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Abstract

Full Text

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INTERACTION OF BROMOCYANOACETIC ESTER WITH AROMATIC ALDEHYDES UNDER THE CONDITIONS OF THE REFORMATSKY AND WIDEQVIST REACTIONS

(Presented by Academician M. M. Shemyakin, February 29, 1964)

Previously (^{1}) we showed that, in the interaction of aromatic aldehydes with bromomalonic ester by the Reformatsky reaction, the principal reaction products are the diethyl esters of the corresponding α,α'-dicarbethoxy-β-arylglutaric acids, together with a small amount of arylidenemalonic esters. It was of interest to study the possibility of using bromocyanoacetic ester as the halogen-containing component of the Reformatsky reaction. There is only one mention of such a reaction.

Fig. 1. NMR spectrum of 2,3-dicyano-2,3-dicarbethoxy-1-phenylcyclopropane (in carbon tetrachloride)

In 1929, Bacher (^{2}) described the preparation of benzylidenecyanoacetic ester in the interaction of benzyl with bromocyanoacetic ester by the Reformatsky reaction.

The interaction of benzaldehyde with bromocyanoacetic ester and zinc in a molar ratio of 1:1:1.2 under conditions analogous to those described earlier (1 hour of boiling in tetrahydrofuran (^{1})) is accompanied by strong resinification; benzylidenecyanoacetic ester (I) is obtained in 19% yield, and a colorless crystalline substance, $C_{17}H_{16}N_2O_4$, in 12% yield, which, as will be shown below, proved to be 2,3-dicyano-2,3-dicarbethoxy-1-phenylcyclopropane (II). When the amount of bromocyanoacetic ester and zinc is doubled (i.e., at a ratio of 1:2:2.4), the yield of I increases somewhat (25%), while the yield of II decreases (6%); whereas when only the amount of bromocyanoacetic ester is doubled (ratio 1:2:1.2), the yield of I does not change, and that of II sharply increases (55%), with a considerable decrease in resinification. Carrying out the reaction for 4.5 hours at 5-

10° and at the indicated ratio of reagents gives approximately the same result (yield of I 20%, and of II—52%).

The structure of II follows from the analytical data and from the presence in the IR spectrum of an absorption band at 1005 cm^{-1}, characteristic of cyclopropane derivatives (^{3}). The correctness of this formula was confirmed by mass-spectrometric determination of the molecular weight (312)* and by the data of the NMR spectrum (Fig. 1),

* The data of the mass-spectrometric study of II and its derivatives will be published separately.

Table 1

Arylidene cyanoacetic esters

Nos.	R	Yield*, %	B.p. (°C (mm)) of fraction II	M.p. (from alcohol) (°C)	M.p. according to literature data (°C)
I	H	19	124—152 (0.12)	47—48	49 (6)[4]
II	*n*-Cl	3	154—182 (0.35)	90—91	92 (6)
III	*o*-Cl	14	138—169 (0.2)		
IV	*n*-CH_3O	39	158—178 (0.15)	81—82	83 (6)
V	*o*-CH_3O	29	150—173 (0.18)	75—76	76—77 (7)

* Yield is given calculated for fraction II.

Table 2

2,3-Dicyano-2,3-dicarbethoxy-1-arylcyclopropanes

Nos.	R	Yield (%)	B.p. (°C (mm))	M.p. (°C)	Found (%) C	Found (%) H	Found (%) Cl	Found (%) N
I	H[1]	55	162—164 (0.15)	97—88	65.17	5.07		8.71
I	H[1]	55	162—164 (0.15)	97—88	65.04	5.11		8.80

Nos.	R	Yield (%)	B.p. (°C (mm))	M.p. (°C)	Found (%) C	Found (%) H	Found (%) Cl	Found (%) N
II	*n*-Cl[2]	68	176–178 (0.05)	95–96	58.80	4.56	10.25	8.21
II	*n*-Cl[2]	68	176–178 (0.05)	95–96			10.15	8.16
III	*o*-Cl[2]	57	163 (0.08)[4]		59.00	4.40	10.38	8.06
III	*o*-Cl[2]	57	163 (0.08)[4]		59.11	4.52	10.41	7.94
IV	*n*-CH_3O[3]	31	186–188 (0.15)		63.17	5.29		8.13
IV	*n*-CH_3O[3]	31	186–188 (0.15)		63.11	5.16		8.11
V	*o*-CH_3O[3]	49	173–174 (0.1)		63.24	5.34		8.14
V	*o*-CH_3O[3]	49	173–174 (0.1)		63.34	5.50		8.05

[1] $C_{17}H_{16}N_2O_4$. Calculated, %: C 65.37; H 5.16; N 8.96.
[2] $C_{17}H_{15}ClN_2O_4$. Calculated, %: C 58.87; H 4.37; Cl 10.22; N 8.07.
[3] $C_{18}H_{18}N_2O_5$. Calculated, %: C 63.15; H 5.29; N 8.17.
[4] n_D^{20} 1.5300.

Table 3

Characteristic bands in the IR spectra of 2,3-dicyano-2,3-dicarbethoxy-1-arylcyclopropanes (in cm^{-1})

Nos.	R	C N	C=O	C-O	Character of substitution of the benzene ring: mono-	Character of substitution of the benzene ring: 1,2-di	Character of substitution of the benzene ring: 1,4-di	Cyclopropane ring
I	H	2255	1760	1264	700			1005
I	H			1204	748			
II	*n*-Cl	2260	1763	1250			856	1006
II	*n*-Cl			1214				
III	*o*-Cl	2260	1755	1260		760		1000–1020
III	*o*-Cl			1220				
IV	*n*-CH_3O	2255	1760	1250			853	1008*
IV	*n*-CH_3O			1208				
V	*o*-CH_3O	2260	1758	1258		758		1008*
V	*o*-CH_3O			1208				

* Shoulder.

in which the peak with $\tau = 5.8$ can be due only to the presence of the methine hydrogen of the cyclopropane ring.

The general character of the reaction studied by us was confirmed in examples of *o*- and *p*-chloro-, as well as *o*- and *p*-methoxybenzaldehydes. In all cases the reaction proceeded analogously to that described above for unsubstituted benzaldehyde, and, along with the corresponding arylidenecyanoacetic esters, usually obtained in insignificant yields (Table 1), the corresponding II were obtained (Table 2). Their structure is confirmed by analytical data and IR spectra (Table 3). The presence of the cyclopropane ring is indicated by the absorption band in the range 1000-1020 cm^{-1} (3) in the spectra of all the compounds studied. The latter is absent in the IR spectra of the diethyl esters of α, α'-dicarbethoxy-β-arylglutaric acids, studied by us earlier (1), which are close to II in structure but do not contain a cyclopropane ring.

2,3-Dicyano-2,3-dicarbethoxy-1-arylcyclopropanes have not been described in the literature; only their analogs are known. Thus, in 1963 Hart and Freeman (4), by the interaction of aldehydes with bromomalononitrile in an aqueous-alcoholic medium in the presence of iodide ions (by the Wideqvist reaction (5)), obtained a series of 2,2,3,3-tetracyano-1-alkyl(aryl)cyclopropanes. The structure of these compounds was proved on the basis of NMR spectral data, the peaks due to the methine hydrogen of the cyclopropane ring being located in approximately the same region as in II (for 2,2,3,3-tetracyano-1-phenylcyclopropane $\tau = 5.07$).

We carried out the interaction of benzaldehyde with bromocyanoacetic ester under the conditions of the Wideqvist reaction (4, 5) and, in 46% yield, obtained a substance identical with II in melting point and IR spectral data. We carried out an analogous reaction with *p*-chlorobenzaldehyde and obtained the *p*-chloro-substituted II, identical with that obtained by the Reformatsky method.

The NMR spectrum of II was recorded by V. I. Sheichenko, to whom the authors express their deep gratitude.

Experimental part

Interaction of aromatic aldehydes with bromocyanoacetic ester by the Reformatsky method. To a mixture of 0.1 mole of aldehyde, 8 g of activated zinc (1), 0.3 g of sublimate, and 50 ml of dry tetrahydrofuran, 0.2 mole of bromocyanoacetic ester is added dropwise over 30 min. As the latter is added, the temperature gradually rises and the reaction mass begins to boil. Boiling is continued for another 30 min, the mixture is cooled to 5–10°, and the solution is decanted from the unreacted zinc into a mixture of 50 ml of acetic acid and 150 g of ice. Then 30 ml of benzene is added, the mixture is stirred for 20 min, the organic layer is separated, it is washed with 30 ml of water, and the aqueous layer is extracted twice with benzene (35 ml each). The combined extract is washed with sodium bisulfite solution (2 portions of 100 ml), 10% soda solution, and repeatedly with water to strictly neutral reaction, dried over magnesium sulfate, and the solvents are distilled off under reduced pressure in a stream of nitrogen. The residue is distilled in vacuo in a stream of nitrogen, collecting three fractions: I—consisting of unreacted aldehyde and cyanoacetic ester; II—of arylidenecyanoacetic ester; and III—of 2,3-dicyano-2,3-dicarbethoxy-1-arylcyclopropane. In a number of cases fractions II and III crystallize on trituration with alcohol. The results of the experiments are given in Tables 1 and 2.

Interaction of benzaldehyde with bromocyanoacetic ester by the Wideqvist method. To a solution of 8.52 g (0.08 mole) of benzaldehyde and 30.72 g (0.16 mole) of bromocyanoacetic ester in 100 ml of alcohol, with stirring over 30 min, a solution of 28 g of potassium iodide in 75 ml of water is added; this is accompanied by a slight

with an increase in temperature (to ~30°) and the liberation of iodine. A precipitate gradually begins to fall out in the form of needles; it is filtered off after 48 hours and washed with alcohol. Yield of 2,3-dicyano-2,3-dicarbethoxy-1-phenylcyclopropane: 11.6 g (46%), m.p. 97–98° (from alcohol).

Analogously, from 0.01 mole of *p*-chlorobenzaldehyde and 0.02 mole of bromocyanoacetic ester in 20 ml of alcohol, 1.1 g (32%) of 2,3-dicyano-2,3-dicarbethoxy-1-(*p*-chlorophenyl)cyclopropane is obtained, m.p. 95–96°.

IR spectra were recorded on a UR-10 spectrophotometer in a paste with Vaseline oil. The NMR spectrum was recorded on a JNMC-60 high-resolution spectrometer in a solution of carbon tetrachloride.

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