Some New Addition Reactions of Acetylenecarboxylic Acids and Their Esters

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1960

SovietRxiv

Abstract

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Chemistry

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Some New Addition Reactions of Acetylenecarboxylic Acids and Their Esters

(Presented by Academician M. I. Kabachnik on 18 III 1960)

In the course of work on the synthesis of compounds with potential physiological activity, we have carried out reactions of acetylenecarboxylic acids with: a) arylsulfinic acids, b) cyclic thioamides, and c) cyclic amidines.

a) **Reaction of acetylenedicarboxylic acid (ADC) and its esters with arylsulfinic acids.**
ADC and its esters in many reactions show similarity to benzoquinone. Evidently, this is connected with the presence in these compounds of related conjugated systems

$$O{=}C{-}C{\equiv}C{-}C{=}O \quad \text{and} \quad O{=}C{-}C{=}C{-}C{=}O.$$

Thus, like quinone ([1–5]), ADC adds alcohols and phenols ([6,7]), mercapto compounds ([8,9]), and amines ([10,11]). One of the characteristic reactions of benzoquinone is the addition reaction of arylsulfinic acids ([12,13]). For ADC, a similar reaction, as far as we know, has not been described in the literature. It turned out that ADC reacts smoothly upon heating in glacial acetic acid with arylsulfinic acids; the methyl and ethyl esters of ADC react similarly, but in methanolic solution. As a result of the reaction, crystalline sulfones were obtained which, according to analytical data, are products of the addition of two molecules of sulfinic acids to ADC.

Upon heating with a solution of caustic potash, the disulfones obtained are smoothly hydrolyzed with elimination of sulfinic acids, which were identified in the form of adducts with benzoquinone. The disulfones obtained from ADC esters (compounds 2, 3, 5, 6, Table 1) readily react with Na, which indicates the presence of an "acidic" hydrogen in the group

$$-OC-CH-SO_2-.$$

In the IR spectrum of compounds 1, 2, 4, 5, strong absorption bands were found in the region 1335–1320 cm^{-1} and 1154–1150 cm^{-1}, characteristic of asymmetric and symmetric vibrations of the SO_2 group ([15]). In the spectrum of compound 1 (Table 1), bands are absent in the region 1464–1407 cm^{-1}, which

could be assigned to scissoring vibrations of the CH_2 group ([15]). All this makes it possible to propose structure (I)* for the addition products (Table 1).

b) **Reactions of acetylenecarboxylic acids and their esters with cyclic thioamides.**
It is of interest to determine whether compounds containing a potential thiol group, namely cyclic thioamides such as benzthiazolin-2 and benzimidazolin-2, can react with acetylenecarboxylic acids similarly to mercaptans. We carried out the reaction of interaction of the indicated–

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* Addition to both carbon atoms of the triple bond of ADC also occurs in other cases, for example, in the reaction of ADC and its methyl ester with thioacetic acid ([14]).

Table 1

Products of addition of arylsulfinic acids to acetylenedicarboxylic acid and its esters
ROOC–CH(SO_2Ar)–CH(SO_2Ar)–COOR (I)

No.	R	Ar	Name	m.p., °C	Yield, %	Empirical formula	Cl, % found	C, % calc.	H, % found	H, % calc.	S, % found	S, % calc.
1	H	C_6H_5	α,α'-Di-(phenylsulfonyl)succinic acid	189–190 (dec. comp.)	31	$C_{16}H_{14}O_8S_2$		48.28	3.29	3.52	15.95	16.07
2	CH_3	C_6H_5	Dimethyl ester of α,α'-di-(phenylsulfonyl)succinic acid	172–174	38	$C_{18}H_{18}O_8S_2$		50.75	4.11	4.23	15.10	15.05
3	C_2H_5	C_6H_5	Diethyl ester of α,α'-di-(phenylsulfonyl)succinic acid	124–126	34	$C_{20}H_{22}O_8S_2$		52.80	4.77	4.84	14.03	14.10

No.	R	Ar	Name	m.p., °C	Yield, %	Empirical formula	C, % found	C, % calc.	H, % found	H, % calc.	S, % found	S, % calc.
4	H	C_6H_5	α,α'-Di-(*p*-tolylsulfonyl)succinic acid	182–184 (decomp.)	33	$C_{18}H_{18}O_8S_2$	50.51	50.75	4.01	4.23	15.00	15.05
5	CH_3	*p*-CH_3–C_6H_4	Dimethyl ester of α,α'-di-(*p*-tolylsulfonyl)succinic acid	171–172	67	$C_{20}H_{22}O_8S_2$	52.96	52.80	4.88	4.84	14.06	14.10
6	C_2H_5	*p*-CH_3–C_6H_4	Diethyl ester of α,α'-di-(*p*-tolylsulfonyl)succinic acid	164–166	95	$C_{22}H_{26}O_8S_2$	54.74	54.70	5.44	5.40	13.30	13.28
7	H	*p*-NO_2–C_6H_4	α,α'-Di-(*p*-nitrophenylsulfonyl)succinic acid	192–194 (decomp.)	76	$C_{16}H_{12}O_{12}N_2S_2$ *	38.51	38.33	2.61	2.46	12.89	13.20

* Found % N 5.65. Calculated % 5.73.

Table 2

Products of addition of cyclic thioamides to acetylenecarboxylic acids and their esters

No.	R	R′	X	Name	m.p., °C	Yield, %	Empirical formula	N, % found	N, % calc.	S, % found	S, % calc.
1	H	H	S	β-(2-Benzthiazolylthio)acrylic acid	190–191 (decomp.)	57	$C_{10}H_7O_2NS_2$ *	5.70	5.89	27.15	26.96
2	H	C_2H_5	S	Ethyl ester of β-(2-benzthiazolylthio)acrylic acid	78–80	55	$C_{12}H_{11}O_2NS_2$ **	5.05	5.28	24.31	24.15
3	H	H	NH	β-(2-Benzimidazolylthio)acrylic acid	198–200 (decomp.)	63	$C_{10}H_8O_2N_2S$	12.72	12.73	14.50	14.51
4	H	C_2H_5	NH	Ethyl ester of β-(2-benzimidazolylthio)acrylic acid	177–178	89	$C_{12}H_{12}O_2N_2S$	10.37	11.22	12.94	12.80
5	COOH	H	S	2-Benzthiazolylthiofumaric acid	154–156 (decomp.)	67	$C_{11}H_7O_4NS_2$	5.22	4.98	22.73	22.75
6	COOH	H	NH	2-Benzimidazolylthiofumaric acid	196–197 (decomp.)	80	$C_{11}H_8O_4N_2S$	10.76	10.60	12.16	12.12

* Found %: C 50.81; H 2.83. Calculated %: C 50.60; H 2.95.
** Found %: C 54.33; H 4.35. Calculated %: C 54.30; H 4.15.

Addition products of cyclic amines to acetylenecarboxylic esters

$$R{-}C{\equiv}CH{-}COOR' \quad (III)$$

$$N\langle\ \rangle$$

Table 3

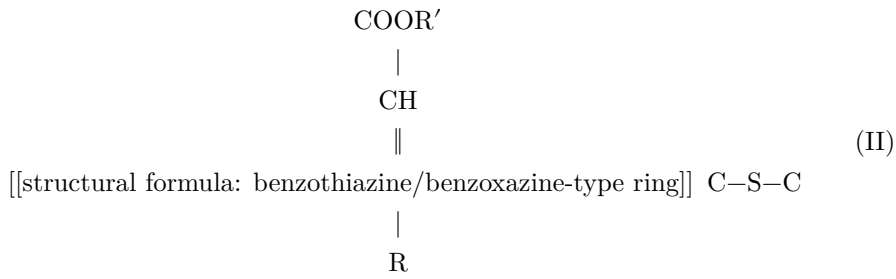
No.	R	R′	–N	Name	b.p., °C/mm	m.p., °C	Yield, %	Empirical formula	Cal. % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
1	H	C_2H_5	aziridinyl	Ethyl ester of β-(N-ethylenimino)acrylic acid *	65 – 67/3	–	51	$C_7H_{11}O_2N$	59,83 59,60		8,10	7,80	9,41	9,93
2	CH_3	C_2H_5	aziridinyl	Ethyl ester of β-(N-ethylenimino)crotonic acid **	75 – 76/3	–	59	$C_8H_{13}O_2N$	62,07 61,80		8,60	8,38	9,31	9,04
3	C_6H_5	C_2H_5	aziridinyl	Ethyl ester of β-(N-ethylenimino)cinnamic acid ***	135 – 136/3	–	71	$C_{13}H_{15}O_2N$	71,85 71,90		6,95	6,92	6,46	6,45
4	COOCH$_3$	CH_3	aziridinyl	Dimethyl ester of N-ethyleniminofumaric acid	71 – 72	–	16	$C_8H_{11}O_4N$	52,12 51,89		6,11	5,95	7,56	7,57

No.	R	R′	–N	Name	b.p., °C/mm	m.p., °C	Yield, %	Empirical formula	Cal. % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
5	H	C_2H_5	pyrrolidyl-	Ethyl ester of β-(N-pyrrolidyl)acrylic acid	41 – 43		55	$C_9H_{15}O_2N$	63,82	63,80	8,99	8,85	8,05	8,25
6	CH_3	C_2H_5	pyrrolidyl-	Ethyl ester of β-(N-pyrrolidyl)crotonic acid	28 – 30		70	$C_{10}H_{17}O_2N$	65,32	65,55	9,35	9,28	7,51	7,64
7	C_6H_5	C_2H_5	pyrrolidyl-	Ethyl ester of β-(N-pyrrolidyl)cinnamic acid	58 – 60		78	$C_{15}H_{19}O_2N$	73,31	73,46	7,84	7,75	5,98	5,71
8	COOCH$_3$	CH_3	pyrrolidyl-	Dimethyl ester of N-pyrrolidylfumaric acid	69 – 71		54	$C_{10}H_{15}O_4N$	56,05	56,30	6,80	7,04	6,72	6,57
9	H	C_2H_5	morpholyl-	Ethyl ester of β-(N-morpholyl)acrylic acid	29 – 31		67	$C_9H_{15}O_3N$	58,15	58,30	8,41	8,11	7,92	7,56

No.	R	R′	–N	Name	b.p., °C/mm	m.p., °C	Yield, %	Empirical formula	Cal. % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
10	CH_3	C_2H_5	morpholyl	Ethyl ester of β-(N-morpholyl)crotonic acid	31 – 33		69	$C_{10}H_{17}O_3N$	60,26	60,25	8,56	8,54	7,31	7,02
11	C_6H_5	C_2H_5	morpholyl	Ethyl ester of β-(N-morpholyl)cinnamic acid	49 – 51		68	$C_{15}H_{19}O_3N$	68,07	68,98	7,50	7,28	5,66	5,37
12	COOCH$_3$	CH_3	morpholyl	Dimethyl ester of N-morpholylfumaric acid	57 – 59		52	$C_{10}H_{15}O_5N$	52,29	52,48	6,67	6,54	5,85	6,11

$*$ n_D^{20} 1,4843, d_4^{20} 1,0277. $**$ n_D^{20} 1,4938, d_4^{20} 1,0040. $***$ n_D^{20} 1,5673, d_4^{20} 1,0817.

thiones with ADC and its esters, and also with propiolic acid and its ester, in ethyl acetate or alcohol on heating. In this way well-crystallizing substances were obtained, which are products of addition of one molecule of a cyclic thioamide to acetylenecarboxylic acids and their esters, of structure (II) (Table 2).



(II)

In the IR spectra of the compounds obtained, 1, 3, 5, 6 (Table 2), in the region 1900-800 cm^{-1}, absorption bands at 960-920 cm^{-1} were found, which should be assigned to CH vibrations at a double bond with trans disposition of the substituents [15], and weak bands in the region 700-670 cm^{-1}, attributable to stretching vibrations of the sulfide group [16]. Thus, it has been shown that cyclic thioamides are capable, in addition reactions, of giving derivatives of the thiol form. Since, under the conditions of carrying out the reaction, a substantial shift of the thione form into the equilibrium thiol form is unlikely, the reaction evidently proceeds with "transfer of the reaction center" [17].

c) **Reactions of esters of acetylenecarboxylic acids with cyclic secondary amines.** The literature contains brief information on the addition of piperidine to esters of acetylenecarboxylic acids [6,11,18,19]. Reactions with other cyclic secondary amines have not been described. We have carried out reactions of the esters of acetylenedicarboxylic, tetrolic, propiolic, and phenylpropiolic acids with ethylenimine, pyrrolidine, and morpholine. In connection with the above-mentioned analogy of ADC with benzoquinone, these compounds (especially the compounds with ethylenimine) may be of interest, since ethylenimino-benzoquinones exhibit antitumor action [20].

The reactions were carried out by interaction of amines with esters of acetylenecarboxylic acids in the cold. The products obtained are colorless viscous oils which, on standing, crystallize into low-melting crystalline substances*. The elemental composition of the substances does not change upon transition from the liquid state to the crystalline state. IR-spectroscopic data make it possible to assume that the liquid products have a cis structure, while crystallization is associated with transition to the trans form. (For the solid substances, absorption bands were found in the region 990-960 cm^{-1}, characteristic of CH at a double bond with trans disposition of the groups [15].) According to elemental-analysis data, the products obtained should be assigned the general formula (III) (Table 3).

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Received
5 III 1960

REFERENCES

1. E. Knoevenagel, C. Bückel, Ber., **34**, 3993 (1901).
2. J. Snell, A. Weissberger, J. Am. Chem. Soc., **61**, 450 (1939).
3. M. Schubert, J. Am. Chem. Soc., **69**, 712 (1947).
4. F. Kehrmann, Ber., **23**, 897 (1890).
5. W. Anslow, H. Raistrick, J. Chem. Soc., **1939**, 1446.
6. F. Feist, Lieb. Ann., **345**, 100 (1906).
7. L. Owen, J. Chem. Soc., **1945**, 385.
8. B. Weibull, Arkiv Kemi, **3**, 225 (1951).
9. A. Blomquist, J. Wolinsky, J. Org. Chem., **23**, 551 (1958).
10. Ch. Moureu, I. Lazennec, Zbl., **1907**, 1, 25; C. R., **143**, 596 (1906).
11. F. Gray et al., J. Am. Chem. Soc., **73**, 3577 (1951).
12. O. Hinsberg, Ber., **27**, 3259 (1894).
13. J. Walker, J. Chem. Soc., **1945**, 630.
14. L. Owen, M. Sultanbawa, J. Chem. Soc., **1949**, 3109.
15. V. West, *Application of Spectroscopy in Chemistry*, Foreign Literature Publishing House, 1959, pp. 439, 455, 461.
16. L. Bellamy, *Infrared Spectra of Molecules*, Foreign Literature Publishing House, 1957, p. 409.
17. A. N. Nesmeyanov, M. I. Kabachnik, *ZhOKh*, **25**, 41 (1955).
18. S. Ruhemann, A. Cunnington, J. Chem. Soc., **75**, 954 (1899).
19. F. Straus, W. Voss, Ber., **59**, 1681 (1926).
20. W. Gauss, Ber., **91**, 2216 (1958).

* The exception is the products of the reaction of ethylenimine with esters of propiolic, tetrolic, and phenylpropiolic acids (compounds 1-3, Table 3), which do not crystallize.

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