The Formation of Acetylenic Bond by the Elimination Reaction of Some Enol-esters. II. Fission of C–C Bond in α, β-Acetylenic Carbonyl Compounds by the Action of Amide Anion

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The nucleophilic addition of various bases to the triple bond of α,β-acetylenic carbonyl compounds has been well known. Benzoylphenylacetylene (I), for example, readily adds amines[1] or alcohols[2] in the presence of the corresponding alcoholates giving β-amino- or β-alkoxy-chalcones, respectively. Therefore the reagents and the reaction conditions, which do not cause such addition reaction, had to be found out for the study of the elimination reaction of enol-esters to yield acetylenic compounds.

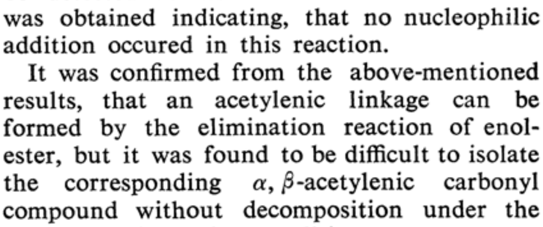
Sodium amide was first examined, because its action on the ketone I had never been known. The ketone I was treated with sodium amide in liquid ammonia resulting in the formation of phenylacetylene (II), benzoic acid (III) and benzamide (IV), while any substance arising from the addition reaction could not be detected at all.

$$\underset{\text{(I)}}{2\,C_6H_5C\equiv CCOC_6H_5} \rightarrow \underset{\text{(II)}}{2\,C_6H_5C\equiv CH} + \underset{\text{(III)}}{HO_2CC_6H_5} + \underset{\text{(IV)}}{H_2NCOC_6H_5}$$

This fact suggests the breaking of the bond between the acetylenic carbon and the carbonyl carbon atoms. Only an example of such a bond fission has been reported in which acetylphenylacetylene is decomposed to phenylacetylene and acetic acid by the action of aqueous potassium hydroxide[3]. Under similar condition, the ketone I decomposed to yield acetophenone and benzoic acid possibly via dibenzoylmethane which was produced by the hydration of the triple bond[3].

Benzoylphenylacetylene (I) was recovered unchanged in an 80% yield when it was treated with liquid ammonia in the absence of sodium amide, indicating the essential role of amide anion for the bond fission of the acetylenic ketone. If the reaction proceeds in one step by the attack of amide anion to the carbonyl carbon displacing phenylethynyl anion, only phenylacetylene (II) and benzamide (IV) ought to be produced and the corresponding free acid should not be obtained at all. The possibility of the hydrolysis of the amide IV in the course of the isolation of the reaction products was excluded by the fact that the amide IV was recovered unchanged in about 75% yield and the acid III was obtained only in a minor quantity, when IV was treated in the same manner as in the isolation procedure. Therefore, the formation of the free acid III seems to be involved in the main reaction path, but detailed studies were not undertaken.

Diphenyl 1, 3-diphenyl-2-propen-1-on-3-yl phosphate (V)[4] was treated with four equivalents of sodium amide in liquid ammonia. Expectedly, phenylacetylene (II) and benzamide (IV) were obtained. Also diphenyl β-methoxycarbonyl-α-styryl phosphate (VI)[4] was treated with sodium amide affording phenylacetylene (II). Phenylpropiolic acid (VII, R=H) or its derivative (VII, R=CH_3 or NH_2) could not be detected at all.



$$\underset{\text{(V)}}{C_6H_5\underset{OPO(OC_6H_5)_2}{C}=CHCOC_6H_5} \rightarrow \underset{\text{(II)}}{C_6H_5C\equiv CH} + \underset{\text{(IV)}}{H_2NCOC_6H_5}$$

$$\underset{\text{(VI)}}{C_6H_5\underset{OPO(OC_6H_5)_2}{C}=CHCO_2CH_3} \rightarrow \underset{\text{(VII)}}{(C_6H_5C\equiv CCO_2R)} \rightarrow \underset{\text{(II)}}{C_6H_5C\equiv CH}$$

Also no basic material was obtained indicating, that no nucleophilic addition occured in this reaction.

It was confirmed from the above-mentioned results, that an acetylenic linkage can be formed by the elimination reaction of enol-ester, but it was found to be difficult to isolate the corresponding α,β-acetylenic carbonyl compound without decomposition under the above stated reaction condition.

Further studies on the elimination reaction will be reported in the following paper.

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[1] E. André, *Compt. rend.*, **152**, 525 (1911); E. André, *Ann. chim.*, [8] **29**, 569 (1913); E. R. Watson, *J. Chem. Soc.*, **85**, 1319 (1904).

[2] M. C. Dufraisse and P. Gérald, *Bull. soc. chim. France*, [4] **31**, 1285 (1922); M. C. Dufraisse and A. Gillet, *Ann. chim.*, [10] **6**, 295 (1926).

[3] C, Moureu and R. Delange, *Compt. rend.*, **130**, 1259 (1900).

[4] M. Nakagawa, G. Nakaminami, F. Ogura and H. Ono, This Bulletin, **35**, 1485 (1962).

Experimental*

Reaction of Benzoylphenylacetylene (I) with Sodium Amide in Liquid Ammonia. — A solution of the ketone I[5] (4.1 g., 0.02 mol.) in dry tetrahydrofuran (50 ml.) was added dropwise to a stirred suspension of sodium amide (0.022 mol.) in liquid ammonia (50 ml.) during 45 min. After stirring for a further 3 hr., ammonium chloride (1.5 g.) was added with stirring, and the ammonia was removed. Ether (50 ml.) and then saturated aqueous sodium chloride solution (50 ml.) were added to the stirred mixture under cooling by ice. A small amount of insoluble material was filtered off and washed with ether. The ethereal solution was separated from the aqueous solution, (solution A), washed successively with sodium chloride solution (solution B), dilute sulfuric acid (solution C), and sodium chloride solution, and dried ($MgSO_4$). The oily residue, obtained by removal of the solvent through a Widmer column, separated crystals on standing. A small amount of light petroleum was added to complete the crystallization. Recrystallization of the solid (0.25 g., 10%) from aqueous methanol and then from benzene afforded benzamide as colorless plates, m. p. 126.5~128°C, which was undepressed on admixture with the authentic specimen.

Distillation (at 75.5~77.5 mmHg) of the unsolidified fraction gave phenylacetylene as colorless liquid (0.7 g.) which was converted to the mercury compound according to the usual way[6]. It was recrystallized 3 times from ethanol as colorless plates, m. p. 123~124.5°C, which showed no depression in the melting point on admixture with the authentic specimen[6]. The yield of the mercury compound was 1.0 g. (25% based on the ketone I) in a fairly pure state.

A solid was separated, on acidification with sulfuric acid (Congo red) from the combined solutions of A and B. The solid was separated by filtration, and the filtrate was extracted with ether. The ethereal solution was concentrated to give a further crop of the solid (combined yield, 1.2 g., 49%). Sublimation of the solid under reduced pressure afforded benzoic acid as colorless plates, m. p. 121~122°C, undepressed on admixture with the authentic specimen.

The solution C was made alkaline with dilute sodium hydroxide and extracted with ether to give orange crystals which could not be identified owing to its minor quantity.

Treatment of Benzoylphenylacetylene (I) with Liquid Ammonia. — A solution of the ketone I (2.0 g., 0.01 mol.) in dry tetrahydrofuran (30 ml.) was added dropwise while stirring to liquid ammonia (50 ml.). After stirring for 5 min., ammonium chloride (0.6 g., 0.011 mol.) was added in a portion, and the mixture was stirred for a further $4\frac{1}{4}$ hr. The ammonia was evaporated, water (50 ml.) and ether (50 ml.) were added to the residue under stirring. The ethereal solution was washed successively with dilute sodium hydroxide solution, water, dilute sulfuric acid and water, and dried (Na_2SO_4). The solvent was evaporated and the residue was distilled giving a yellow liquid (1.6 g., 80%), b. p. 153.5~160°C/2 mmHg. The infrared spectrum of the liquid was identical with that of an authentic specimen of I. The entire liquid crystallized when seeded with a piece of crystal of ketone I.

Reaction of Diphenyl 1, 3-Diphenyl-2-propen-1-on-3-yl Phosphate (V) with Sodium Amide. — A solution of the phosphate V[4] (4.6 g., 0.01 mol.) in dry tetrahydrofuran was added dropwise to a stirred suspension of sodium amide (0.04 mol.) in liquid ammonia (45 ml.) during a period of 15 min. The reaction mixture was stirred for $3\frac{1}{2}$ hr., and the ammonia was evaporated. A saturated solution of sodium chloride was added to the residue under stirring and cooling (ice-bath). A small amount of insoluble material was removed by filtration, and the aqueous layer was extracted with ether. The combined organic solutions were washed with sodium chloride solution, and dried (Na_2SO_4). The solvent was evaporated, and the residue deposited a solid on standing. Light petroleum was added to complete the deposition. The solid (0.8 g., 66%) was separated and then recrystallized 3 times from benzene to give benzamide as white plates, m. p. 126~127°C, which was undepressed on admixture with the authentic specimen.

Found: C, 69.43; H, 5.95; N, 11.37. Calcd. for C_7H_7ON: C, 69.40; H, 5.83; N, 11.56%.

Distillation of the unsolidified part gave phenylacetylene as a colorless liquid, b. p. 60~100°C (bath)/75~77.5 mmHg, which was converted to the mercury derivative according to the usual method[6]. Recrystallization of the mercury compound gave colorless needles or plates, m. p. 123.5~124.5°C, undepressed on admixture with authentic specimen.

The Reaction of Diphenyl β-Methoxycarbonyl-α-styryl Phosphate (VI) with Sodium Amide. —A solution of the phosphate VI[4] (15.0 g., 0.037 mol.) in dry ether (500 ml.) was added dropwise to a stirred suspension of sodium amide (0.2 mol.) in liquid ammonia (250 ml.) during $1\frac{3}{4}$ hr. The mixture was stirred for $1\frac{1}{4}$ hr. The ammonia was evaporated, and a solution of ammonium chloride (12.0 g.) in water (38 ml.) was added to the residue under stirring and cooling (ice-bath). A small amount of insoluble material was filtered and washed with ether. The organic layer separated from the lower (solution A) was washed successively with dilute sodium hydroxide solution (solution B) and water, and dried. The ethereal solution was worked up yielding phenylacetylene (1.05 g., 28%) as a colorless liquid, b. p. 72~73°C/73~73.5 mmHg, whose infrared spectrum and mercury derivative (colorless needles or plates, m. p. 123~124°C) were identical with those of the authentic specimen.

Phenylpropiolic acid or its derivatives were not detected at all whether in the solution A nor in the residue in the distilling flask.

Phenol was obtained from the ether-extract of

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* All melting points and boiling points are not corrected.

5) E. André, *Ann. chim.*, [8] **29**, 564 (1913). Cf., K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, **1946**, 39.

6) J. R. Johnson and W. L. McEwen, *J. Am. Chem. Soc.*, **48**, 471 (1926).

the acidified solution B. Benzoylation by Schotten-Baumann's method afforded phenyl benzoate (4.1 g., 28% based on VI), which was crystallized from ethanol yielding light yellow needles, m. p. 67.5~69.5°C, undepressed on admixture with authentic specimen.

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