REACTION OF TETRACYANOETHYLATED KETONES WITH ALDEHYDES. SYNTHESIS OF 3-IMINO-2,6-DIOXABICYCLO[2.2.2]OCTANES

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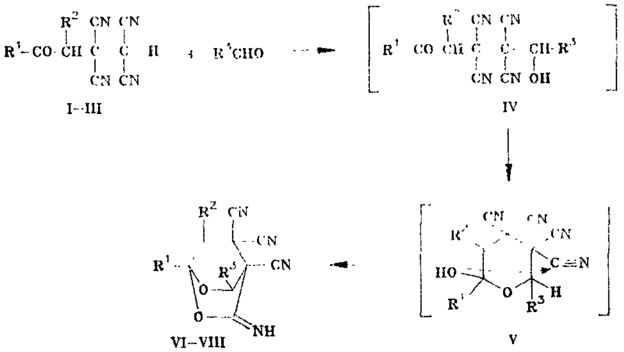
The products of the addition of tetracyanoethylene to ketones react smoothly with aliphatic, aromatic, and heterocyclic aldehydes to give 4,8,8-tricyano-3-imino-2,6-dioxabicyclo[2.2.2]octanes. The structures of the reaction products were confirmed by ^{13}C, IR, and mass spectral data.

In [1] it was shown that the aliphatic and aliphatic-aromatic ketones upon reaction with tetracyanoethylene (TCE) in the presence of "molecular silver" form tetracyanoethylation products. According to the data in [2, 3], cyano-substituted pyridones can be obtained by the action of alcohols on the latter, whereas tetracyanourethanes can be obtained upon reaction with aryl isocyanates [2, 3].

We have recently established that the reaction of TCE with ketones can be realized in the presence of water and alcohols or under the influence of UV light [4]. Since we have recently shown [5-9] that cyano-substituted 2-amino-4,5-dihydrofurans are formed in the reaction of symmetrical tetracyanoethane with carbonyl compounds, it seemed of interest to study the pathway of the reaction of tetracyanoethylated ketones I-III with aldehydes. We found that freshly prepared ketones I-III in an alcoholic medium, even at room temperature, react smoothly with aliphatic, aromatic, and heterocyclic aldehydes to give, apparently, unstable carbinols IV, which undergo initial cyclization to cyano-substituted 2-hydroxypyrans V and then to 3-imino-2,6-dioxabicyclo[2.2.2]octanes VI-VIII.

In the IR spectra of VI-VIII (Table 2) one observes intense absorption bands at 3250-3320 cm^{-1}, which are characteristic for an amino group, as well as bands of stretching vibrations of a C=N group at 1710-1725 cm^{-1} [10, 11].

Scheme 1



I, VI $R^1=CH_3$, $R^2=H$; II, VII $R^1=R^2=CH_3$; III, VIII $R^1+R^2=(CH_2)_4$

Two signals are characteristic for the ^{13}C NMR spectra of VI and VII (see Table 3): the signal of the carbon atom bonded to the imino group at 154-159 ppm and the signal of the carbon atom bonded to the two oxygen atoms at 94-107 ppm. The assignment was made by means of recording of the spectra under off-resonance conditions and by means of the spectra of the structural analog [12].

The presence of a low-intensity peak (W_M = 0.1-1.5%, Tables 4 and 5) of the molecular (M^+) or, more often, the protonated molecular ion (MH^+) is characteristic for the mass spec-

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TABLE 1. Characteristics of Substituted 2,6-Dioxabicyclo-[2.2.2]octanes VIa, b, VIIa-h, and VIIIa-h

Compounds	R^3	mp, °C	Reaction time, h	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
VIa	H	108—113 (dec.)	0,5	55,5	3,8	25,8	$C_{10}H_8N_4O_2$	55,5	3,7	25,9	84
VIb	C_2H_5	112—114	1	59,2	4,9	23,1	$C_{12}H_{12}N_4O_2$	59,0	4,9	22,9	89
VIIa	H	151—153	0,6	57,5	4,5	24,3	$C_{11}H_{10}N_4O_2$	57,4	4,3	24,3	92
VIIb	CH_3	128—130	0,4	59,2	5,1	22,7	$C_{12}H_{12}N_4O_2$	59,0	5,0	22,9	95
VIIc	C_2H_5	124—126	0,8	60,5	5,4	21,6	$C_{13}H_{14}N_4O_2$	60,5	5,4	21,7	95
VIId	C_3H_7	148—150	0,6	61,8	5,6	20,7	$C_{14}H_{16}N_4O_2$	61,8	5,9	20,6	92
VIIe	i-C_3H_7	105—106	0,3	61,9	6,0	20,4	$C_{14}H_{16}N_4O_2$	61,8	5,9	20,6	91
VIIf	2-Furyl	154—155 (dec.)	1	60,9	4,2	19,0	$C_{15}H_{12}N_4O_2$	60,8	4,0	18,9	90
VIIg	C_6H_5	175—177	4	66,8	4,6	18,1	$C_{17}H_{14}N_4O_2$	66,7	4,6	18,3	94
VIIh	3-$NO_2C_6H_4$	173—174	3	58,2	3,8	19,9	$C_{17}H_{13}N_5O_4$	58,1	3,7	19,9	94
VIIIa	H	127—129	1,3	61,1	4,7	22,0	$C_{13}H_{12}N_4O_2$	60,9	4,7	21,9	91
VIIIb	CH_3	151—152	0,4	62,3	5,1	20,7	$C_{14}H_{14}N_4O_2$	62,2	5,2	20,7	91
VIIIc	C_2H_5	170—172	1	63,5	5,6	19,8	$C_{15}H_{16}N_4O_2$	63,4	5,6	19,7	92
VIIId	C_3H_7	134—136	0,8	64,5	5,8	18,8	$C_{16}H_{18}N_4O_2$	64,4	6,0	18,8	93
VIIIe	i-C_3H_7	169—172	1,5	64,7	6,2	18,6	$C_{16}H_{18}N_4O_2$	64,4	6,0	18,8	90
VIIIf	2-Furyl	164—166 (dec.)	0,5	63,4	4,5	17,2	$C_{17}H_{14}N_4O_3$	63,3	4,3	17,4	86
VIIIg	C_6H_5	180—184	3,5	68,7	4,9	16,7	$C_{19}H_{16}N_4O_2$	68,7	4,8	16,9	91
VIIIh	3-$NO_2C_6H_4$	166—167	3,3	60,6	4,1	18,4	$C_{19}H_{15}N_5O_4$	60,5	4,0	18,6	96

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[a] Compounds VIa, b, VIIa, c-e, g, and VIIIb-e, g from iso-C_3H_7OH; VIIb and VIIIf from $CH_3COOC_2H_5$; VIIf from C_3H_7OH—$CH_3COOC_2H_5$ (1:1); VIIh from $CH_3COOC_2H_5$—$(CH_3)_2CO$ (1:1); VIIIa from $(CH_3)_2CO$—C_6H_{12} (1:1); and VIIIh from dioxane.

TABLE 2. IR and Mass Spectra of VIa, b, VIIa-h, and VIIIa-h

Compound	IR spectrum, cm^{-1}	Mass spectra[a] (relative intensities, %)
VIa	3290, 2265, 1720	217 (0,4)[b], 173 (8), 149 (16), 83 (29), 73 (40), 71 (39), 69 (52), 67 (26), 60 (37), 57 (100), 55 (96)
VIb	3285, 2270, 1720	245 (1)[b], 201 (11), 187 (4), 186 (8), 160 (4), 158 (4), 96 (14), 59 (65), 58 (40), 43 (100), 41 (13)
VIIa	3320, 2270, 1720	245 (1)[b], 201 (11), 187 (4), 186 (8), 160 (4), 158 (4), 96 (14), 59 (65), 58 (40), 43 (100), 41 (13)
VIIb	3280, 2262, 1720	245 (1)[b], 201 (8), 200 (16), 186 (10), 110 (43), 109 (33), 93 (25), 72 (11), 61 (25), 45 (25), 43 (100)
VIIc	3330, 3295, 2265, 1720	259 (2)[b], 215 (7), 200 (4), 110 (100), 109 (37), 93 (76), 72 (29), 61 (42), 59 (79), 57 (13), 43 (29)
VIId	3300, 2268, 1720	273 (2)[b], 229 (12), 200 (13), 110 (100), 109 (25), 93 (32), 73 (82), 72 (42), 61 (27), 55 (62), 43 (25)
VIIe	3300, 2270, 1720	273 (4)[b], 229 (78), 137 (27), 135 (20), 120 (27), 110 (100), 109 (20), 93 (51), 72 (55), 61 (51), 56 (49)
VIIf	3290, 3170, 3140, 2270, 1725	296 (5), 253 (4), 200 (8), 182 (20), 144 (36), 98 (9), 97 (100), 96 (37), 95 (20), 72 (6), 43 (91)
VIIg	3282, 3273, 2270, 1719	307 (0,8)[b], 127 (2), 108 (7), 107 (100), 106 (11), 105 (18), 79 (30), 77 (40), 72 (32), 51 (31), 50 (13)
VIIh	3290, 2270, 1720	351 (1), 173 (10), 152 (41), 151 (68), 150 (65), 146 (22), 105 (33), 77 (18), 76 (20), 51 (20), 43 (100)
VIIIa	3300, 3270, 2270, 1712	257 (2)[b], 213 (69), 171 (42), 161 (17), 144 (36), 141 (50), 135 (30), 107 (100), 106 (30), 67 (30), 55 (33)
VIIIb	3280, 2268, 1725	271 (3)[b], 227 (100), 226 (89), 185 (26), 183 (74), 182 (26), 136 (40), 135 (100), 107 (58), 98 (58), 55 (53)
VIIIc	3290, 2265, 1715	285 (2)[b], 255 (8), 241 (40), 226 (55), 183 (37), 136 (50), 135 (32), 107 (25), 98 (32), 59 (100), 41 (45)
VIIId	3250, 3195, 2265, 1720	299 (2)[b], 255 (20), 241 (40), 226 (55), 183 (37), 136 (50), 135 (32), 107 (25), 98 (32), 59 (100), 41 (45)
VIIIe	3280, 2265, 1739	299 (4)[b], 255 (100), 226 (55), 200 (19), 183 (27), 163 (19), 136 (80), 135 (20), 98 (62), 56 (67), 55 (47)
VIIIf	3290, 3170, 3140, 2270, 1720	322 (6), 226 (16), 199 (19), 182 (17), 172 (16), 144 (21), 98 (28), 97 (100), 96 (43), 95 (43), 41 (32)
VIIIg	3285, 2270, 1710	332 (10), 226 (24), 199 (17), 193 (11), 108 (38), 107 (40), 106 (51), 105 (100), 98 (54), 79 (51), 77 (91)
VIIIh	3296, 3290, 2270, 1720	377 (3), 226 (37), 198 (16), 161 (17), 152 (100), 151 (60), 150 (76), 105 (34), 77 (84), 51 (45)

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[a] The peaks of the molecular (protonated molecular) ion and the 10 most intense peaks are presented. [b] Protonated molecular ion.

TABLE 3. ^{13}C NMR Spectra of VIa, b and VIIIa-h

Compound	Chemical shift, ppm							
	$C_{(1)}$	$C_{(3)}$	$C_{(4)}$ ($C_{(8)}$)	$C_{(5)}$	$C_{(7)}$	$C_{(8)}$ ($C_{(4)}$)	$C_{(9)}$	$C_{(10, 11)}$
VIa	107,59	158,53	48,98	66,40	43,37	39,54	110,88	114,44; 113,06
VIb	95,40, 94,70[a],	159,73	52,47[a], 51,31[a]	72,40 70,48	46,94, 44,75	36,82[a], 35,47[a]	113,66, 113,58	115,06; 117,89, 118,62; 118,65
VIIa	97,24	155,82	51,14	64,06	46,15	33,72	109,89	112,75; 109,21
VIIb	109,05	155,71	53,59	70,24	45,83	45,45	110,16	112,83; 110,34
VIIc	108,81	155,60	53,84	74,28	45,88	44,54	110,24	112,80; 110,43
VIId	108,92	155,55	53,79	73,07	45,86	44,70	110,26	112,85; 110,51
VIIe	108,56	155,71	54,68	77,58	45,75	43,05	110,72	112,83; 110,56
VIIf	109,70	154,91	b	69,94	45,91	b	111,31	111,21; 113,01

[a] Signals of the cis and trans isomers. [b] The signals of the $C_{(4)}$ and $C_{(8)}$ atoms cannot be identified because of the low concentration of the solution of VIIf in d_6-DMSO.

TABLE 4. Intensities of the Peaks of the Principal Characteristic Ions in the Mass Spectra of V and VII ($\%\Sigma_{39}$)

Compound	W_M[a]	F_1	F_3	F_4	F_5	F_6	F_7	F_8	F_9
VIb	0,37	3,26	11,11	3,92	—	1,89	18,30	2,35	28,10
VIIa	0,68	2,66	—	1,69	13,69	9,37	—	0,75	29,56
VIIb	0,39	2,01	2,13	10,48	8,15	6,21	6,21	1,47	24,45
VIIc	0,31	1,17	1,94	16,45	6,06	12,55	12,99	2,28	4,54
VIId	0,33	1,67	5,68	13,38	3,34	4,35	11,04	1,77	3,34
VIIe	0,46	8,23	5,76	10,50	2,05	5,35	2,26	1,60	1,64
VIIf	1,43	0,76	8,00	—	—	—	21,33	—	19,42
VIIh	0,17	0,11	12,01	—	—	—	7,14	—	17,53

[a] $W_M = (\Sigma I_M/\Sigma_{39})\cdot 100\%$.

TABLE 5. Intensities of the Peaks of the Principal Characteristic Ions in the Mass Spectra of VIII ($\%\Sigma_{39}$)

Compound	W_M[a]	F_1	F_2	F_4	F_6	F_7	F_8	F_{10}	F_{11}	F_{12}
VIIIa	0,14	6,66	0,90	0,61	2,93	—	1,28	9,60	2,93	3,20
VIIIb	0,16	5,85	3,38	2,31	5,85	3,08	5,23	3,38	1,78	3,08
VIIIc	0,22	4,08	3,31	5,10	3,31	10,20	5,61	2,55	1,09	1,68
VIIId	0,26	2,67	3,34	4,01	2,22	12,92	5,12	1,49	0,86	7,79
VIIIe	0,32	7,55	4,72	6,04	1,51	1,54	4,15	0,38	0,77	3,59
VIIIf	1,25	0,30	—	—	1,12[b]	15,21	0,34	6,62[c]	6,62[d]	2,14
VIIIg	1,47	0,10	—	—	8,40[b]	3,69	0,28	4,70[c]	9,24[d]	1,61
VIIIh	0,41	—	—	—	—	9,95	—	6,02[c]	7,59[d]	1,25

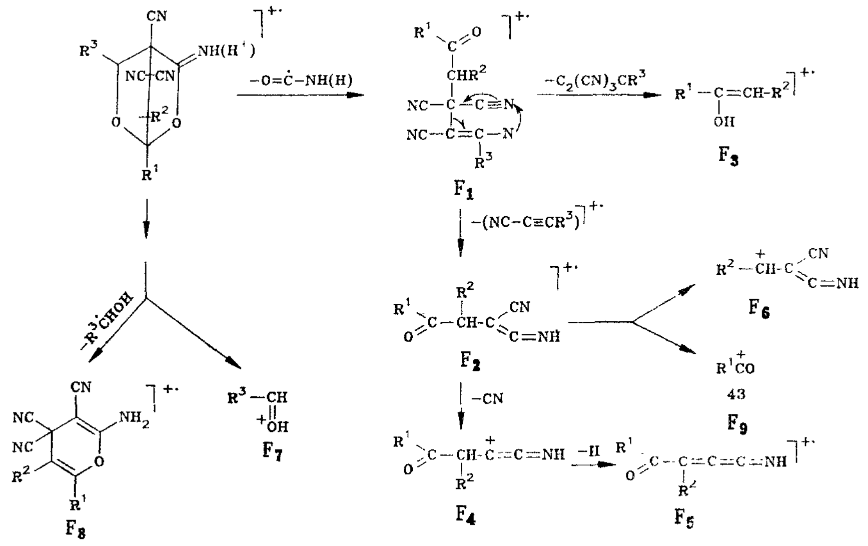
[a] $W_M = (\Sigma I_M/\Sigma_{39})\cdot 100\%$. [b] $[F_7 = 2H—CO]^+$. [c] $[F_7—H]^+$. [d] $[F_7—2H—CO]^+$.

tra of VI-VIII. The latter is evidently formed in the ionization chamber due to ion-molecular reactions. The elementary compositions of M^+ and MH^+ are confirmed by the results of the high-resolution mass spectra. In all likelihood, protonation is realized at the nitrogen atom of the imino group, since we have observed monotypic character of the subsequent fragmentation of the F^1 ion (Scheme 2), which is formed as a result of the elimination by the M^+ or MH^+ ions of the resulting HNCO or H_2NCO fragments, respectively. The most intense peaks in the mass spectra of VI and VII are the peaks of F_3, F_6, F_7, and F_9 ions, whereas the overall fraction of the F_1—F_9 ions in the total ion current constitutes 37-69%, which indicates high selectivity of the fragmentation.

The fragmentation of the molecular (protonated) ions of VIII proceeds via a similar scheme; however, in addition, one observes additional pathways of fragmentation of the F_3—F_5 ions associated with cleavage of the cyclohexane fragment and the formation of $CH_2C{\equiv}O^+$ (F_{12}), $[F_4—C_2H_5]^+$ (F_{10}), and $[F_5—C_2H_5]^+$ (F_{11}) ions. In the case of aryl- and hetaryl-substituted VIIIa-h, owing to the migration of the site of localization of the charge in M^+ on the aromatic substituent, the fraction of F_1—F_{12} ions in the total ion current decreases; however, the intensities of the peaks of the $[F_7—H]^+$, $[F_7—2H]^+$, and $[F_7—2H—CO]^+$ increases sharply. In the case of VIIhv the $[F_7—H]^+$ ion subsequently initially loses an NO_2 group (m/z 105, $\%\Sigma_{39}$ 3.40), and only then the CO molecule (m/z 77, $\%\Sigma_{39}$ 8.4).

Thus the reaction of tetracyanoethylated ketones with aldehydes may serve as a convenient preparative method for the synthesis of diverse derivatives of 3-imino-2,6-dioxabicylo[2.2.2]octane.

Scheme 2



EXPERIMENTAL

Monitoring of the course of the reaction was realized by TLC on plates of the Silufol type (UV-254) in an ethyl acetate—hexane system (3:1) with development by iodine vapors. The ^{13}C NMR spectra were recorded with a Bruker WH-90 apparatus at an operating frequency of 22.63 MHz with hexamethyldisiloxane (HMDS) as the standard.

The high- and low-resolution mass spectra were obtained with a Varian MAT-212 spectrometer at an ionization energy of 70 eV.

Synthesis of VI-VIII. A 55-60-mmole sample of the aldehydes* in 10 ml of isopropyl alcohol was added in a single portion at room temperature with stirring in a nitrogen atmosphere to a suspension of 50 mmole of freshly prepared and dried tetracyano ketone I-III in 50 ml isopropyl alcohol; in the process we observed a small exothermic effect. A 150-200-ml sample of water was added to the reaction mixture,† the product was separated, washed with water, dried, and recrystallized.

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*Excess aldehyde does not interfere with the reaction; in the case of solid aldehydes the reagent ratio was 1:1.

†In most cases the product was isolated in the form of crystals prior to dilution with water.

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REACTION OF 2-AMINOBENZOXAZOLES WITH COMPOUNDS WITH ACTIVATED MULTIPLE BONDS

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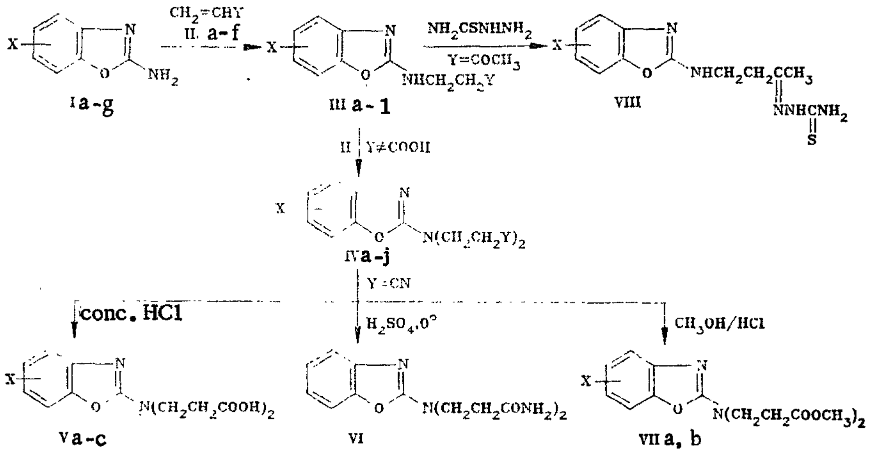
The reaction of 2-aminobenzoxazoles with activated alkenes of the acrylic acid type and its derivatives and methyl vinyl ketone proceeds in the presence of basic catalysts to give products of mono- and diaddition at the exocyclic nitrogen atom. The reaction of 5(6)-substituted 2-aminobenzoxazoles with esters of propyl and acetylenedicarboxylic acids in the absence of catalysts leads to the production of condensed 2-oxopyrimidines. The effect of substituents and the reaction conditions on the course of the process was investigated.

A considerable number of reactions involving the addition of heterocyclic amines to compounds that contain multiple carbon—carbon bonds have been described in the literature. The possibility of the synthesis, on the basis of these reactions, of new condensed heterocyclic compounds with potential pharmacological activity have continued to be of interest to synthetic chemists.

Continuing our study of the reactions of condensed 2-aminooxazoles with compounds with activated multiple bonds [1, 2], we have studied the reaction of 2-aminobenzoxazoles (Ia) and its derivatives (Ib-g) with activated alkenes and alkynes: esters of acrylic acid (IIa, b), acrylonitrile (IIc), acrylamide (IId), acrylic acid (IIe), methyl vinyl ketone (IIf), dimethyl acetylenedicarboxylate (IXa), and ethyl propiolate (IXb).



I a X=H; b X=5-CH_3; c X=5-Cl; d X=5-NO_2; e X=6-Cl; f X=6-Br; g X=6-NO_2;
II a Y=$COOCH_3$; b Y=$COOC_2H_5$; c Y=CN; d Y=$CONH_2$; e Y=COOH; f Y=$COCH_3$;
IIIa, c, g, k X=H; b, i X=5-Cl; d X=6-Cl; e X=6-Br; f, j X=5-NO_2; h, *l* X=5-CH_3;
a Y=$COOC_2H_5$; b Y=$COOCH_3$; c-f Y=CN; g-i Y=$COCH_3$; j-*l* Y=COOH; IVa, d, i
X=H; b, e X=5-CH_3; c-f X=5-Cl; g, j X=6-Cl; h X=6-Br; a-c Y=$COOCH_3$; d-h
Y=CN; i, j Y=$COCH_3$; V a X=H; b X=5-CH_3; c X=6-Cl; VI X=H; VIIIa X=H; b
X=5-Cl

We have found that 2-aminobenzoxazoles react with activated alkenes only upon heating in the presence of basic catalysts. The reaction proceeds with the formation of products of mono- (III) and diaddition (IV) at the exocyclic nitrogen atom. The yields of III and IV depend substantially on the structures of the reagents and the reaction conditions.

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