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1957

SovietRxiv

Abstract

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Chemistry

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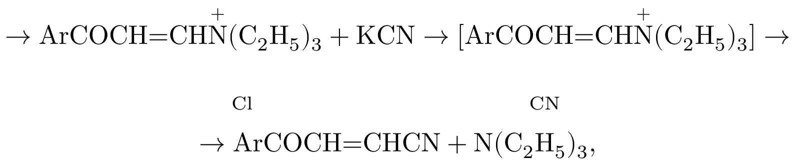
BETA-CYANOVINYL KETONES

Earlier, in our work together with N. K. Kochetkov, the varied use of β-chlorovinyl ketones for obtaining heterocyclic systems was shown ([1]). The synthesis of the corresponding cyanides would obviously broaden these possibilities still further. Although the chlorine atom in β-chlorovinyl ketones, despite its vinylic position, undergoes nucleophilic substitutions ([2]), and, for example, the corresponding iodides and rhodanides are readily obtained by exchange, exchange with cyanide salts could not be carried out ([3]). In nonpolar media the reaction does not proceed; in polar media resinification occurs.

We succeeded in obtaining β-cyanovinyl ketones through quaternary β-acylvinyltrialkylammonium salts ([4–6]). The latter are readily formed by the action of β-chlorovinyl ketones on tertiary amines.

$$\mathrm{RCOCH{=}CHCl + N(R_1)_3 \rightarrow RCOCH{=}CH\overset{+}{N}(R_1)_3 \cdot Cl^-}.$$

β-Acylvinyltrialkylammonium salts, under the action of potassium cyanide in aqueous solution, exchange the trialkylammonium group for cyano. Thus, β-benzoylvinyltriethylammonium chloride in aqueous medium readily reacts with potassium cyanide to form phenyl-β-cyanovinyl ketone (yield 77% of theory) and triethylamine. Other aryl-β-cyanovinyl ketones were obtained in an analogous manner in good yields.



$$\rightarrow \mathrm{ArCOCH{=}CH\underset{Cl}{\overset{+}{N}}(C_2H_5)_3 + KCN \rightarrow [ArCOCH{=}CH\underset{CN}{\overset{+}{N}}(C_2H_5)_3]} \rightarrow$$

$$\rightarrow \mathrm{ArCOCH{=}CHCN + N(C_2H_5)_3},$$

where $\mathrm{Ar} = \mathrm{C_6H_5},\ \mathrm{O{-}ClC_6H_4{-}},\ \mathrm{n\text{-}BrC_6H_4{-}}$.

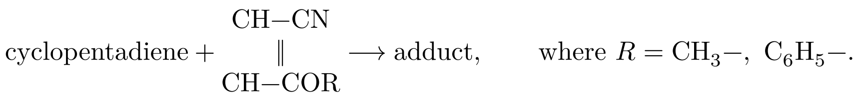
For more rapid removal of aryl-β-cyanovinyl ketones from the alkaline solution, the reaction was carried out in an aqueous-ether or aqueous-benzene medium, so that, as they formed, the aryl-β-cyanovinyl ketones passed into the organic layer.

Alkyl-β-cyanovinyl ketones could be obtained only by the action of potassium cyanide on aqueous solutions of β-acylvinyltrimethylammonium chloride salts.

The reaction with potassium cyanide was carried out in an aqueous–benzene medium. The β-acylvinyltrimethylammonium cyanide salt formed in this process readily decomposes on heating on a water bath, and trimethylamine is removed as a gas from the reaction mass. In addition, it is very important to note that the reaction must be carried out in a buffer solution of trimethylamine hydrochloride, since alkyl-β-cyanovinyl ketones change very rapidly under the action of aqueous alkali solutions. In this way we obtained methyl-, ethyl-, and propyl-β-cyanovinyl ketones, but in lower yields than aryl-β-cyanovinyl ketones.

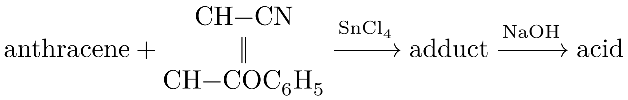
This variant, used also for the synthesis of aryl-β-cyanovinyl ketones—with the sole difference that cooling is employed—gives the most satisfactory results. In this case phenyl-β-cyanovinyl ketone was obtained in almost quantitative yield and was sufficiently pure. It is also interesting to note that by this procedure *p*-nitrophenyl-β-cyanovinyl ketone was obtained, whereas the method involving the use of triethylamine gave no positive results.

The structure of the cyanovinyl ketones obtained is confirmed by the following reactions. β-Cyanovinyl ketones give semicarbazones. Owing to the presence of an active double bond, they readily enter into the Diels–Alder reaction. With cyclopentadiene, methyl- and phenyl-β-cyanovinyl ketones react on heating, as a result of which the corresponding adducts are formed.



$$\text{cyclopentadiene} + \begin{array}{c}\mathrm{CH{-}CN}\\ \| \\ \mathrm{CH{-}COR}\end{array} \longrightarrow \text{adduct}, \qquad \text{where } R = \mathrm{CH_3}-,\ \mathrm{C_6H_5}-.$$

The 2-benzoyl-3-cyanobicyclo-(2,2,1)-heptene-5 isolated as a result of this reaction was saponified to the corresponding acid. In addition, an adduct of phenyl-β-cyanovinyl ketone with anthracene was obtained in the presence of stannic chloride (7). This adduct was saponified to β-benzoyl-α,β-endo-9,10-dihydroanthracenepropionic acid, previously obtained by Barnett and co-workers (8).



$$\text{anthracene} + \begin{array}{c}\mathrm{CH{-}CN}\\ \| \\ \mathrm{CH{-}COC_6H_5}\end{array} \xrightarrow{\mathrm{SnCl_4}} \text{adduct} \xrightarrow{\mathrm{NaOH}} \text{acid}$$

Thus we have established that quaternary salts of β-acylvinylammonium can be used in the ketovinylation reaction. This is also confirmed by the fact that the reaction of β-propionylvinyltrimethylammonium chloride with sodium sulfide gives di-(β-propionylvinyl) sulfide in good yield.

$$\mathrm{C_3H_7COCH{=}CHN^+(CH_3)_3Cl^-} + \mathrm{Na_2S} \rightarrow \mathrm{(C_3H_7COCH{=}CH)_2S} + \mathrm{N(CH_3)_3} + \mathrm{NaCl}.$$

Experimental Part

Alkyl-β-cyanovinyl ketones. To a solution of 0.1 mol of alkyl-β-chlorovinyl ketone in 100 ml of absolute acetone, while cooling with solid carbon dioxide with acetone, with stirring, was added about 10 ml of liquid trimethylamine. A white precipitate formed. The reaction mixture was left for 30 min at room temperature; then the precipitate was filtered off and rapidly and thoroughly washed with absolute acetone. The yield of β-acylvinyltrimethylammonium chloride was almost quantitative (β-acetylvinyltrimethylammonium chloride: m.p. 135–136°).

Found, %: C 51.30; H 8.66; Cl 21.64; N 8.39
$C_7H_{14}ONCl$. Calculated, %: C 51.37; H 8.62; Cl 21.71; N 8.56

For the synthesis of β-cyanovinyl ketones, the quaternary salts isolated from the reaction were used without additional purification. To a solution of 5 g of trimethylamine hydrochloride in 5 ml of water were added the obtained β-acylvinyltrimethylammonium chloride, 150 ml of benzene, and 0.1 mol of potassium cyanide. The reaction mixture was vigorously stirred and heated on a water bath. When the bath temperature reached 50–60°, a solution was added dropwise···

tion of 0.05 mol of potassium cyanide in 15 ml of water. With the first drops of the potassium cyanide solution, evolution of gaseous trimethylamine was observed. After the vigorous foaming had ceased, the benzene layer was carefully decanted, and a fresh portion of benzene (100 ml) was added to the flask. Heating and stirring were continued. After an hour this operation was repeated, and so on 3–4 times. The collected benzene solutions were dried over sodium sulfate and, after distillation of the benzene, were distilled in vacuo. The main fraction was the alkyl-β-cyanovinyl ketones. Their semicarbazones were obtained by the usual method and recrystallized from alcohol (Table 1).

Table 1

Alkyl-β-cyanovinyl ketones and their semicarbazones	MR_D found	MR_D calc.	Yield, %	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
$CH_3COCH{=}CHCN$, b.p. 73°/11 mm, m.p. 27°; n_D^{27} 1.4590; d_4^{27} 1.0050	25.87	24.65	40.3	62.86	63.15	5.41	5.26	14.93	14.73
Semicarbazone, m.p. 227–228° (decomp.)	–	–	–	47.37	47.36	5.48	5.26	36.94	36.84
$C_2H_5COCH{=}CHCN$, b.p. 77°/8 mm; n_D^{20} 1.4620; d_4^{20} 0.9814	30.57	29.27	21.7	65.79	66.03	6.62	6.42	12.87	12.84
Semicarbazone, m.p. 187–188° (decomp.)	–	–	–	50.61	50.60	5.95	6.02	33.79	34.07

Alkyl-β-cyanovinyl ketones and their semicarbazones	MR_D found	MR_D calc.	Yield, %	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
$C_3H_7COCH{=}CHCN$, b.p. 85–85.5° (8 mm); n_D^{20} 1.4594; d_4^{20} 0.9593	35.14	33.88	54.6	68.12	68.29	7.46	7.33	11.42	11.38
Semicarbazone, m.p. 158–159°	–	–	–	53.04	53.33	6.53	6.66	31.06	31.11

Aryl-β-cyanovinyl ketones. Variant A. To a solution of 5 g of trimethylamine hydrochloride in 5 ml of water was added the quaternary ammonium salt obtained from 0.1 mol of an aryl-β-chlorovinyl ketone and 10 ml of liquid trimethylamine by the method described above. Then 100–150 ml of benzene was poured in, and, with stirring and cooling, a solution of 0.15 mol of potassium cyanide in 30 ml of water was added dropwise. After one hour the benzene layer was decanted and a fresh portion of benzene (50 ml) was added. This operation was repeated 3 times. The collected benzene solutions were washed with 5% hydrochloric acid, and after drying over sodium sulfate the benzene was removed in vacuo. The remaining crystalline substance is the aryl-β-cyanovinyl ketone (Table 2).

Table 2

Aryl-β-cyanovinyl ketone	Yield, % var. A	Yield, % var. B	m.p., °C	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.	Hal, % found	Hal, % calc.
$C_6H_5COCH=CHCN$*	94	89	82	76.47	76.43	4.65	4.46	8.99	8.98	–	–
o-$ClC_6H_4COCH=CHCN$	97	59.08	140-143	62.66	62.66	3.19	3.13	7.19	7.31	18.68	18.53
n-$BrC_6H_4COCH=CHCN$	–	44.07	155-156.5	51.09	50.87	2.65	2.54	5.75	5.94	34.05	33.87
n-$NO_2C_6H_4COCH=CHCN$	77	–	147-150	59.17	59.45	3.01	2.97	–	–	–	–

* The semicarbazone was obtained by the usual method, decomp. temp. 183° (from alcohol).

Found, %: C 56.84; H 5.25; N 23.93
$C_{11}H_{10}ON_4 \cdot H_2O$. Calculated, %: C 56.89; H 5.17; N 24.13

Variant B. To 0.1 mol of an aryl-β-chlorovinyl ketone in 50 ml of abs. acetone, with cooling, 10.1 g of triethylamine was slowly added. After 1.5–2 hours the precipitate of β-arylvinyltriethylammonium chloride that had formed was filtered off and quickly washed with abs. acetone. The resulting salt was dissolved in 30 ml of water, 200 ml of ether or benzene was added, and, with vigorous stirring and cooling with ice water, a solution of 0.51 mol of potassium cyanide in 50 ml of water was added dropwise. As a result of further treatment, as described in Variant A, the corresponding aryl-β-cyanovinyl ketones were obtained (see Table 2).

2-Acetyl-3-cyanobicyclo(2,2,1)heptene-5. To a solution of 2 g of methyl β-cyanovinyl ketone in 10 ml of dry benzene, 1.5 g of cyclopentadiene was added. After the spontaneous heating had ceased, the mixture was heated for 2 hours on a water bath. The next day, after removal of the benzene, the residue was distilled in vacuo. Yield 2.3 g (68% of theory), b.p. 145-146°/13-12 mm. A yellowish viscous liquid, n_D^{20} 1.4962, d_4^{20} 1.091. MR_D found 43.18. MR_D calculated 43.34.

Found, %: C 74.60; H 6.94; N 8.83
$C_{10}H_{11}ON$. Calculated, %: C 74.53; H 6.83; N 8.80

2-Benzoyl-3-cyanobicyclo(2,2,1)heptene-5. Obtained analogously from 2 g of phenyl β-cyanovinyl ketone and 1 g of cyclopentadiene in 5 ml of dry benzene. Yield 1.8 g (64.3% of theory), m.p. 87-88° (from alcohol).

Found, %: C 80.81; H 5.74; N 6.34
$C_{15}H_{13}ON$. Calculated, %: C 80.71; H 5.83; N 6.27

2-Benzoylbicyclo(2,2,1)heptene-5-carboxylic acid-3. A mixture of 0.48 g of 2-benzoyl-3-cyanobicyclo(2,2,1)heptene-5, 0.2 g of caustic potash, 5 ml of alcohol, and 2 ml of water was heated on a water bath until evolution of ammonia had completely ceased. The reaction mass was diluted with water and filtered. The filtrate was acidified with hydrochloric acid, and the oil that separated was extracted with ether. The ether extracts were washed with water; after drying over sodium sulfate, the ether was distilled off. The residue was an oil, which crystallized on rubbing. Yield 0.4 g (76.9% of theory), m.p. 108–109° (from aqueous alcohol).

Found, %: C 74.38; H 5.83
$C_{15}H_{14}O_3$. Calculated, %: C 74.37; H 5.78

Nitrile of β-benzoyl-α,β-endo-9,10-dihydroanthracenepropionic acid. To a solution of 1 g of phenyl β-cyanovinyl ketone in 30 ml of dry benzene, 1.13 g of anthracene and 2 g of anhydrous stannic chloride were added. The mixture was heated to boiling for 15 min and decomposed with dilute hydrochloric acid. The benzene layer was separated, and the aqueous layer was extracted with benzene. The benzene solution was washed with water, dried over sodium sulfate, and the benzene was evaporated in vacuo. After recrystallization from benzene, the residue gave 1.7 g of substance (yield 79.8% of theory), m.p. 203–204°.

Found, %: C 86.10; H 5.12; N 4.02
$C_{24}H_{17}ON$. Calculated, %: C 85.94; H 5.07; N 4.17

The nitrile of β-benzoyl-α,β-endo-9,10-dihydroanthracenepropionic acid, after saponification with alcoholic alkali, gives β-benzoyl-α,β-endo-9,10-dihydroanthracenepropionic acid with m.p. 232° (from alcohol).

Literature data (8): m.p. 234°. A mixed melting-point test gives no depression of the melting point.

Di-(β-propionylvinyl) sulfide was obtained by adding a solution of 0.1 mole of sodium sulfide to a solution of 0.2 mole of β-propionylvinyltrimethylammonium chloride in water. Yield 88.13%, m.p. 80° (from alcohol).

Found, %: C 63.72; H 7.94; S 14.36
$C_{12}H_{18}O_2S$. Calculated, %: C 63.71; H 7.96; S 14.15

Institute of Organoelement Compounds
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Received
12 III 1957

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Note: Figure translations are in progress. See original paper for figures.

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