The Reactions of Benzoyl Cyanide with Trivalent Phosphorus Compounds

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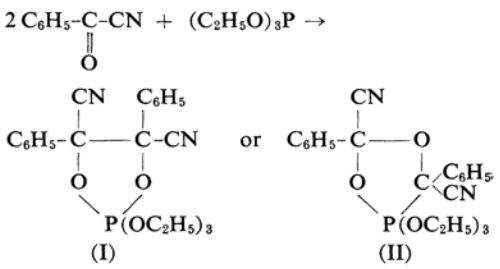
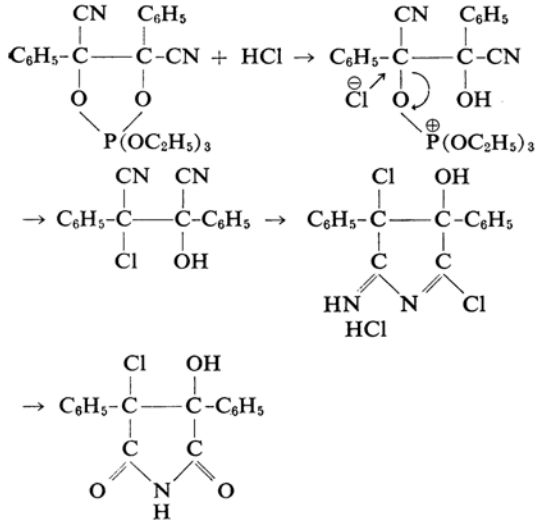
The deoxygenation reactions of isocyanates,[1] diphenyl ketone,[1] and benzil[2] by means of trivalent phosphorus compounds have been described in previous papers. In the present study, the reactions of benzoyl cyanide with trivalent phosphorus compounds will be examined. When triethyl phosphite is added to two equivalents of benzoyl cyanide in anhydrous benzene at room temperature, the reaction takes place exothermically. After the mixture is warmed to 50°C for 30 min., a white solid is obtained in a high yield. An elemental analysis shows that this product is a 2 : 1 adduct.



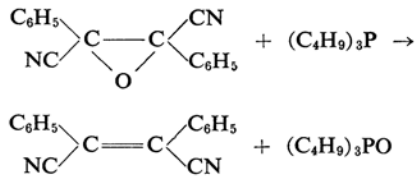
In order to confirm this structure, it was hydrolyzed in concentrated hydrochloric acid; 3,4-diphenyl-3-chloro-4-hydroxysuccinimide, whose infrared spectrum has characteristic bonds for carbonyl (1790 and 1720 cm^{-1}), for NH (3270 cm^{-1}) and for OH (3430 cm^{-1}), was thus obtained in a 62% yield. Mark[3] and Ramirez[4] reported that tris-dimethylamino phosphane or triethyl phosphite reacts with 2 mol. of aldehydes to form 2 : 1 adducts which

1) T. Mukaiyama, H. Nambu and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962).
2) T. Mukaiyama, H. Nambu and T. Kumamoto., ibid., **29**, 2243 (1964).
3) V. Mark, *J. Am. Chem. Soc.*, **85**, 1884 (1963).
4) F. Ramirez, A. V. Patwardhan and S. R. Heller, ibid., **86**, 514 (1964).

posses phosphorus-carbon bond. However, in the present case the structure of the adduct may be designated as I, since the hydrolysis product obtained adove may be expected only from I through decomposition as is sketched below:



When the adduct was heated in xylene, it decomposed into α,α'-dicyanostilbene oxide (70%) and triethyl phosphate (100%). The former compound could be identified by its infrared spectrum which has characteristic absorption bonds attributable to the epoxide ring (1260, 870 and 790 cm^{-1}), and by the fact of its conversion to *cis*-α,α'-dicyanostilbene when treated with tri-*n*-butylphosphine at 160°C.

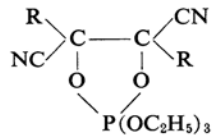


It has been reported by Wittig[5] that an inverted olefin is a predominant product when the epoxide is deoxygenated by tertiary phosphine. This suggests that the epoxide obtained above is in the trans-form. Similar adducts were obtained in the cases of *p*-nitro, *p*-chloro and *p*-methyl phenyl derivatives; they decomposed into the corresponding epoxides when they were refluxed in toluene or xylene (see Tables I and II).

In the case of *p*-anisoyl cyanide, however, a similar adduct was not obtained; rather α,α'-dicyano-*p*,*p'*-dimethoxystilbene was formed in a 64% yield.

Next, the reaction was attempted by using tri-*n*-butylphosphine in place of the triethyl phosphite used in the above experiment. When tri-*n*-butylphosphine was added drop-by-drop to an equimolar amount of benzoyl cyanide at room temperature, a red color was formed with a violent evolution of heat. After the solvent had been removed, a large amount of white crystals were obtained from the tarry reaction mixture. This product was shown to be *cis*-α,α'-dicyanostilbene by means of elemental analysis, its melting point[6] and its infrared spectrum (2400 cm^{-1} for nitrile; 1600, 1580, 1500, 1470, 770 and 700 cm^{-1} for the

TABLE I. THE SYNTHESIS OF 2:1 ADDUCT FROM THE REACTION OF AROYL CYANIDES WITH TRIETHYL PHOSPHITE



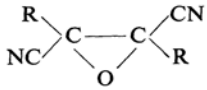
R	Yield, %	M. p., °C		Analysis C, %	H, %	N, %	P, %
C_6H_5-	97	117	Found	61.29	6.08	6.58	7.45
			Calcd.	61.68	5.84	6.54	7.24
p-CH_3-C_6H_4-	66	84	Found	62.98	6.40	6.32	7.01
			Calcd.	63.15	6.36	6.14	6.79
p-Cl-C_6H_4-	99	111—113	Found	53.13	4.41	5.76	*
			Calcd.	53.12	4.62	5.63	
p-NO_2-C_6H_4-	74	131 dec.	Found			10.81	5.82
			Calcd.			10.81	5.63

* Due to its sublimation property, the analysis of phosphorus of this compound could not be carried out.

5) G. Wittig and W. Haag, *Ber.*, **88**, 1654 (1955); C. B. Scott, *J. Org. Chem.*, **22**, 1118 (1957); M. J. Boskin and D. B. Denney, *Chem. & Ind.*, **1959**, 330.

6) L. Chalanay and E. Knoevenagel, *Ber.*, **25**, 289 (1892).

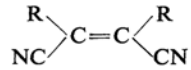
TABLE II. THE DECOMPOSITIONS OF 2 : 1 ADDUCTS INTO EPOXIDES AND TRIETHYL PHOSPHATE



R	Yield, %	M. p., °C		Analysis C, %	Analysis H, %	Analysis N, %	$(C_2H_5O)_3PO$, %
C_6H_5-	70	162[a]	Found	78.22	4.20	11.39	91
			Calcd.	78.03	4.09	11.38	
p-CH_3-C_6H_4-	22	150[b]	Found	78.43	5.03	10.40	98
			Calcd.	78.81	5.14	10.21	
p-Cl-C_6H_4-	20	168[c]	Found	61.12	2.39	9.10	77
			Calcd.	60.95	2.54	8.88	
p-NO_2-C_6H_4-	76	190[d]	Found	57.22	2.34	16.82	71
			Calcd.	57.15	2.40	16.66	

The reactions were carried out by heating in xylene for 1.5 hr.
a) Recrystallized from ethanol. b) Recrystallized from ether.
c) Recrystallized from ethyl acetate. d) Recrystallized from benzene.

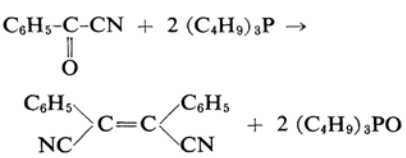
TABLE III. THE REACTIONS OF AROYL CYANIDES WITH TRI-*n*-BUTYLPHOSPHINE



R	Yield, %	M. p., °C		Analysis C, %	Analysis H, %	Analysis N, %
C_6H_5-	39	159[a]	Found	83.23	4.47	12.23
			Calcd.	83.45	4.38	12.17
p-CH_3-C_6H_4-	19	197[a]	Found	83.67	5.68	11.04
			Calcd.	83.69	5.46	10.85
p-CH_3O-C_6H_4-	40	188[b]	Found	74.65	5.15	9.69
			Calcd.	74.47	4.86	9.65
p-Cl-C_6H_4-	20	184[c]	Found	64.34	2.61	9.49
			Calcd.	64.21	2.67	9.36

a) Recrystallized from ethanol. b) Recrystallized from benzene.
c) Recrystallized from ethyl acetate.

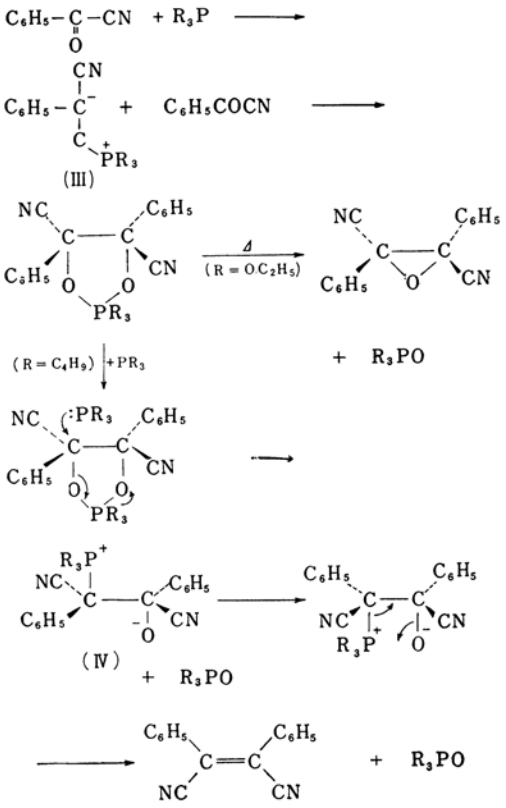
monosubstituted benzene ring). In order to ascertain whether the epoxide is an intermediate of this reaction, the deoxygenation of α,α'-dicyanostilbene oxide by tri-*n*-butylphosphine was next attempted under similar moderate conditions. However, the expected deoxygenation could not be observed, and the epoxide was recovered almost quantitatively. The results show that the epoxide is not a probable intermediate in this olefin formation. Similar results were observed in the cases of various *p*-substituted benzoyl cyanides, where the corresponding α,α'-dicyano olefines were obtained in 18—40% yields (see Table III).



The mechanisms of these reactions may be considered to be as follows; initially, benzoyl cyanide reacts with the trivalent phosphorus compound to form an adduct such as III, which may be stabilized by the strong electron-attracting effect of the cyano group. This is in turn transformed into 2 : 1 adduct by the electrophilic attack of another molecule of benzoyl cyanide. The electrophilic attack may occur at this stage so that two large groups, e. g., the phenyl group, conform in trans-position. Thus, the triethyl phosphite adduct, which is pyrolyzed, gives *trans*-epoxide, as is shown below.

In the case of tri-*n*-butylphosphine, the reaction may proceed through a similar adduct. The substitution reaction is expected to occur by the nucleophilic attack of the tertiary phosphine, accompanied by the elimination of the phosphine oxide. In the intermediate IV,

since the $>P^+$ part and $-O^-$ part are situated on opposite sides, it is necessary to rotate along the central carbon-carbon bond in order to accomplish the Wittig-type elimination of the tertiary phosphine oxide. Thus, *cis*-olefin may be formed predominantly.



Experimental

The Reaction of Benzoyl Cyanide with Triethyl Phosphite. — A solution of triethyl phosphite (0.415 g., 0.0025 mol.) in 10 ml. of anhydrous benzene was added slowly to benzoyl cyanide (0.655 g., 0.005 mol.) in 20 ml. of anhydrous benzene at 50°C under nitrogen atmosphere. After this mixture had stood for 30 min. at 50°C, the benzene was distilled off in vacuo, and the solidified residue was recrystallized from ligroin. The 2 : 1 adduct (1.04 g., 97% ; m. p. 117°C) was obtained.

By a similar procedure, the corresponding adducts were obtained from *p*-methyl, *p*-chloro and *p*-nitro phenyl derivatives.

The Reaction of Benzoyl Cyanide with Tri-*n*-butylphosphine.—A solution of tri-*n*-butylphosphine (6.06 g., 0.03 mol.) in 10 ml. of anhydrous ether was added drop-by-drop to benzoyl cyanide (3.93 g., 0.03 mol.) in 20 ml. of anhydrous ether under cooling in an ice-salt bath. Then the bath was removed and the reaction mixture was kept for one day at room temperature. After the evaporation of the ether at reduced pressure, the deposited solid was filtered and recrystallized from ethanol. α,α'-Dicyanostilbene (1.35 g., 39% ; m. p. 160°C) was thus obtained. By the distillation of the residue, tri-*n*-butylphosphine oxide (4.00 g., 61% ; b. p. 125—130°C/0.5 mmHg) was then obtained.

The Decomposition of the Adduct.—The benzoyl cyanide-triethyl phosphite adduct (4.30 g.) was dissolved in anhydrous xylene and refluxed for 1.5 hr. Then the solvent was removed in vacuo and the reaction mixture was distilled, giving triethyl phosphate (1.80 g., 98% ; b. p. 105—107°C/22 mmHg). The residue was solidified by cooling it and then recrystallized from ethanol. α,α'-Dicyanostilbene oxide (1.75 g., 70% ; m. p. 162°C) was thus obtained.

The Hydrolysis of the Adduct.—When 10 ml. of concentrated hydrochloric acid was added to the adduct (1.00 g.), it turned into a yellow oil. After it had then been refluxed for an hour, the deposited white solid was filtered and recrystallized twice from benzene.

Found : C, 63.11 ; H, 4.37 ; N, 5.03. Calcd. for $C_{16}H_{12}NO_3Cl$: C, 63.68 ; H, 3.98 ; N, 4.64%.

The Conversion of α,α'-Dicyanostilbene Oxide into α,α'-Dicyanostilbene.—A mixture of α,α'-dicyanostilbene oxide and tri-*n*-butylphosphine was heated at 160°C for 5 min. in nitrogen atmosphere. The reaction took place violently, and the reaction mixture turned black. After it had then been washed with ether, α,α'-dicyanostilbene (m. p. and m. m. p. 158—160°C) was obtained in a 48% yield.

No similar reaction could be observed at room temperature or at 100°C.

Summary

The reactions of various *p*-substituted benzoyl cyanides with trivalent phosphorus compounds have been studied. They react with triethyl phosphite to form 2 : 1 adducts which, upon being heated in xylene, decomposed into the corresponding dicyanostilbene oxide and triethyl phosphate. The reaction with tri-*n*-butylphosphine, on the other hand, gives *cis*-dicyanostilbene derivatives. These reactions can be explained by a mechanism through similar intermediates.

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