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Reactions of Substituted 2,3,7-Triazabicyclo[3.3.0]oct-3-ene-4-carboxylic Acid Esters with Halogens*

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Abstract—Substituted 2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylic acid esters react with chlorine and bromine to give the corresponding 4-halo-2,3,7-triazabicyclo[3.3.0]oct-2-ene-4-carboxylates. Heating of the latter to 120°C under reduced pressure leads to elimination of nitrogen molecule and formation of 6-halo-3-azabicyclo[3.1.0]hexane-6-carboxylates.

1-Halogen-substituted cyclopropanecarboxylic acid esters are synthesized most frequently by reactions of geminal dihalocyclopropanes with organolithium compounds and subsequent treatment of 1-halocyclopropyllithium with carbon dioxide [1], by reactions of diazo compounds with α-haloacrylic acid esters [2], and by reactions of diazohaloacetic acid esters with unsaturated compounds [3]. In the present communication we report on the synthesis of 1-halo-1-cyclopropanecarboxylates via thermal elimination of nitrogen from dihydropyrazoles [4].

1-Substituted 7-aryl-6,8-dioxo-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylic acid esters **Ia**–**In** were obtained from the corresponding diazoacetates and *N*-substituted maleimides [5]. The reactions of esters **I** with chlorine in chloroform at 0°C gave 69–84% of 7-aryl-4-chloro-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]-oct-2-ene-4-carboxylates as mixtures of *endo* (**IIa**–**IIg**) and *exo* isomers (**IIIa**–**IIIg**) at a ratio of (7–10):1 (Scheme 1). The reaction mixtures obtained from esters **Ia**–**Ie** also contained some amount (up to 10%) of cyclopropane derivatives formed by elimination of nitrogen from the corresponding dihydropyrazoles.

Pure *endo* isomers **IIa**, **IIb**, **IId**, and **IIe** were isolated by crystallization. The structure of esters **IIa**–**IIg** was derived from the data of elemental analysis and spectral measurements (Tables 1, 2). Compounds **IIa**–**IIe** showed in the ^{1}H NMR spectra a singlet from 5-H in the region δ 3.6–3.8 ppm; the corresponding signal of *exo* isomers **IIIa**–**IIIe** was observed in a stronger field (at δ 3.43 ppm). The ^{1}H NMR spectra of compounds **IIf** and **IIg** having no substituent in the bridgehead position contain a signal from the 1-H proton at δ 6.3–6.5 ppm. The position of this signal is typical of protons on C^3 in 4,5-dihydro-3*H*-pyrazoles. The 5-H signal is located at δ 4.0–4.2 ppm. The corresponding signals of *exo* isomers **IIIf** and **IIIg** are observed at δ 6.5–6.8 and 3.8–4.0 ppm, respectively. In the ^{13}C NMR spectrum of ester **IIe** the C^4 signal appears at δ_C 105.4 ppm. The UV spectra of **IIb**, **IIe**, and **IIf** are characterized by absorption in the region 320–330 nm, which also supports their structure.

The reaction with chlorine of ester **Ih** having an electron-donor methoxy group in the aromatic ring is accompanied by chlorination of the aromatic substituent. As a result, a 3.5:1 mixture of *endo* and *exo* isomers **IIh** and **IIIh** is formed. The structure of compounds **IIh** and **IIIh** was proved by the elemental analyses (Table 1) and spectral data (Table 2).

Heating of pyrrolopyrazoles **IIa**–**IIh** and **IIIa**–**IIIh** at 120°C under reduced pressure resulted in elimination of nitrogen and formation of substituted 6-chlorobicyclo[3.1.0]hexane-6-carboxylic acid esters as mixtures of *endo* (**IVa**–**IVh**) and *exo* isomers (**Va**–**Vh**) in up to 87% yield. ^{1}H NMR study of the reaction mixtures showed that thermolysis of *endo* isomers **II** gives only *endo*-cyclopropanes **IV**, whereas from *exo* isomers **III** mixtures of isomeric cyclopropanes **IV** and **V** are obtained. Thus thermolysis of isomeric mixture **II**/**III** is accompanied by considerable increase of the fraction of *endo* isomer **IV** in the

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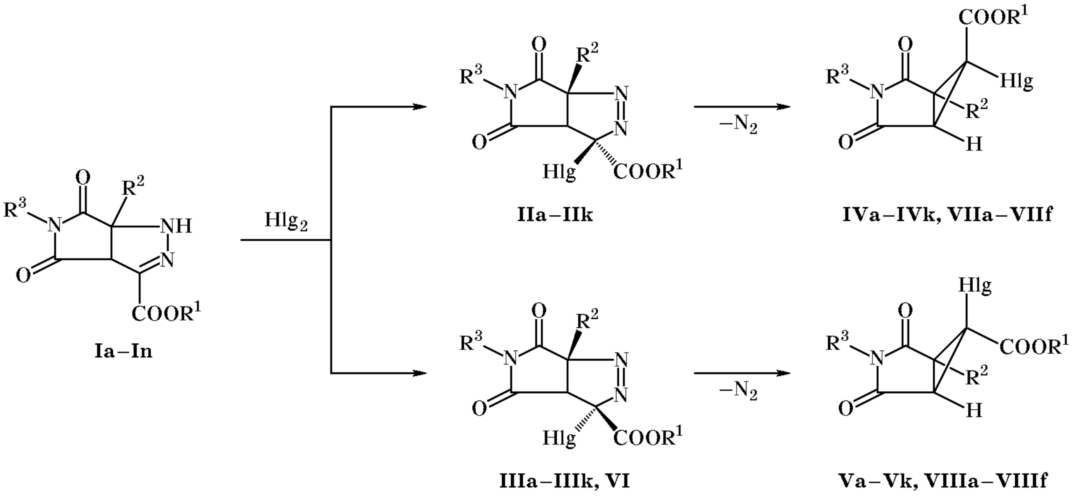
Scheme 1.



I, R^1 = Et, R^2 = Me, R^3 = 4-MeC_6H_4 (**a**); R^1 = R^2 = Me, R^3 = 3,4-$Me_2C_6H_3$ (**b**); R^1 = R^2 = Me, R^3 = 4-MeC_6H_4 (**c**); R^1 = R^2 = Me, R^3 = 3-$CF_3C_6H_4$ (**d**); R^1 = R^2 = Me, R^3 = 4-BrC_6H_4 (**e**); R^1 = Et, R^2 = H, R^3 = *cyclo*-C_6H_{11} (**f**); R^1 = Et, R^2 = H, R^3 = 3-ClC_6H_4 (**g**); R^1 = Et, R^2 = H, R^3 = 4-$MeOC_6H_4$ (**h**); R^1 = Me, R^2 = 4-ClC_6H_4, R^3 = 4-ClC_6H_4 (**i**); R^1 = Me, R^2 = 4-ClC_6H_4, R^3 = Ph (**j**); R^1 = Me, R^2 = 4-ClC_6H_4, R^3 = 4-MeC_6H_4 (**k**); R^1 = Me, R^2 = R^3 = 4-MeC_6H_4 (**l**); R^1 = Me, R^2 = 3-$NO_2C_6H_4$, R^3 = 4-ClC_6H_4 (**m**); R^1 = R^2 = Me, R^3 = 3,4-$Cl_2C_6H_3$ (**n**); **II–V**, R^1 = Et, R^2 = Me, R^3 = 4-MeC_6H_4, Hlg = Cl (**a**); R^1 = R^2 = Me, R^3 = 3,4-$Me_2C_6H_3$, Hlg = Cl (**b**); R^1 = R^2 = Me, R^3 = 4-MeC_6H_4, Hlg = Cl (**c**); R^1 = R^2 = Me, R^3 = 3-$CF_3C_6H_4$, Hlg = Cl (**d**); R^1 = R^2 = Me, R^3 = 4-BrC_6H_4, Hlg = Cl (**e**); R^1 = Et, R^2 = H, R^3 = *cyclo*-C_6H_{11}, Hlg = Cl (**f**); R^1 = Et, R^2 = H, R^3 = 3-ClC_6H_4, Hlg = Cl (**g**); R^1 = Et, R^2 = H, R^3 = 3-Cl-4-$MeOC_6H_3$ (**h**); **IV**, **V**, R^1 = Me, R^2 = R^3 = 4-ClC_6H_4, Hlg = Cl (**i**); R^1 = Me, R^2 = 4-ClC_6H_4, R^3 = Ph, Hlg = Cl (**j**); R^1 = Me, R^2 = 4-ClC_6H_4, R^3 = 4-MeC_6H_4, Hlg = Cl (**k**); **VI**, R^1 = Et, R^2 = Me, R^3 = 4-MeC_6H_4, Hlg = Br; **VII**, **VIII**, R^1 = Et, R^2 = Me, R^3 = 4-MeC_6H_4, Hlg = Br (**a**); R^1 = Me, R^2 = 4-ClC_6H_4, R^3 = Ph, Hlg = Br (**b**); R^1 = Me, R^2 = R^3 = 4-MeC_6H_4, Hlg = Br (**c**); R^1 = Me, R^2 = 4-ClC_6H_4, R^3 = 4-MeC_6H_4, Hlg = Br (**d**); R^1 = Me, R^2 = 3-$NO_2C_6H_4$, R^3 = 4-ClC_6H_4, Hlg = Br (**e**); R^1 = R^2 = Me, R^3 = 3,4-$Cl_2C_6H_3$, Hlg = Br (**f**).

products. Pure *endo* isomers **IVa**, **IVb**, and **IVd**–**IVg** and *exo* isomer **Ve** were isolated by column chromatography. Compounds **Ii**–**Ik** having an aromatic substituent on C^1 reacted with chlorine in dichloroethane at 0°C to afford directly *endo*-cyclopropane carboxylates **IVi**–**IVk**. Presumably, the initially formed dihydropyrazole with an aryl group in the bridgehead position is unstable, and it loses nitrogen even at 0°C. The structure of products **IV** and **V** was confirmed by the data of elemental analysis (Table 1) and spectral measurements (Tables 2, 3). In the IR spectra of these compounds we observed an ester carbonyl band at 1720 cm^{-1}. The position of the 5-H signal in the ^1H NMR spectra of **IV** and **V** strongly depends on the R^2 substituent: when R^2 = Me, it is located at δ 3.4–3.5 ppm for *endo* isomers **IVa**–**IVk** and 2.8–2.9 ppm for *exo* isomers **Va**–**Vk**; when R^2 = Ar, the 5-H signal shifts downfield to ~4.0 ppm due to deshielding effect of the benzene ring.

Treatment of ester **Ia** with bromine in chloroform at 60°C gave a mixture of products from which we isolated by crystallization 36% of ethyl *exo*-4-bromo-1-methyl-6,8-dioxo-7-(4-tolyl)-2,3,7-triazabicyclo[3.3.0]oct-2-ene-4-carboxylate (**VI**). Heating of **VI** at 120°C under reduced pressure resulted in elimination of nitrogen and formation of a mixture of *endo* and *exo* isomers **VIIa** and **VIIIa** at a ratio of 1 : 3.

By reactions of pyrrolopyrazoles **Ij**–**In** with bromine in acetic acid at 70°C we obtained mixtures of *endo*- and *exo*-6-bromo-2,4-dioxo-3-azabicyclo[3.1.0]hexane-6-carboxylates **VIIb**–**VIIf** and **VIIIb**–**VIIIf**. The ratio of *endo* and *exo* isomers was 2.3 (**VIIb**/**VIIIb**), 0.7 (**VIIc**/**VIIIc**), 0.9 (**VIId**/**VIIId**), 1.1 (**VIIe**/**VIIIe**), and 12 (**VIIf**/**VIIIf**). The structure of brominated cyclopropanes **VII** and **VIII** was established on the basis of their elemental compositions and spectral data. The signal from the CH proton of the cyclopropane ring in the ^1H NMR spectra of *endo* isomers **VIIa**–**VIIf** was observed in a weaker field relative to the corresponding signal of the *exo* isomers due to deshielding effect of the *cis*-bromine atom, δ, ppm: 3.58 (**VIIa**), 3.90–4.10 (**VIIb**–**VIIe**), 3.43 (**VIIf**) and 2.85 (**VIIIa**), 3.42–3.60 (**VIIIb**–**VIIIe**), 2.90 (**VIIIf**).

Our results suggest a mechanism involving electrophilic substitution of hydrogen at the nitrogen atom

Table 1. Yields, melting points, and elemental analyses of compounds **II**–**VIII** and **XIII**

Compound no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
IIa	69	98–99[a]	55.01	4.43	11.88	$C_{16}H_{16}ClN_3O_4$	54.94	4.58	12.02
IIb	68	96–98[a]	55.07	4.32	11.94	$C_{16}H_{16}ClN_3O_4$	54.94	4.58	12.02
IIc/IIIc	84	111–112[a]	53.91	4.33	12.34	$C_{15}H_{14}ClN_3O_4$	53.66	4.17	12.52
IId	70	102–104[a]	46.37	2.71	10.52	$C_{15}H_{11}ClF_3N_3O_4$	46.22	2.82	10.78
IIe	71	109–111[a]	41.89	2.51	10.31	$C_{14}H_{11}BrClN_3O_4$	41.96	2.75	10.49
IIf/IIIf	78	101–103[a]	51.47	5.72	12.69	$C_{14}H_{18}ClN_3O_4$	51.30	5.50	12.83
IIg/IIIg	83	116–118[a]	47.01	3.15	11.59	$C_{14}H_{11}Cl_2N_3O_4$	47.20	3.09	11.80
IIh/IIIh	79	120–122[a]	46.67	3.56	10.61	$C_{15}H_{13}Cl_2N_3O_5$	46.64	3.37	10.88
IVa	73	97–98	59.86	5.07	4.27	$C_{16}H_{16}ClNO_4$	59.73	4.98	4.36
IVb	76	114–115	59.61	5.01	4.19	$C_{16}H_{16}ClNO_4$	59.73	4.98	4.36
IVc/Vc	81	131–133	58.64	4.53	4.31	$C_{15}H_{14}ClNO_4$	58.55	4.55	4.55
IVd	73	103–104	50.01	2.99	3.65	$C_{15}H_{11}ClF_3NO_4$	49.80	3.04	3.87
IVe	73	151–153	45.18	3.03	3.58	$C_{14}H_{11}BrClNO_4$	45.12	2.95	3.76
IVf	72	116–118	56.18	6.00	4.46	$C_{14}H_{18}ClNO_4$	56.10	6.01	4.67
IVg	59	82–83	51.12	3.63	4.09	$C_{14}H_{11}Cl_2NO_4$	51.23	3.35	4.27
IVh	77	205–207	50.18	3.71	3.69	$C_{15}H_{13}Cl_2NO_5$	50.29	3.63	3.91
IVi	94	179–181	53.71	3.04	3.03	$C_{19}H_{12}Cl_3NO_4$	53.73	2.82	3.29
IVj	88	201–202	58.67	3.49	3.46	$C_{19}H_{13}Cl_2NO_4$	58.46	3.33	3.59
IVk	91	207–209	59.44	4.02	3.31	$C_{20}H_{15}Cl_2NO_4$	59.42	3.71	3.47
Ve	14	112–113	45.04	2.99	3.51	$C_{14}H_{11}BrClNO_4$	45.12	2.95	3.76
VI	36	118–120	48.97	4.29	10.25	$C_{16}H_{16}BrN_3O_4$	48.74	4.06	10.66
VIIa/VIIIa	61	87–89	52.61	4.33	3.69	$C_{16}H_{16}BrNO_4$	52.46	4.37	3.82
VIIb/VIIIb	76	149–152	52.51	3.07	3.14	$C_{19}H_{13}BrClNO_4$	52.48	2.99	3.22
VIIc/VIIIc	72	109–111	58.92	4.32	2.88	$C_{21}H_{18}BrNO_4$	58.89	4.24	3.27
VIId/VIIId	81	141–143	53.61	3.48	2.72	$C_{20}H_{15}BrClNO_4$	53.54	3.37	3.12
VIIe/VIIIe	69	98–99	47.18	2.79	5.83	$C_{19}H_{12}BrClN_2O_6$	47.58	2.52	5.84
VIIf/VIIIf	63	163–165	41.32	2.75	3.23	$C_{14}H_{10}BrCl_2NO_4$	41.31	2.48	3.44
XIIIa	91	155–157	57.82	5.87	21.69	$C_{14}H_{17}N_3O_4$	57.73	5.84	21.99
XIIIb	89	164–165	50.59	4.70	17.90	$C_{10}H_{11}N_3O_4$	50.63	4.67	17.71
XIIIc	52	194–196	59.13	4.01	14.54	$C_{14}H_{11}N_3O_4$	58.95	3.89	14.72
XIIId	64	216–218	60.04	4.26	14.37	$C_{15}H_{13}N_3O_4$	60.20	4.38	14.03
XIIIe	68	202–203	52.94	3.04	12.95	$C_{14}H_{10}ClN_3O_4$	52.60	3.13	13.14
XIIIf	72	215[a]	45.84	3.01	11.44	$C_{14}H_{10}BrN_3O_4$	46.18	2.77	11.53
XIIIg	94	222–224	55.39	3.63	13.84	$C_{14}H_{10}FN_3O_4$	55.46	3.32	13.86
XIIIh	86	147–149	52.64	3.21	12.99	$C_{14}H_{10}ClN_3O_4$	52.59	3.13	13.15
XIIIi	73	210–212	51.14	3.15	17.08	$C_{14}H_{10}N_4O_6$	50.92	3.05	16.96
XIIIj	44	211–213	45.63	3.12	10.43	$C_{15}H_{12}BrN_3O_5$	45.71	3.07	10.66
XIIIk	48	128–130	61.58	5.02	13.17	$C_{16}H_{15}N_3O_4$	61.34	4.83	13.41
XIIIl	82	221–223	51.38	3.49	11.86	$C_{15}H_{12}ClN_3O_5$	51.51	3.43	12.02

[a] With decomposition.

with formation of *N*-halogen derivative **IX**, homolytic cleavage of the Hlg–N bond in **IX**, and reaction of allylic radical **X** with the second halogen molecule to give isomeric products **II** and **III** (Scheme 2).

The reduction of chlorocyclopropanes **IVi**–**IVk** with zinc in glacial acetic acid was nonstereospecific and yielded *endo*/*exo*-isomeric methyl cyclopropanecarboxylates **XIa**–**XIc** and **XIIa**–**XIIc** at a ratio of 1 : 1 (Scheme 3). The ^1H NMR spectra of mixtures **XI**/**XII** contained doublets from the cyclopropane ring protons at δ 3.2 and 2.9 ppm ($J = 8$ Hz) and δ 3.5 and 3.0 ppm ($J = 3$ Hz) for the *endo* and *exo* isomers,

Table 2. IR and ^{1}H NMR spectra of compounds **II–VIII** and **XIII**

Comp. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm (J, Hz)
IIa	1030, 1110, 1140, 1250, 1300, 1380 s, 1450, 1520, 1720 v.s, 3050	7.28 d (2H, 8), 7.15 d (2H, 8), 4.42 q (2H, 7), 3.74 s (1H), 2.40 s (3H), 2.01 s (3H), 1.42 t (3H, 7)
IIb	910, 1020, 1110, 1140, 1250, 1300, 1380 s, 1460, 1510, 1720 v.s, 3050	7.28–6.98 (3H), 4.01 s (3H), 3.75 s (1H), 2.29 s (6H), 2.01 s (3H)
IIc[a]	940, 1050, 1110, 1140, 1260, 1310, 1380 s, 1450, 1510, 1720 v.s, 3050	7.33–7.06 (4H), 4.05 s (3H), 3.75 s (1H), 2.42 s (3H), 2.03 s (3H)
IId	900, 1010, 1100, 1140, 1180 s, 1330, 1370, 1460, 1490, 1720 v.s, 3050	7.75–7.45 (4H), 4.04 s (3H), 3.81 s (1H), 2.02 s (3H)
IIe[b]	890, 1020, 1080, 1110, 1130, 1260, 1380 s, 1460, 1490, 1720 v.s, 3050	7.63 d (2H, 8), 7.15 d (2H, 8), 4.03 s (3H), 3.75 s (1H), 2.01 s (3H)
IIf[a]	910, 1040, 1110, 1150, 1270, 1300, 1370 s, 1400, 1460, 1720 v.s, 2940 s	6.31 d (1H, 8), 4.32 m (2H), 3.98 d (1H, 8), 3.76 m (1H), 2.06–1.09 (15H)
IIg[a, c]	910, 1020, 1050, 1110, 1240, 1300, 1370 s, 1440, 1480, 1590, 1730 v.s, 3050	7.61–7.22 (4H), 6.52 d (1H, 8), 4.35 m (2H), 4.23 d (1H, 8), 1.30 t (3H, 7)
IIh[a]	910, 1030, 1070, 1100, 1270 s, 1380, 1440, 1510 s, 1720 v.s, 3050	7.33–7.15 (3H), 6.47 d (1H, 8), 4.35 m (2H), 4.19 d (1H, 8), 3.88 s (3H), 1.30 t (3H, 7)
IVa	870, 930, 970, 1030, 1060, 1150, 1260, 1290, 1390 s, 1460, 1520, 1730 v.s, 3050	7.26 d (2H, 8), 7.17 d (2H, 8), 4.36 q (2H, 7), 3.45 s (1H), 2.40 s (3H), 1.65 s (3H), 1.38 t (3H, 7)
IVb	880, 940, 990, 1010, 1080, 1140, 1170, 1280 s, 1380 s, 1450, 1510, 1720 v.s, 2960, 3050	7.25 m (1H), 7.03 m (2H), 3.93 s (3H), 3.46 s (1H), 2.29 s (6H), 1.64 s (3H)
IVc	890, 940, 1040, 1110, 1140, 1260, 1300, 1380 s, 1450, 1520, 1720 v.s, 3050	7.27 d (2H, 8), 7.18 d (2H, 8), 3.92 s (3H), 3.46 s (1H), 2.39 s (3H), 1.65 s (3H)
IVd	920, 990, 1020, 1080, 1140 s, 1250, 1300, 1330, 1380 s, 1460, 1500, 1720 v.s, 3050	7.0–7.52 (4H), 3.94 s (3H), 3.51 s (1H), 1.67 s (3H)
IVe	900, 990, 1020, 1080, 1140, 1260, 1290 s, 1380 s, 1440, 1490, 1730 v.s, 3050	7.61 d (2H, 8), 7.20 d (2H, 8), 3.95 s (3H), 3.49 s (1H), 1.66 s (3H)
IVf	900, 970, 990, 1020, 1050, 1120, 1270 s, 1370 s, 1460, 1720 v.s, 2940 s	4.30 q (2H, 7), 3.91 m (1H), 3.18 s (2H), 2.06 m (2H), 1.82 m (2H), 1.60 m (1H), 1.34 t (3H, 7), 1.5 m (3H)
IVg	960, 1030, 1070, 1260 s, 1390, 1420, 1450, 1470, 1510 s, 1720 v.s, 3050	7.42–7.19 (4H), 4.38 q (2H, 7), 3.41 s (2H), 1.37 t (3H, 7)
IVh	960, 1030, 1070, 1260 s, 1390, 1420, 1450, 1470, 1510 s, 1740 v.s, 3050	7.37 d (1H, 3), 7.18 d.d (1H, 6, 3), 6.99 d (1H, 6), 4.35 q (2H, 7), 3.93 s (3H), 3.41 s (2H), 1.38 t (3H, 7)
IVi	910, 1020, 1090, 1160, 1250, 1290, 1380 s, 1490 s, 1600, 1720 v.s, 3050	7.48–7.27 (8H), 4.03 s (1H), 3.57 s (3H)
IVj	920, 980, 1020, 1090, 1160, 1250, 1290, 1380 s, 1500 s, 1600, 1720 v.s, 3050	7.52–7.31 (9H), 4.04 s (1H), 3.57 s (3H)
IVk	920, 980, 1020, 1090, 1160, 1250, 1290, 1380 s, 1440, 1520, 1720 v.s, 3050	7.45 s (4H), 7.28 d (2H, 8), 7.17 d (2H, 8), 4.02 s (1H), 3.56 s (3H), 2.40 s (3H)
Ve	900, 990, 1020, 1080, 1140, 1260, 1290 s, 1380 s, 1440, 1490, 1720 v.s, 3050	7.59 d (2H, 8), 7.18 d (2H, 8), 3.81 s (3H), 2.86 s (1H), 1.83 s (3H)
VI[d]	930, 1110, 1140, 1260, 1380 s, 1450, 1520, 1720 v.s, 3050	7.23 d (2H, 8), 7.07 d (2H, 8), 4.30 m (2H), 3.58 s (1H), 2.38 s (3H), 1.97 s (3H), 1.25 t (3H, 7)

Table 2. (Contd.)

Comp. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm (*J*, Hz)
VIIa[a]	1020, 1090, 1120, 1280, 1380 s, 1450, 1520, 1720 v.s, 3050	7.25 d (2H, 8), 7.08 d (2H, 8), 4.35 q (2H, 7), 3.39 s (1H), 2.37 s (3H), 1.63 s (3H), 1.38 t (3H, 7)
VIIb[a]	840, 910, 1020, 1100, 1160, 1290, 1380 s, 1440, 1500, 1600, 1720 v.s, 2970	7.51–7.23 (9H), 3.98 s (1H), 3.54 s (3H)
VIIc[a]	840, 910, 1030, 1100, 1160, 1290, 1380 s, 1440, 1520, 1720 v.s, 2960	7.45–7.12 (8H), 3.95 s (1H), 3.50 s (3H), 2.46–2.37 (6H)
VIId[a]	850, 910, 1020, 1100, 1290, 1380 s, 1440, 1520, 1600, 1720 v.s, 2950	7.48–7.09 (8H), 3.97 s (1H), 3.54 s (3H), 2.40 s (3H)
VIIe[a]	840, 880, 910, 1020, 1100, 1160, 1280, 1380 s, 1440, 1500, 1540, 1720 v.s, 2960	8.36 m (2H), 7.95 d (1H, 3), 7.88 d (1H, 3), 7.73 t (1H, 3), 7.62 t (1H, 3), 7.46 m (2H), 7.33 d (1H, 3), 7.22 d (1H, 3), 4.09 s (1H), 3.56 s (3H)
VIIf	870, 920, 1040, 1080, 1140, 1260, 1290, 1380 s, 1480, 1590, 1720 v.s, 2950	7.54 m (2H), 7.26 m (1H), 3.92 s (3H), 3.43 s (1H), 1.64 s (3H)
XIIIa	900, 950, 1040, 1090, 1170, 1330 s, 1460, 1610, 1730 v.s, 2950, 3410	15.22 br.s (1H), 4.35 q (2H, 7), 3.86 m (1H), 2.02 m (3H), 1.80–1.55 (4H), 1.31 t (3H, 7)
XIIIb	890, 1020 s, 1120, 1160, 1250, 1320 s, 1370, 1450, 1600, 1720 v.s, 3040, 3400	14.15 br.s (1H), 4.41 q (2H, 7), 3.63 q (2H, 7), 1.42 t (3H, 7), 1.20 t (3H, 7)
XIIIc	1030, 1090, 1110, 1240, 1320 s, 1360 s, 1730 v.s, 3040, 3400	15.44 br.s (1H), 7.52–7.30 (5H), 4.40 q (2H, 7), 1.34 t (3H, 7)
XIIId	1035 s, 1090, 1110, 1235, 1320 s, 1360 s, 1730 v.s, 3030, 3400	15.40 br.s (1H), 7.32 d (2H, 8), 7.26 d (2H, 8), 4.40 q (2H, 7), 2.37 s (3H), 1.34 t (3H, 7)
XIIIe	1035 s, 1095, 1235, 1320 s, 1355 s, 1495, 1735 v.s, 3040, 3400	15.50 br.s (1H), 7.60 d (2H, 8), 7.44 d (2H, 8), 4.40 q (2H, 7), 1.34 t (3H, 7)
XIIIf	1030, 1080, 1110, 1240, 1320, 1360, 1490, 1730 v.s, 3040, 3400	15.50 br.s (1H), 7.73 d (2H, 8), 7.38 d (2H, 8), 4.40 q (2H, 7), 1.34 t (3H, 7)
XIIIg	940, 1030, 1080, 1110, 1160, 1250, 1320, 1360, 1450, 1510, 1600, 1740 v.s, 3050, 3400	15.40 br.s (1H), 7.52–7.21 (4H), 3.50 q (2H, 7), 1.36 t (3H, 7)
XIIIh	930, 1030, 1070, 1120, 1160, 1240, 1320, 1380, 1450, 1510, 1610, 1730 v.s, 3050, 3400	15.48 br.s (1H), 7.59–7.39 (4H), 4.40 q (2H, 7), 1.34 t (3H, 7)
XIIIi	1030, 1120, 1240, 1320, 1345 s, 1530, 1730 v.s, 3035, 3395	15.53 br.s (1H), 8.39 d (2H, 9), 7.73 d (2H, 9), 4.41 q (2H, 7), 1.35 t (3H, 7)
XIIIj	1030 s, 1095, 1250, 1320 s, 1355 s, 1730 v.s, 3030, 3400	15.43 br.s (1H), 7.20 s (1H), 7.18 d (1H, 8), 7.12 d (1H, 8), 4.38 q (2H, 7), 2.35 s (3H), 2.09 s (3H), 1.36 t (3H, 7)
XIIIk	1035 s, 1090, 1110, 1260, 1300, 1320, 1480, 1500, 1735 v.s, 3040, 3400	15.43 br.s (1H), 7.66 d (1H, 2), 7.42 d.d (1H, 7, 2), 7.28 d (1H, 7), 4.40 q (2H, 7), 3.91 s (3H), 1.34 t (3H, 7)
XIIIl	900, 1040, 1090, 1110, 1170, 1250, 1330, 1360, 1450, 1500, 1590, 1720 v.s, 3050, 3400	15.41 br.s (1H), 7.44 d (1H, 3), 7.26 d.d (1H, 9, 3), 7.04 d (1H, 9), 4.53 q (2H, 7), 1.49 t (3H, 7)

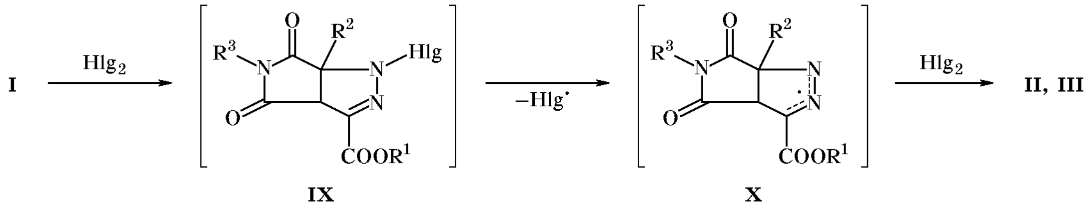
[a] Mixture of *endo* and *exo* isomers.

[b] ^{13}C NMR spectrum, δ_C, ppm: 169.6, 167.9, 164.8, 132.9, 130.1, 128.1, 123.8, 105.4, 103.6, 55.7, 51.5, 10.2.

[c] ^{13}C NMR spectrum, δ_C, ppm: 167.4, 165.2, 163.2, 134.6, 131.2, 130.0, 129.4, 126.2, 121.2, 104.4, 95.7, 64.9, 45.1, 13.6.

[d] ^{13}C NMR spectrum, δ_C, ppm: 169.9, 169.4, 163.1, 139.9, 130.4, 128.4, 126.4, 101.3, 94.8, 65.2, 57.1, 21.6.

Scheme 2.



respectively. Compounds **XIa**–**XIc** and **XIIa**–**XIIc** were identical to those reported previously [6]. Nonstereospecific reduction of bromocyclopropanes with zinc was also reported in [7].

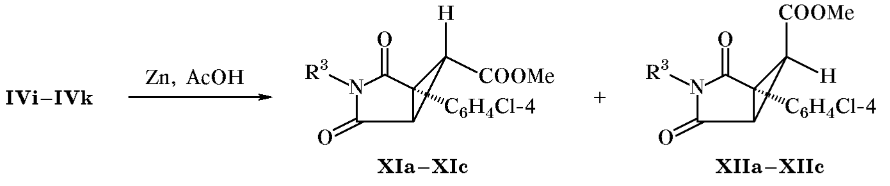
As shown above, compounds **Ij**–**In** having a substituent in the bridgehead position react with bromine in acetic acid at 70°C to give isomeric bromocyclopropanes **VIIb**–**VIIf** and **VIIIb**–**VIIIf**. On the other hand, bromination of compounds **If** and **Io**–**Iv** (which lack substituent on C^1) in acetic acid or chloroform on heating yields pyrrolopyrazoles **XIIIa**–**XIIIl** (Scheme 4). The sane products were obtained by the action of triethylamine on chlorinated compounds **IIf**, **IIg**, and **IIh**. The structure of compounds **XIIIa**–**XIIIl** is confirmed by their elemental analyses and IR and ^{1}H NMR spectra (Tables 1, 2). In the IR spectra of **XIIIa**–**XIIIl** we observed absorption at 3400 cm^{-1} due to stretching vibrations of the NH bond, and their ^{1}H NMR spectra contain a signal at δ 15.5 ppm belonging to the NH proton. The reaction of compound **Ih** with bromine at 70°C is accompanied by substitution of hydrogen in the aromatic ring by bromine to afford product **XIIIj**. Introduction of bromine into the aromatic ring was also observed for compound **Iv** at 70°C, whereas at 20°C pyrrolopyrazole **XIIIk** is formed.

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrophotometer from 2% solutions in chloroform. The ^{1}H NMR spectra were recorded on a Bruker AM-300 instrument (300 MHz) from 2% solutions in $CDCl_3$ or DMSO-d_6.

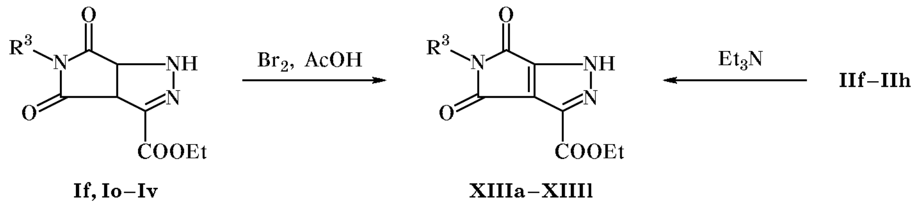
Ethyl 4-chloro-1-methyl-6,8-dioxo-7-(4-tolyl)-2,3,7-triazabicyclo[3.3.0]oct-2-ene-4-carboxylate (IIa). A stream of gaseous chlorine was passed at 0°C through a solution of 0.35 g (1.1 mmol) of compound **Ia** in 30 ml of dry chloroform until saturation (~1 min). The solvent was removed under reduced pressure at room temperature, and the residue was recrystallized from methanol. Yield of **IIa** 0.31 g

Scheme 3.



R^3 = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**).

Scheme 4.



If, **XIIIa**, R^3 = *cyclo*-C_6H_{11}; **Io**, **XIIIb**, R^3 = Et; **Ip**, **XIIIc**, R^3 = Ph; **Iq**, **XIIId**, R^3 = 4-MeC_6H_4; **Ir**, **XIIIe**, R^3 = 4-ClC_6H_4; **Is**, **XIIIf**, R^3 = 4-BrC_6H_4; **It**, **XIIIg**, R^3 = 4-FC_6H_4; **IIg**, **XIIIh**, R^3 = 3-ClC_6H_4; **Iu**, **XIIIi**, R^3 = 4-$NO_2C_6H_4$; **XIIIj**, R^3 = 4-CH_3O-3-BrC_6H_3; **Iv**, **XIIIk**, R^3 = 2,4-$Me_2C_6H_3$; **IIh**, **XIIIl**, R^3 = 3-Cl-4-$MeOC_6H_3$.

Table 3. Chemical shifts of some protons in the ^{1}H NMR spectra of compounds **IIIa–IIIh**, **Vb–Ve**, **VIIIa–VIIIf**, δ, ppm (*J*, Hz)

Compound no.	5-H	$COOCH_3$
IIIa	3.43 s	3.88 s
IIIb	3.42 s	3.88 s
IIIc	3.43 s	3.89 s
IIId	3.45 s	3.91 s
IIIe	3.43 s	3.89 s
IIIf	6.52 d (*J* = 8)[a]	3.88 d (*J* = 8)
IIIg	6.78 d (*J* = 8)[a]	4.02 d (*J* = 8)
IIIh	6.83 d (*J* = 8)[a]	4.04 d (*J* = 8)
Vb	2.83 s	3.83 s
Vc	2.84 s	3.82 s
Vd	2.88 s	3.82 s
Ve	2.86 s	3.81 s
VIIIa	2.85 s	4.24 q (*J* = 7),[b] 1.21 t (*J* = 7)
VIIIb	3.46 s	3.87 s
VIIIc	3.42 s	3.86 s
VIIId	3.44 s	3.86 s
VIIIe	3.60 s	3.88 s
VIIIf	2.90 s	3.80 s

[a] 1-H.
[b] C_2H_5.

(71%). Esters **IIb**–**IIg** and **IIIb**–**IIIg** were obtained in a similar way.

Ethyl 6-chloro-1-methyl-2,4-dioxo-3-(4-tolyl)-3-azabicyclo[3.1.0]hexane-6-carboxylate (IVa). Compound **IIa**, 0.20 g (0.57 mmol), was heated at 120°C under a residual pressure of 20 mm until nitrogen no longer evolved (5 min). The resulting material was cooled and recrystallized from methanol. Yield of ester **IVa** 0.134 g. Compounds **IVb**–**IVg** were obtained in a similar way.

Methyl 6-chloro-1-(4-chlorophenyl)-2,4-dioxo-3-phenyl-3-azabicyclo[3.1.0]hexane-6-carboxylate (IVj). A stream of dry gaseous chlorine was passed at 0°C through a solution of 0.3 g (0.78 mmol) of compound **Ij** in 30 ml of anhydrous 1,2-dichloroethane until saturation (~2 min). The solvent was evaporated at room temperature, and the residue was recrystallized from ethanol. Yield of ester **IVj** 0.27 g (88%). Compounds **IVi** and **IVk** were obtained by a similar procedure.

Ethyl 4-bromo-1-methyl-6,8-dioxo-7-(4-tolyl)-2,3,7-triazabicyclo[3.3.0]oct-2-ene-4-carboxylate (VI). A mixture of 0.6 g (2 mmol) of compound **Ia** and 1.6 g of bromine in 30 ml of dry chloroform was heated for 3 h. The mixture was cooled and treated with a solution of Na_2SO_3, the organic phase was separated, dried over $MgSO_4$, and evaporated, and the residue was recrystallized from methanol. Yield of ester **VI** 0.27 g (36%).

Ethyl 6-bromo-1-methyl-2,4-dioxo-3-(4-tolyl)-3-azabicyclo[3.1.0]hexane-6-carboxylate (isomeric mixture VIIa/VIIIa). Ester **VI**, 0.20 g (0.5 mmol), was heated at 130°C under a residual pressure of 20 mm until nitrogen no longer evolved (4 min). The resulting material was cooled and recrystallized from methanol. Yield of **VIIa/VIIIa** 0.11 g (61%).

Methyl 6-bromo-3-(3,4-dichlorophenyl)-1-methyl-2,4-dioxo-3-azabicyclo[3.1.0]hexane-6-carboxylate (VIIf). A mixture of 0.7 g (2 mmol) of compound **In** and 1.6 g of bromine in 20 ml of glacial acetic acid was heated for 5 h at 70°C. The solvent and excess bromine were distilled off, and a mixture of diethyl ether and hexane (1:1) was added to the residue for crystallization. The precipitate was filtered off and recrystallized from ethanol. Yield of ester **VIIf** 0.5 g (63%). Isomer ratio **VIIf**:**VIIIf** 12:1 (before recrystallization). Esters **VIIb**–**VIIe** and **VIIIb**–**VIIIe** were synthesized in a similar way; according to the ^{1}H NMR data, the isomer ratio was 2.3 (**VIIb/VIIIb**), 4.1 (**VIIc/VIIIc**), 0.9 (**VIId/VIIId**), 1.1 (**VIIe/VIIIe**).

Methyl 1-(4-chlorophenyl)-3-phenyl-3-azabicyclo[3.1.0]hexane-6-carboxylate (XIa/XIIa). A mixture of 62 mg (0.25 mmol) of chlorocyclopropane **IVj** and 0.7 g of zinc dust in 15 ml of glacial acetic acid was heated for 1 h. The mixture was cooled and filtered, acetic acid was removed from the filtrate under reduced pressure, the residue was dissolved in chloroform, the chloroform solution was filtered, washed with a 10% solution of Na_2CO_3, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography on silica gel (eluent hexane–ether, 1:2 by volume). Yield of **XIa**/**XIIa** 69%. Isomeric mixtures **XIb**/**XIIb** and **XIc**/**XIIc** were isolated in 71% and 75% yield, respectively.

Ethyl 7-cyclohexyl-6,8-dioxo-3,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylate (XIIIa). A solution of 230 mg (0.8 mmol) of compound **If** and 0.2 ml of bromine in 10 ml of chloroform was heated for 3 h. The mixture was cooled and washed with a solution of $Na_2S_2O_3$, the organic phase was separated, dried over $MgSO_4$, and evaporated, and the residue was recrystallized from hexane–acetone. Yield of ester **XIIIa** 210 mg (91%). Compounds **XIIIb** and **XIIIg** were synthesized in a similar way.

Ethyl 6,8-dioxo-7-phenyl-3,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylate (XIIIc). A mixture of 1 g (3.5 mmol) of compound **Ip** and 1 ml of bromine in 30 ml of acetic acid was heated for 2 h at 60–70°C. The mixture was cooled and poured into 100 ml of water, and the precipitate was filtered off, washed with a solution of $Na_2S_2O_3$ and water, and recrystallized from aqueous ethanol. Yield of **XIIIc** 0.5 g (52%). Esters **XIIId**–**XIIIf** and **XIIIi**–**XIIIk** were synthesized in a similar way.

Ethyl 7-(3-chlorophenyl)-6,8-dioxo-3,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylate (XIIIh). A mixture of 70 mg (0.2 mmol) of compound **IIg** and 40 mg of triethylamine in 7 ml of chloroform was stirred for 2 h. The mixture was washed with 10% hydrochloric acid, and the organic phase was dried over $MgSO_4$. The solvent was evaporated, and the residue was recrystallized from methanol. Yield of ester **XIIIh** 60 mg (86%). Compound **XIIIl** was obtained in a similar way.

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