that the hydrolysis of the biacetyl - trimethyl phosphite adduct in boiling benzene gave trimethyl phosphate.

The carbene, 1, 3-dipolar intermediate, was further demonstrated by the formation of 3, 4, 5-triphenyl-4-oxazoline-2-one when benzil, triethyl phosphite and phenyl isocyanate were allowed to react in the presence of copper powder. By the above reaction, 3, 4, 5-triphenyl-4-oxazoline-2-one and triethyl phosphate were obtained in 23% and 79% yields respectively, as expected.



Furthermore, when the adduct was treated with dicyclohexylcarbodiimide in boiling toluene in the presence of copper powder under nitrogen, 2 - cyclohexylimino - 3 - cyclohexyl - 4, 5 - diphenyl - 4 - oxazoline (72% yield) and triethyl phosphate (89% yield) were obtained.



Next, several reactions of the oxazoline were studied. 2-Cyclohexylimino-3-cyclohexyl-4, 5-diphenyl-4-oxazoline reacts with protonic acids, such as hydrogen chloride, *p*-toluenesulfonic acid, monochloroacetic acid and phenylphosphonic acid, to form the corresponding salts in high yields (see Table II).

On the other hand, 2-cyclohexylimino-3-cyclohexyl-4, 5-diphenyl-4-oxazoline is very stable towards hydrolysis in both basic and acidic media. Further study of the reaction of the oxazoline is now in progress.

Experimental

The Decomposition of the Benzil - Triethyl Phosphite Adduct in the Presence of Cupric Sulfate.—A mixtrue of benzil (4.20 g., 0.02 mol.), triethyl phosphite (3.32 g., 0.02 mol.) and cupric sulfate (2.00 g.) was refluxed in anhydrous toluene (15 cc.) under nitrogen for 5 hr. The removal of the solvent gave a white precipitate. Its recrystallization from benzene gave *cis*-dibenzoylstilbene, 1.12 g., m. p. 215—217°C.

Found C, 86.37; H, 5.24. Calcd. for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19%.

The fractional distillation of filtrate gave triethyl phosphate, 2.89 g. (81%); b. p. 113—115°C/28 mmHg. The addition of a small amount of ether to the residue also gave *cis*-dibenzoylstilbene. It was recrystallized from benzene, 0.48g., m. p. 214—216°C. The total yield of *cis*-dibenzoylstilbene was 41%.

Further, a crystalline was isolated from the residue. Its recrystallization from acetic acid gave tetraphenyl furan, 0.66 g. (18%), m. p. 173—174°C.

Found C, 90.03; H, 5.38. Calcd. for $C_{28}H_{20}O$: C, 90.29; H, 5.41%.

The Decomposition of the Benzil - Triethyl Phosphite Adduct in the Presence of Ethanol and Cupric Sulfate.—A mixture of benzil (2.10 g., 0.01 mol.), triethyl phosphite (1.66 g., 0.01mol.), ethanol (0.46 g., 0.01mol.) and cupric sulfate (1.00 g.) was refluxed in toluene (10 cc.) for 5 hr. under nitrogen. After the cupric sulfate had then been filtered off, the solvent was removed. Then a white precipitate was obtained. Recrystallization from benzene gave dibenzoyldiphenyl ethane, 0.05 g. (3%), m. p. 253—254°C. The residue was distilled in vacuo giving triethyl phosphate, 1.25 g. (69%), 114—116°C/30

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[6] F. Ramirez, R. B. Mitra and N. B. Desai, ibid., **82**, 2652 (1960).

[7] F. Ramirez, O. P. Madan and C. P. Smith, ibid., **87**, 670 (1965).

mmHg, and another fraction, 1.45 g., 141—144°C/ 0.4 mmHg. This was a mixture of benzil and benzoin ethyl ether. By the addition of a small amount of petroleum ether, benzil was recovered, along with benzoin ethyl ether; recrystallization from ligroin gave 0.72 g. (30%); m. p. 59—61°C.

Found C, 79.63; H, 6.98. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

When to the residue of fractional distillation there was added a small amount of diethyl ether, a white precipitate was obtained. It was recrystallized from benzene to give *cis*-dibenzoylstilbene, 0.10 g. (5%); m. p. 213—215°C.

By a similar procedure, various benzoin ethers were obtained from the reactions of benzil, triethyl phosphite and alcohols.

Analogously, anilino desoxybenzoin or benzoin benzoate was obtained from the reaction of benzil, triethyl phosphite and corresponding aniline or benzoic acid (see Table I).

The Decomposition of the Benzil-Triethyl Phosphite Adduct in the Presence of Phenyl Isocyanate and Copper Powder.—A mixture of benzil (2.10 g., 0.01 mol.), triethyl phosphite (1.66 g, 0.01 mol.), phenyl isocyanate (1.19 g., 0.01 mol.) and copper powder (0.50 g.) was refluxed in toluene for 5 hr. under nitrogen. The removal of the solvent gave a white precipitate. This was recrystallized from benzene to give 3, 4, 5-triphenyl-4-oxazoline-2-one, 0.73 g. (23%); m. p. 212—213°C; mixed m. p. 213°C. The filtrate was distilled in vacuo to give triethyl phosphate, 1.43 g. (79%), b. p. 103—105°C/ 20 mmHg.

The Decomposition of the Benzil-Triethyl Phosphite Adduct in the Presence of Dicyclohexylcarbodiimide and Copper Powder.—A mixture of benzil (4.20 g., 0.02 mol.), triethyl phosphite (3.32 g., 0.02 mol.), dicyclohexylcarbodiimide (4.12 g., 0.02 mol.) and copper powder (1.00 g.) was refluxed in toluene (15 cc.) for 5 hr. under nitrogen. After copper powder was filtered, the solvent was removed.

The fractional distillation of the residue gave triethyl phosphate, 3.24 g. (89%); b. p. 103—106°C/ 18 mmHg. The addition of a small amount of ethanol to the residue gave a white precipitate. Recrystallization from ethanol gave 2-cyclohexylimino-3-cyclohexyl-4, 5-diphenyl-4-oxazoline, 5.76 g. (72%); m. p. 133—134°C.

Found C, 80.73; H, 8.28; N, 7.10. Calcd. for $C_{27}H_{32}N_2O$: C, 80.96; H, 8.05; N, 6.99%. ν_{max}^{KBr} 2925, 2855, 1673, 1648, 1595, 1500, 1444, 1363, 1342, 1047, 1020, 984, 736, 698 and 683 cm^{-1}.

The Reaction of 2-Cyclohexylimino-3-cyclohexyl-4, 5-diphenyl-4-oxazoline with Hydrogen Chloride.—Anhydrous hydrogen chloride was passed through a solution of 2-cyclohexylimino-3-cyclohexyl-4, 5-diphenyl-4-oxazoline (2.00 g., 0.005 mol.) in anhydrous ether. A white precipitate was thus obtained. This was recrystallized from ethyl acetate giving 2-cyclohexylimino-3-cyclohexyl-4, 5-diphenyl-4-oxazoline hydrochloride, 3.83 g. (100%); m. p. 234—236°C (decomp.).

By a similar procedure, various salts of 2-cyclohexylimino-3-cyclohexyl-4, 5-diphenyl-4-oxazoline were obtained from the oxazoline and *p*-toluenesulfonic acid, phenylphosphonic acid and monochloroacetic acid respectively (see Table II).

The authors wish to express their hearty thanks to Mr. Takenori Nagaoka for his help during the course of this experiment.