Russian Journal of General Chemistry, Vol. 74, No. 4, 2004, pp. 586–593. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 4, 2004, pp. 642–650.

Functionally Substituted Amides and Esters of 3,4,4-Trichloro-3-butenoic Acid

S. K. Petkevich, E. A. Dikusar, V. I. Potkin, R. V. Kaberdin, K. L. Moiseichuk, A. P. Yuvchenko, and P. V. Kurman

Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, Minsk, Belarus

Received April 12, 2002

Abstract — Substituted amides and esters of 3,4,4-trichloro-3-butenoic acid were prepared by reactions of its chloride with appropriate amines and alcohols. Treatment of 3,4,4-trichloro-3-butenomorpholide and *tert*-butyl 3,4,4-trichloro-3-butenoate results in nucleophilic substitution of the internal chlorine atom with the morpholine residue, accompanied by prototropic allyl rearrangement.

Polychlorobutenoic acids and their derivatives exhibit a wide spectrum of valuable properties. Salts of 2,3,4,4-tetrachloro-2-butenoic acid are active bactericides, herbicides, extractants for rare-earth metals, and polymer fire retardants [1]. Alkyl 2,3,4,4-tetrachloro-3-butenoates (CCl_2=CClCHClCOOR, R = C_{1-6}-alkyl), and also esters and halides of perchloro-3-butenoic and perchloro-2-butenoic acids are used as promoters of Ziegler–Natta catalysts in production of high-molecular-weight polymers and copolymers [2–4].

A convenient procedure was developed previously [5] for preparing 3,4,4-trichloro-3-butenoic acid **II**, an effective herbicide [6], starting from trichloroethylene **I**, which is commercially produced on a large scale. The goal of this study was to prepare substituted amides and esters of acid **II**, containing various functional groups, peroxy group, and residues of natural compounds. These compounds are potentially bioactive, and the presence of various functional groups makes them promising intermediates for organic synthesis. Furthermore, chlorine-substituted peroxides show enhanced thermal stability and adhesive properties, which allows the use of these compounds in production of multilayer composite materials [7].

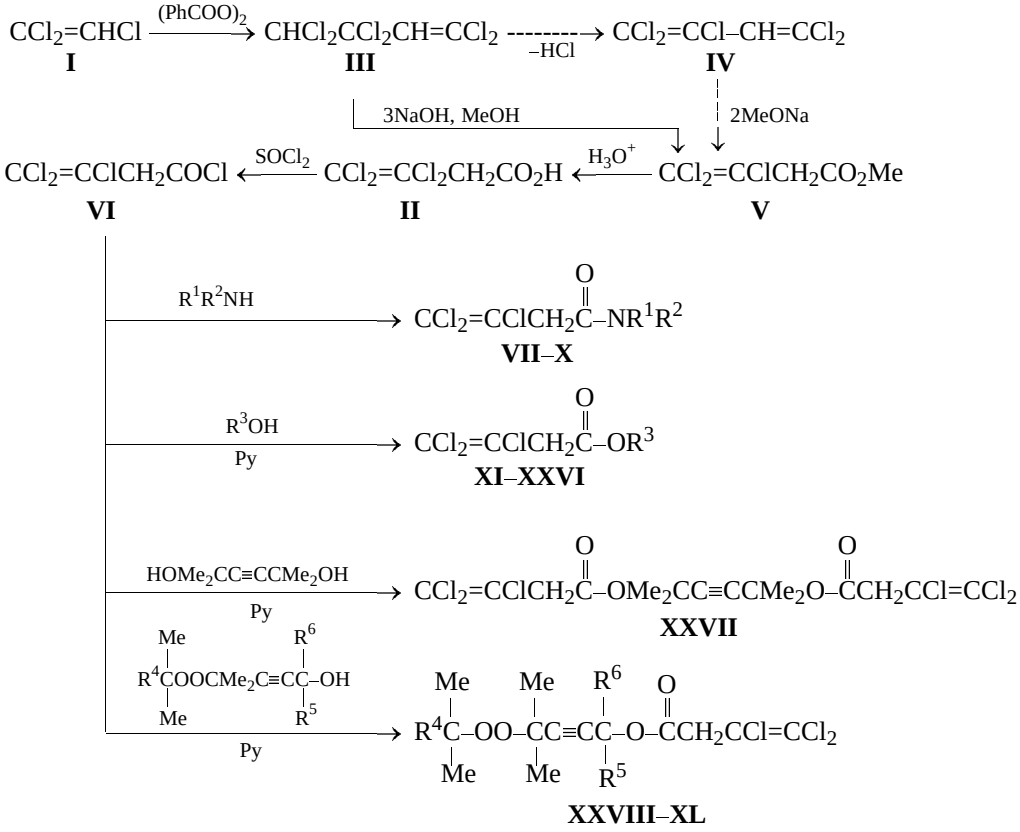
The known route to **II** involves preparation of trichloroethylene dimer **III**, its dehydrochlorination to obtain 2*H*-pentachloro-1,3-butadiene **IV**, and its reaction with sodium methylate, yielding methyl 3,4,4-trichloro-3-butenoate **V**; its subsequent hydrolysis gives the desired acid **II** [5]. The use of higher-molecular-weight alcohols decreases the yield of esters of acid **II**, especially with branched alcohols. The known route to amides of acid **II** involves the reaction of dangerously explosive perchlorobutenyne (formed by dehydrochlorination of **IV**) with amines, followed by acid hydrolysis of the resulting perchlorobuten-1-yn-1-amines [8]. This route, however, is practically unfeasible. It would be more convenient to prepare esters and amides of acid **II** from its chloride **VI**. We simplified the synthesis of **II** and eliminated the step of dehydrochlorination of 1,1,3,3,4,4-hexachloro-1-butene to diene **IV**.

We found that treatment of dimer **III** with a threefold molar excess of methanolic alkali directly afforded methyl 3,4,4-trichloro-3-butenoate **V** in 80% yield. Subsequent hydrolysis of **V** with 20% HCl according to [5] yielded acid **II** whose refluxing with thionyl chloride in CCl_4 gave acid chloride **VI**.

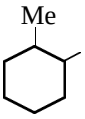
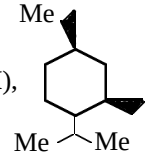
The reactions of acid chloride **VI** with 4-ethoxycarbonylaniline, allylamine, ethanolamine, and morpholine in ether solution at 20–25°C and amine : acid chloride molar ratio of 2 : 1 give the corresponding amides **VII**–**X** in 50–80% yields. With monoethanolamine, the reaction occurs selectively at the amino group of the nucleophile, with the OH group remaining intact.

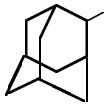
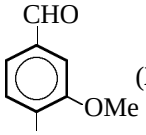
The compositions and structures of the reaction products were determined by elemental analysis, ^{1}H NMR and IR spectroscopy, and mass spectrometry (Tables 1, 2). In the IR spectra of the amides, the amide C=O bond gives strong absorption bands at 1646–1664 cm^{-1}; the N–H bonds in **VII**–**IX** give bands at 3100–3300 cm^{-1}, and the O–H bond in **IX**, a band at 3310 cm^{-1}. The ^{1}H NMR spectra contain a singlet of the CH_2 group of the trichlorobutenoic acid radical (δ 3.51–3.73 ppm) and signals of the hydrocarbon residues of the starting amines; the OH group in **IX** gives a broadened singlet at 1.65 ppm. The mass spectra contain groups of molecular peaks with the

1070-3632/04/7404-0586 ©2004 MAIK "Nauka/Interperiodica"



R^1 = H, R^2 = 4-EtOC(O)C_6H_4 (**VII**), $CH_2CH{=}CH_2$ (**VIII**), CH_2CH_2OH (**IX**); R^1, R^2 = $(CH_2)_2O(CH_2)_2$ (**X**); R^3 = $Me(CH_2)_{13}CH_2$ (**XI**), $Me(CH_2)_{14}CH_2$ (**XII**), Me_3C (**XIII**), $MeCH_2Me_2C$ (**XIV**), $Me(CH_2)_3Me_2C$ (**XV**), $PhMe_2C$ (**XVI**), $HC{\equiv}CCH_2$ (**XVII**), $HC{\equiv}CCH_2CH_2$ (**XVIII**),

$HC{\equiv}C(CH_2)_2CH_2$ (**XIX**), HC≡CMeCH (**XX**), $HC{\equiv}CMe_2C$ (**XXI**),  (**XXII**),  (**XXIII**),  (**XXIV**),

 (**XXV**),  (**XXVI**); R^4 = R^5 = R^6 = Me (**XXVIII**), R^4 = Ph, R^5 = R^6 = Me (**XXIX**); R^4 = R^5 = Me, R^6 = $CH_2CH{=}CH_2$ (**XXX**); R^4 = $MeCH_2CH_2$, R^5 = Me, R^6 = $CH_2CH_2CH{=}CH_2$ (**XXXI**); R^4 = R^5 = Me, R^6 = Ph (**XXXII**); R^4 = Et, R^5 = Me, R^6 = Ph (**XXXIII**); R^4 = $MeCH_2CH_2$, R^5 = Me, R^6 = Ph (**XXXIV**); R^4 = Me, R^5 = R^6 = CD_3 (**XXXV**); R^4 = Et, R^5 = R^6 = CD_3 (**XXXVI**); R^4 = $MeCH_2CH_2$,

R^5 = R^6 = CD_3 (**XXXVII**); R^4 =  , R^5 = R^6 = CD_3 (**XXXVIII**), R^4 = Me, CR^5R^6 =  (**XXXIX**);

R^4 = Me, CR^5R^6=  (**XL**).

isotopic pattern typical of Cl_3 species [9, 10] (intensity ratio 100 : 98 : 32 : 3.5).

Functionally substituted esters of acid **I** are prepared by the reactions of acid chloride **VI** with appropriate alcohols in the presence of pyridine. By this procedure, we prepared esters **XI**–**XL** containing aliphatic, alicyclic, and aromatic residues, triple bond, and methoxy and aldehyde groups. The reaction of **VI** with a dihydric alcohol, 2,5-dimethyl-3-hexyne-2,5-diol, involves both hydroxy groups of the glycol and yields the corresponding polyunsaturated diester **XXVII**. The reactions with peroxy alcohols occur with preservation of the O–O bond and yield the corre-

Table 1. Yields, physicochemical constants, and elemental analyses of amides **VII**–**X** and **XLI** and of esters **XI**–**XL** and **XLII**

Comp. no.	Yield, %	mp, °C, bp, °C (*p*, mm)	d_{20}^{20}	n_D^{20}	Found, %			Formula	Calculated, %			*M*	
					C	H	Cl		C	H	Cl	found [a]	calculated
VII	80	142–144	–	–	46.00	3.78	31.22	$C_{13}H_{12}Cl_3NO_3$	46.39	3.59	31.60	335	336.6
VIII	52	96–97	–	–	36.43	3.84	46.21	$C_7H_8Cl_3NO$	36.79	3.53	46.55	227	228.5
IX	50	134–136	–	–	31.29	3.75	45.43	$C_6H_8Cl_3NO_2$	31.00	3.47	45.75	231	232.5
X	57	82–83	–	–	37.28	4.16	41.01	$C_8H_{10}Cl_3NO_2$	37.17	3.90	41.14	257	258.5
XI	81	28–29	–	–	57.35	8.54	26.32	$C_{19}H_{33}Cl_3O_2$	57.08	8.32	26.60	386.4	399.8
XII	79	39–40	–	–	58.15	8.66	25.48	$C_{20}H_{35}Cl_3O_2$	58.04	8.52	25.70	398.7	413.9
XIII	76	53–54 (0.05)	1.3279	1.4760	39.51	4.68	42.84	$C_8H_{11}Cl_3O_2$	39.13	4.52	43.32	234.1	245.5
XIV	76	64–65 (0.05)	1.2923	1.4790	41.88	5.18	40.70	$C_9H_{13}Cl_3O_2$	41.65	5.05	40.98	248.3	259.6
XV	73	70–71 (0.05)	1.1112	1.4770	46.17	6.04	36.52	$C_{11}H_{17}Cl_3O_2$	45.94	5.96	36.98	281.0	287.6
XVI	79	–	1.1569	1.5365	51.03	4.29	34.23	$C_{13}H_{13}Cl_3O_2$	50.76	4.26	34.58	298.6	307.6
XVII	87	59–60 (0.05)	1.3402	1.5075	37.17	2.45	46.28	$C_7H_5Cl_3O_2$	36.96	2.22	46.76	218.4	227.5
XVIII	82	68–69 (0.05)	1.4264	1.5035	40.12	3.08	43.87	$C_8H_7Cl_3O_2$	39.79	2.92	44.04	235.0	241.5
XIX	81	78–79 (0.05)	1.1596	1.5020	42.56	3.70	41.28	$C_9H_9Cl_3O_2$	42.03	3.55	41.62	248.7	255.5
XX	89	55–56 (0.05)	1.3090	1.4950	40.09	3.02	43.95	$C_8H_7Cl_3O_2$	39.79	2.92	44.04	234.3	241.5
XXI	81	57–58 (0.05)	1.2211	1.4895	42.54	3.68	41.22	$C_9H_9Cl_3O_2$	42.03	3.55	41.62	244.4	255.5
XXII	83	–	1.1389	1.5040	44.71	4.96	38.89	$C_{10}H_{13}Cl_3O_2$	44.23	4.82	39.16	262.4	271.6
XXIII	77	–	1.2180	1.5015	46.54	5.48	37.02	$C_{11}H_{15}Cl_3O_2$	46.26	5.29	37.24	277.2	285.6
XXIV	74	–	1.1473	1.4970	51.72	6.58	32.11	$C_{14}H_{21}Cl_3O_2$	51.32	6.46	32.46	319.1	327.7
XXV	78	50–51	–	–	52.14	5.44	32.36	$C_{14}H_{17}Cl_3O_2$	51.96	5.29	32.86	316.0	323.6
XXVI	76	164 (0.05)	1.4391	1.5745	44.81	3.10	32.49	$C_{12}H_9Cl_3O_4$	44.55	2.80	32.87	312.9	323.6
XXVII	73	–	1.3495	1.5130	40.01	3.46	43.70	$C_{16}H_{16}Cl_6O_4$	39.62	3.32	43.86	460.1	485.0
XXVIII	77	–	1.1349	1.4780	50.11	6.14	27.40	$C_{16}H_{23}Cl_3O_4$	49.82	6.01	27.57	360.9	385.7
XXIX	77	–	1.2207	1.5165	56.64	5.72	23.50	$C_{21}H_{25}Cl_3O_4$	56.33	5.63	23.75	440.0	447.8
XXX	71	–	1.0606	1.4810	54.00	6.51	24.60	$C_{19}H_{27}Cl_3O_4$	53.60	6.39	24.98	417.6	425.8
XXXI	84	–	1.0985	1.4820	55.91	7.03	23.12	$C_{21}H_{31}Cl_3O_4$	55.58	6.88	23.44	439.0	453.8
XXXII	81	–	1.1996	1.5140	56.83	5.70	23.60	$C_{21}H_{25}Cl_3O_4$	56.33	5.63	23.75	438.1	447.8
XXXIII	74	–	1.1508	1.5110	57.45	6.02	22.80	$C_{22}H_{27}Cl_3O_4$	57.22	5.89	23.03	450.2	461.8
XXXIV	82	–	1.2127	1.5120	58.51	6.32	22.05	$C_{23}H_{29}Cl_3O_4$	58.06	6.14	22.35	460.2	475.8
XXXV	85	–	1.1376	1.4760	49.35	7.54	27.03	$C_{16}H_{17}D_6Cl_3O_4$	49.06	7.46	27.15	382.4	391.8
XXXVI	79	–	1.1398	1.4775	50.68	7.84	25.97	$C_{17}H_{19}D_6Cl_3O_4$	50.32	7.70	26.21	391.7	405.8
XXXVII	79	–	1.1899	1.4770	51.88	8.16	25.02	$C_{18}H_{21}D_6Cl_3O_4$	51.50	7.92	25.34	406.3	419.8
XXXVIII	74	–	1.1516	1.4910	55.10	8.26	22.80	$C_{21}H_{25}D_6Cl_3O_4$	54.85	8.11	23.13	438.5	459.9
XXXIX	70	–	1.1332	1.4915	52.67	6.24	25.40	$C_{18}H_{25}Cl_3O_4$	52.51	6.12	25.83	390.7	441.8
XL	71	–	1.1209	1.4940	53.88	6.51	24.61	$C_{19}H_{27}Cl_3O_4$	53.60	6.39	24.98	412.9	425.8
XLI	85	137–138	–	–	46.97	5.98	22.59	$C_{12}H_{18}Cl_2N_2O_3$	46.62	5.87	22.92	308	309.2
XLII	67	36–38	–	–	48.31	6.54	23.75	$C_{12}H_{19}Cl_2NO_3$	48.66	6.47	23.94	295	296.2

[a] The molecular weights of **VII**–**X, XLI**, and **XLII** were determined by mass spectrometry, with the *m/z* values given for ^{35}Cl.

sponding peroxy esters **XXVIII**–**LX**. With deuterated peroxyalkynyl alcohols, we obtained the corresponding deuterated derivatives **XXXV**–**XXXVIII**.

The analytical, ^1H NMR, and IR data for esters **X**–**XL** are listed in Tables 1 and 2. The IR spectra of **XI**–**XL** do not contain ν(OH) bands of the starting alcohols but contain C=O and $(C=C)_{aliph}$ bands at 1730–1775 and 1600–1650 cm^{-1}, respectively. The spectrum of vanillin derivative **XXVI** contains, along with the ν(C=O) band of the ester group, also that of the aldehyde group at 1700 cm^{-1}. The spectra of monosubstituted acetylenes **XVII**–**XXI** contain ν(≡C–H) and ν(C≡C) bands at 3300–3305 and 2120–2135 cm^{-1},

Table 2. IR and ^{1}H NMR spectra of amides **VII**–**X** and **XLI** and of esters **XI**–**XL** and **XLII**

Comp. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm
VII	3248 (NH), 1716 ($C=O_{ester}$), 1664 ($C=O_{amide}$), 1602, 1591 (C=C), 921 (C–Cl)	1.37 t (3H, ^3J 7.1 Hz, Me), 3.73 s (2H, CH_2CCl), 4.34 q (2H, ^3J 7.1 Hz, CH_2O), 7.59 d ($2H_{arom}$, ^3J 8.5 Hz), 7.98 d ($2H_{arom}$, ^3J 8.5 Hz), 8.40 br.s (1H, NH)
VIII	3300 (NH), 1650 (C=O), 1563 (C=C), 927 (C–Cl)	3.57 s (2H, CH_2CCl), 3.91 m (2H, CH_2N), 5.10 m (2H, $=CH_2$), 5.70 m (1H, =CH), 6.10 br.s (1H, NH)
IX	3310 (OH), 3100 (NH), 1649 (C=O), 1565 (C=C), 922 (C–Cl)	1.65 br.s (1H, OH), 3.57 s (2H, CH_2CCl), 3.45 t (2H, CH_2N), 3.73 t (2H, CH_2O), 6.10 br.s (1H, NH)
X	1646 (C=O), 1639 (C=C), 920 (C–Cl)	3.47 m (2H, CH_2N), 3.65 m (8H, $2CH_2O$, CH_2N, CH_2Cl)
XI	1730 (C=O), 1607 (C=C), 921 (C–Cl)	0.87 t (3H, Me, ^3J 4.4 Hz), 1.10–1.85 m [26H, $(CH_2)_{13}$], 3.62 s (2H, CH_2CCl), 4.15 t (2H, CH_2O, ^3J 6.6 Hz)
XII	1730 (C=O), 1606 (C=C), 918 (C–Cl)	0.91 t (3H, Me, ^3J 4.4 Hz), 1.10–1.90 m [28H, $(CH_2)_{14}$], 3.62 s (2H, CH_2CCl), 4.18 t (2H, CH_2O, ^3J 6.3 Hz)
XIII	1741 (C=O), 1608 (C=C), 920 (C–Cl)	1.48 s (9H, Me_3C), 3.53 s (2H, CH_2)
XIV	1741 (C=O), 1607 (C=C), 924 (C–Cl)	0.90 t (3H, Me, ^3J 7.6 Hz), 1.45 s (6H, Me_2C), 1.78 q (3H, Me, ^3J 7.6 Hz), 3.54 s (2H, CH_2CCl)
XV	1742 (C=O), 1609 (C=C), 919 (C–Cl)	0.96 t (3H, Me, ^3J 6.2 Hz), 1.15–1.90 m [6H, $(CH_2)_3$], 1.51 s (6H, Me_2C), 3.58 s (2H, CH_2CCl)
XVI	1746 (C=O), 1603, 1499 (C=C), 925 (C–Cl)	1.82 s (6H, Me_2C), 3.61 s (2H, CH_2), 7.20–7.45 m (5H, Ph)
XVII	3300 (≡C–H), 2131 (C≡C), 1750 (C=O), 1611 (C=C), 925 (C–Cl)	2.52 t (1H, C≡CH, ^4J 2.5 Hz), 3.69 s (2H, CH_2CCl), 4.76 d (2H, CH_2O, ^4J 2.5 Hz)
XVIII	3301 (≡C–H), 2124 (C≡C), 1746 (C=O), 1610 (C=C), 924 (C–Cl)	2.02 t (1H, C≡CH, ^4J 2.6 Hz), 2.56 t.d [2H, CH_2C≡C, $^3J(CH_2)$ 6.8, ^4J(C≡CH) 2.6 Hz], 3.66 s (2H, CH_2CCl), 4.27 t (2H, CH_2O, ^3J 6.8 Hz)
XIX	3302 (≡C–H), 2120 (C≡C), 1745 (C=O), 1613 (C=C), 924 (C–Cl)	1.67–2.46 m [5H, C≡CH and $(CH_2)_2$C≡C], 3.64 s (2H, CH_2CCl), 4.27 t (2H, CH_2O, ^3J 6.2 Hz)
XX	3302 (≡C–H), 2126 (C≡C), 1747 (C=O), 1612 (C=C), 924 (C–Cl)	1.54 d (3H, Me, ^3J 6.7 Hz), 2.50 d (1H, C≡CH, ^4J 2.2 Hz), 3.65 s (2H, CH_2CCl), 5.49 q.d [1H, C*H*Me, ^3J(Me) 6.7, ^4J(C≡CH) 2.2 Hz]
XXI	3302 (≡C–H), 2123 (C≡C), 1749 (C=O), 1609 (C=C), 921 (C–Cl)	1.70 s (6H, Me_2C), 2.57 s (1H, C≡CH), 3.60 s (2H, CH_2CCl)
XXII	1742 (C=O), 1607 (C=C), 923 (C–Cl)	1.20–2.00 m [10H, $(CH_2)_5$], 3.61 s (2H, CH_2CCl), 4.70–4.95 m (1H, CH)
XXIII	1740 (C=O), 1609 (C=C), 920 (C–Cl)	0.94 d (3H, Me, ^3J 1.5 Hz), 1.05–2.10 m (9H, C_6H_9), 3.65 s (2H, CH_2CCl), 4.90–5.05 m (1H, CHO)
XXIV	1740 (C=O), 1612 (C=C), 920 (C–Cl)	0.82 d (3H, Me^7, ^3J 6.5 Hz), 0.95 d (6H, Me_2C^8, ^3J 6.7 Hz), 0.90–2.23 m (9H, C^1H, C^2H_2, C^4H, C^5H_2, C^6H_2, C^8H), 3.6 s (2H, CH_2CCl), 4.78 d.t (1H, C^3H, $^3J_{aa}$ 10.1, $^3J_{ae}$ 4.7 Hz)
XXV	1755 (C=O), 1603 (C=C), 933 (C–Cl)	1.10–2.15 m (14H, Ad), 3.65 s (2H, CH_2CCl), 4.90–5.05 m (1H, CHOAd-1)
XXVI	1774 (C=O), 1700 (HC=O), 1601, 1502 (C=C), 924 (C–Cl)	3.90 s (3H, MeO), 3.92 s (2H, CH_2CCl), 7.18–7.54 m (3H, C_6H_3), 9.94 s (1H, CHO)
XXVII	1750 (C=O), 1610 (C=C), 925 (C–Cl)	1.65 s (12H, $2Me_2C$), 3.57 s (4H, $2CH_2CCl$)
XXVIII	2121 (C≡C), 1753 (C=O), 1609 (C=C), 923 (C–Cl), 879 (O–O)	1.23 s (9H, Me_3COO), 1.43 s (6H, Me_2COO), 1.65 s [6H, $Me_2CO(O)$], 3.54 s (2H, CH_2CCl)
XXIX	1751 (C=O), 1605, 1498 (C=C), 924 (C–Cl), 875 (O–O)	1.46 s (6H, Me_2COO), 1.60 s (6H, $OOMe_2CC{\equiv}C$), 1.70 s [6H, $Me_2 \cdot CO(O)$], 3.56 s (2H, CH_2CCl), 7.15–7.58 m (5H, Ph)
XXX	1752 (C=O), 1644, 1614 (C=C), 921 (C–Cl), 880 (O–O)	1.24 s (9H, Me_3COO), 1.46 s (6H, Me_2C), 1.70 s (3H, Me), 1.75–2.50 m [4H, $(CH_2)_2$], 3.56 s (2H, CH_2CCl), 4.88–5.18 m (2H, $C=CH_2$), 5.60–6.10 m (1H, C=CH)

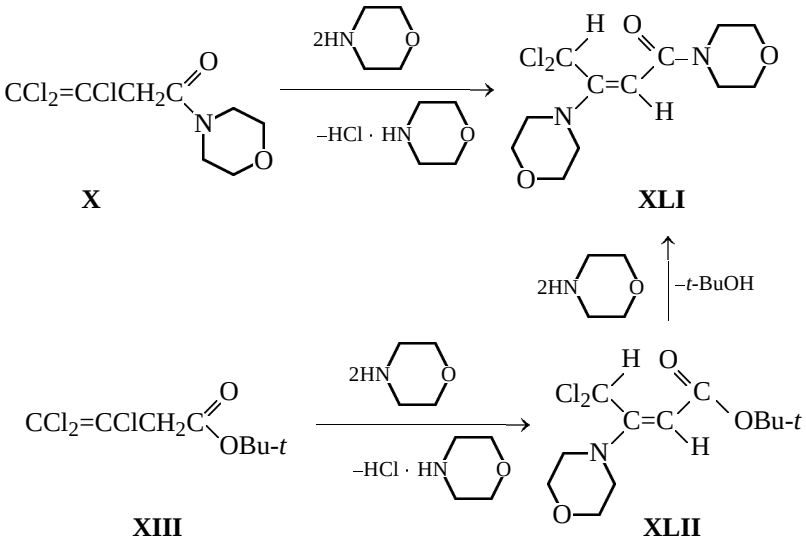
Table 2. (Contd.)

Comp. no.	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm
XXXI	1751 (C=O), 1645, 1612 (C=C), 921 (C–Cl), 878 (O–O)	0.87 t [3H, *Me*$(CH_2)_2$, ^3J 5.5 Hz], 1.20 s (6H, Me_2COO), 1.32–1.60 m [4H, Me$(CH_2)_2$], 1.45 s (6H, Me_2C), 1.70 s (3H, MeCC≡C), 1.75–2.45 m [4H, (C*H*$_2)_2$CH=C), 3.56 s (2H, CH_2CCl), 4.83–5.18 m (2H, C=C*H*$_2$), 5.60–6.10 m (1H, C=CH)
XXXII	1756 (C=O), 1605, 1496 (C=C), 922 (C–Cl), 862 (O–O)	1.27 s (9H, Me_3COO), 1.55 s (6H, Me_2C), 1.92 s (3H, Me), 3.62 s (2H, CH_2CCl), 7.15–7.80 m (5H, Ph)
XXXIII	1756 (C=O), 1602, 1496 (C=C), 923 (C–Cl), 860 (O–O)	0.90 t (3H, *Me*CH_2, ^3J 6.9 Hz), 1.21 s (9H, Me_3COO), 1.53 s (6H, Me_2C), 1.54 q (2H, C*H*$_2$Me, ^3J 6.9 Hz), 1.90 s [6H, $Me_2CO(O)$], 3.60 s (2H, CH_2CCl), 7.22–7.72 m (5H, Ph)
XXXIV	1755 (C=O), 1606, 1497 (C=C), 923 (C–Cl), 865 (O–O)	0.90 t [3H, *Me*$(CH_2)_2$, ^3J 5.7 Hz], 1.23 s (9H, Me_3COO), 1.38–1.70 m [4H, $(CH_2)_2$], 1.52 s (6H, Me_2C), 1.89 s (3H, Me), 3.58 s (2H, CH_2CCl), 7.22–7.72 m (5H, Ph)
XXXV	2245 (C–D), 2130 (C≡C), 1751 (C=O), 1610 (C=C), 921 (C–Cl), 879 (O–O)	1.25 s (9H, Me_3COO), 1.45 s (6H, Me_2C), 3.56 s (2H, CH_2CCl)
XXXVI	2244 (C–D), 2130 (C≡C), 1751 (C=O), 1612 (C=C), 920 (C–Cl), 877 (O–O)	0.89 t (3H, *Me*CH_2, ^3J 7.3 Hz), 1.20 s (6H, Me_2COO), 1.44 s (6H, Me_2C), 1.50 q (2H, C*H*$_2$Me, ^3J 7.3 Hz), 3.56 s (2H, CH_2CCl)
XXXVII	2245 (C–D), 2131 (C≡C), 1752 (C=O), 1608 (C=C), 920 (C–Cl), 876 (O–O)	0.90 t [3H, *Me*$(CH_2)_2$, ^3J 5.8 Hz], 1.21 s (9H, Me_3COO), 1.31–1.60 m [4H, $(CH_2)_2$], 1.44 s (6H, Me_2C), 3.56 s (2H, CH_2CCl)
XXXVIII	2132 (C≡C), 2247 (C–D), 1752 (C=O), 1607 (C=C), 919 (C–Cl), 872 (O–O)	0.88–1.95 m (11H, C_6H_{11}), 1.17 s (6H, Me_2COO), 1.44 s (6H, Me_2C), 3.56 s (2H, CH_2CCl)
XXXIX	1751 (C=O), 1608 (C=C), 922 (C–Cl), 876 (O–O)	1.25 s (9H, Me_3COO), 1.45 s (6H, Me_2C), 1.52–2.35 m [8H, $(CH_2)_4$], 3.56 s (2H, CH_2CCl)
XL	1753 (C=O), 1610 (C=C), 923 (C–Cl), 875 (O–O)	1.24 s (9H, Me_3COO), 1.40–2.15 m [10H, $(CH_2)_5$], 1.48 s (6H, Me_2C), 3.56 s (2H, CH_2CCl)
XLI	1575 (C=O), 1613 (C=C), 757 (C–Cl)	3.35 m (2H, CH_2N), 3.60 m (8H, $2CH_2N$, $2CH_2O$), 3.80 m (4H, $2CH_2O$), 4.88 s (1H, =CH)
XLII	1684 (C=O), 1582 (C=C), 762 (C–Cl)	1.54 s (9H, Me_3C), 3.62 m (4H, $2CH_2N$), 3.78 (4H, CH_2O), 4.70 s (1H, =CH), 8.43 s (1H, $CHCl_2$)

respectively. In the spectra of peroxides **XXVIII**–**XL**, the O–O stretching vibrations give rise to a band at 860–880 cm^{-1}. The spectra of deuterated peroxides **XXXV**–**XXXVIII** contain C–D absorption bands at 2245–2247 cm^{-1}.

The ^1H NMR spectra of esters **XI**–**XL** contain singlets of the CH_2 groups of the acid residue in the range δ 3.5–3.8 ppm and signals of the hydrocarbon radicals of the initial alcohols (Table 2).

The amides and esters synthesized contain chlorine atoms replaceable by nucleophilic agents, which allows synthesis of various functional derivatives. We examined the possibility of nucleophilic substitution of chlorine atoms in these compounds with morpholide **X** and *tert*-butyl 3,4,4-trichloro-3-butenoate **XIII** as examples. The pattern of the reactions of **X** and **XIII** with morpholine in refluxing ester at the amide (butenoate) : morpholine molar ratio of 1 : 2 is nontrivial; substitution of the internal chlorine atom by the morpholine residue is accompanied by a prototropic allyl rearrangement, affording, respectively, 3-morpholino-4,4-dichloro-2-butenomorpholide **XLI** in 85% yield and *tert*-butyl 3-morpholino-4,4-dichloro-2-butenoate **XLII** in 67% yield. At the morpholine : acid derivative molar ratio of 1 : 4, in refluxing benzene, ester **XIII** reacts with morpholine both at the chlorinated residue and at the ester group to give amide **XLI**. The reaction is accompanied by extensive tarring, and the yield of **XLI** in this case does not exceed 32%. Minor amounts of amino ester **XLII** were detected in the reaction mixture by gas chromatography–



mass spectrometry. Amide **XLI** was also obtained in 44% yield from the reaction of morpholine with ester **XLII** prepared in advance.

In the IR spectra of **XLI** and **XLII**, the C=O vibrations are manifested at 1575 and 1684 cm^{-1}, respectively. The decreased ν(C=O) frequency in the spectra of **XLI** and **XLII**, compared to the starting amide **X** and ester **XIII**, is due to conjugation of the C=O group with the enamine moiety [11]. The occurrence of the allyl rearrangement is confirmed by the absence in the ^1H NMR spectra of **XLI** and **XLII** of the signal from the CH_2 group of the acid residue at δ 3.50–3.95 ppm and by appearance of two singlets at δ 4.70–4.88 and 8.35–8.43 ppm, corresponding to the =CH and $CHCl_2$ groups, respectively. Our assignments are consistent with published data for related β-amino-γ,γ-dichlorocrotonic acid derivatives and suggest that compounds **XLI** and **XLII** are formed as *E* isomers: the dichloromethyl proton signal is observed at δ 7.90–9.15 ppm, and the vinyl =CH– signal, at δ 4.35–5.85 ppm, whereas in the spectra of the *Z* isomers the singlets of both groups are observed at δ 4.4–6.5 ppm [12, 13]. The significant downfield shift of the $CHCl_2$ signal in the spectra of the *E* isomers is due to formation of an intramolecular hydrogen bond between the dichloromethyl hydrogen atom and the C=O oxygen atom.

The mass spectra of amide **XLI** and ester **XLII** contain molecular peak groups; the intensity ratio of the two major isotopic components (100 : 65) is typical of Cl_2 species [9, 10].

The thermal stability of peroxy esters **XXVIII**–**XL** was evaluated by thermal analysis [14]. The thermogravimetric data show that the weight loss occurs in two or three steps depending on the stability of the peroxides. In the first step starting at 92–135°C, decomposition of all the peroxy esters occurs with a pronounced exothermic effect; the subsequent steps occur without significant thermal effects and largely correspond to removal of volatile decomposition products.

Peroxy esters **XXVIII**, **XXIX**, **XXXIX**, and **XL** show the highest thermal stability. They start to decompose at a noticeable rate only at 130–135°C; the first step has a maximum at 170–182°C and is complete at 175–192°C (weight loss 37–47%). The least thermally stable are peroxy esters **XXXII**–**XXXIV**. They start to decompose even at 92–100°C. The three steps of their decomposition from 92–100 to 235–260°C are less resolved; the total weight loss is 62–63%. Deuterated peroxides **XXXV**–**XXXVIII** are comparable in the thermal stability with peroxides **XXVIII** and **XXIX** and start to decompose at 117–132°C. In the series of peroxides **XXXV**–**XXXVIII**, compounds **XXXV**–**XXXVII** with *tert*-alkylperoxy groups show higher thermal stability (decomposition starts at 125–132°C) than compound **XXXVIII** with the cycloalkylperoxy group (decomposition starts at 117°C). In turn, compound **XXXV** with the *tert*-butylperoxy group is somewhat more stable than the related compounds with the *tert*-pentylperoxy (**XXXVI**) and 1,1-dimethylbutylperoxy (**XXXVII**) groups (decomposition starts at 132, 128, and 125°C, respectively), which is consistent with the results of quantum-chemical calculations and kinetic studies for branched peroxy alkynes [15, 16].

EXPERIMENTAL

The IR spectra were recorded on a Protege-460 Fourier spectrometer. Samples of **VII**–**XII**, **XXV**, **XLI**, and **XLII** were prepared as KBr pellets, and samples of **XIII**–**XXIV** and **XXVI**–**XL**, as thin films.

The ^{1}H NMR spectra were taken on a Tesla-567A spectrometer (100 MHz) in $CDCl_3$; the chemical shifts were measured relative to TMS. The mass spectra were obtained on an MKh-1320 mass spectrometer at the ionizing electron energy of 50 eV. The GC–MS analysis was performed on a Hewlett–Packard GC/MS-5890/5972 device.

The thermal properties of peroxy esters **XXVIII**–**XL** were studied on a Paulik–Paulik–Erdey derivatograph in an Ar atmosphere at a linear heating rate of 7 deg min^{-1}. The sample weight was 100 mg (DTA 1/10, DTG 1/10).

The compound purity was checked by TLC on Silufol (20 cm) plates, eluent hexane–ether, 3 : 1, developer *N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride. The column chromatography was performed on Al_2O_3 L 40/250 μm, Brockmann grade II, neutral; eluent hexane–ether, 3 : 1. The molecular weights of the compounds were determined cryoscopically in benzene.

The starting peroxy alcohols were prepared according to [17–19]. Iodometric determination of available oxygen in peroxides **XXVIII**–**XL** using concentrated HCl [20] gave overestimated results [21].

1,1,3,3,4,4-Hexachloro-1-butene **III** was prepared by radical dimerization of trichloroethylene **I** under the action of benzoyl peroxide [22].

Methyl 3,4,4-trichloro-3-butenoate V. To a solution of 12 g of NaOH in 150 ml of methanol, we added dropwise with stirring 26.3 g of 1,1,3,3,4,4-hexachloro-1-butene **III**, avoiding warming up above 40°C. The reaction mixture was stirred for 1 h, 50 ml of HCl was added, and the mixture was diluted with water and extracted with methylene chloride. The extract was dried over $MgSO_4$, the solvent was removed, and the residue was vacuum-distilled. Ester **V** was obtained in a yield of 16.3 g (80%); its characteristics were in agreement with published data [5].

3,4,4-Trichloro-3-butenoic acid **II** was prepared by hydrolysis of ester **V** according to [5].

3,4,4-Trichloro-3-butenoyl chloride VI. To a solution of 2.86 g of 3,4,4-trichloro-3-butenoic acid **II** in 10 ml of CCl_4, we added dropwise 3.3 ml of thionyl chloride; the mixture was refluxed until evolution of HCl ceased. The solvent and excess thionyl chloride were distilled off, and the residue was vacuum-distilled. Chloride **VI** was obtained; yield 2.99 g (95%), bp 38–39°C (1 mm), d_4^{20} 1.558, n_D^{20} 1.5135. IR spectrum, ν, cm^{-1}: 761, 792 (C–Cl), 1607 (C=C), 1800 (C=O). ^{1}H NMR spectrum, δ, ppm: 4.12 s (2H, CH_2). Found, %: C 23.02; H 1.37; Cl 68.55. [*M*] 206 (for ^{35}Cl). $C_4H_2Cl_4O$. Calculated, %: C 23.11; H 0.97; Cl 68.22. *M* 207.87.

3,4,4-Trichloro-3-butenamides VII–**X.** A mixture of 10 mmol of chloride **VI** and 20 mmol of appropriate amine in 50 ml of absolute diethyl ether was stirred at 20–25°C for 3 h. The amine hydrochloride precipitate was filtered off, the solvent was removed from the filtrate, and the solid residue was washed with water and hexane and purified by recrystallization from 80% aqueous ethanol.

3,4,4-Trichloro-3-butenoic acid esters XI–**XL.** A solution of 10 mmol of chloride **VI** in 20 ml of absolute diethyl ether was added at 0–5°C to a solution of 10 mmol of appropriate alcohol in 50 ml of absolute diethyl ether. After that, 10 mmol of pyridine was added with vigorous stirring. The mixture was stirred at 20–23°C for 4 h and allowed to stand at this temperature for 18 h. The precipitate of pyridine hydrochloride was filtered off, and the filtrate was diluted with diethyl ether, washed with water and 5% $NaHCO_3$ solution, and dried over $CaCl_2$. The solvent was removed. Compounds **XIII**–**XV**, **XVII**–**XXI**, and **XXVI** were isolated by vacuum distillation, and **XVI**, **XXII**–**XXV**, and **XXVII**–**XL**, by column chromatography on Al_2O_3.

(*E*)-3-Morpholino-4,4-dichloro-2-butenomorpholide XLI. *a*. A solution of 2.58 g of amide **XII** and 1.75 g of morpholine in 50 ml of diethyl ether was refluxed for 5 h. The precipitate of morpholine hydrochloride was filtered off, the solvent was removed from the filtrate, and the solid residue was washed with water and hexane and recrystallized from diethyl ether–hexane, 1 : 3. Yield of **XLI** 2.62 g (85%), mp 137–138°C.

b. A mixture of 2.46 g of ester **XIII** and 3.49 g of morpholine in 50 ml of benzene was refluxed for 20 h, the precipitate of morpholine hydrochloride was filtered off, and the filtrate was washed with water, dried over $MgSO_4$, and concentrated to 1/5 of the initial volume. Amide **XLI** was isolated chromatographically on an Al_2O_3 column, yield 32%.

***tert*-Butyl (*E*)-3-morpholino-4,4-dichloro-2-butenoate XLII** was prepared similarly to **XLI** by method *a* from ester **XIII** and morpholine in 1 : 2 molar ratio. The reaction mixture was refluxed for 14 h, after which the solvent was removed and amino ester **XLII** was isolated chromatographically on an Al_2O_3 column; yield 67%.

REFERENCES

1. US Patent 3803189, 1974, *Ref. Zh. Khim.*, 1975, 50363P.
2. FRG Patent 2921220, 1980, *Chem. Abstr.*, 1981, vol. 94, 83622u.
3. FRG Patent 2925012, 1980, *Chem. Abstr.*, 1981, vol. 94, 156335q.
4. FRG Patent 1534599, 1968, *Chem. Abstr.*, 1969, vol. 71, 13992.
5. Ol'dekop, Yu.A., Kaberdin, R.V., and Zhidkov, Yu.N., *Zh. Org. Khim.*, 1978, vol. 14, no. 3, p. 484.
6. Shcheglov, Yu.V., Nikishin, G.I., Dyusenov, M.I., Musikaev, D.A., Yakovets, V.I., and Yakovets, V.P., USSR Inventor's Certificate no. 218563, 1967, *Byull. Izobret.*, 1968, no. 17.
7. Dikusar, E.A., Yuvchenko, A.P., Vashkevich, E.V., Kozlov, N.G., Potkin, V.I., and Moiseichuk, K.L., *Zh. Org. Khim.*, 1999, vol. 35, no. 3, p. 396.
8. Roedig, A. and Foure, M., *Chem. Ber.*, 1976, vol. 109, no. 6, p. 2159.
9. Takhistov, V.V., *Prakticheskaya mass-spektrometriya organicheskikh soedinenii* (Practical Mass Spectrometry of Organic Compounds), Leningrad: Leningr. Gos. Univ., 1977.
10. Takhistov, V.V., Rodin, A.A., and Maksimova, B.N., *Usp. Khim.*, 1991, vol. 60, no. 10, p. 2143.
11. Bellamy, L.J., *The Infra-Red Spectra of Complex Molecules*, New York: Wiley, 1957.
12. Roedig, A. and Ritschel, W., *Lieb. Ann.*, 1983, no. 1, p. 13.
13. Roedig, A. and Ritschel, W., *Chem. Ber.*, 1983, vol. 116, no. 4, p. 1595.
14. Wendlandt, W.Wm., *Thermal Methods of Analysis*, New York: Interscience, 1964.
15. Yuvchenko, A.P., Dikusar, E.A., Kozlov, N.G., Zelenkovskii, V.M., Prokopchuk, N.R., Filanchuk, A.P., and Moiseichuk, K.L., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 1, p. 111.
16. Denisov, E.T., *Konstanty skorosti gomoliticheskikh reaktsii* (Rate Constants of Homolytic Reactions), Moscow: Nauka, 1971.
17. Yuvchenko, A.P., Dikusar, E.A., and Moiseichuk, K.L., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 1, p. 81.
18. Yuvchenko, A.P., Dikusar, E.A., Zhukovskaya, N.A., and Moiseichuk, K.L., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 2, p. 291.
19. Yuvchenko, A.P., Dikusar, E.A., and Moiseichuk, K.L., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 5, p. 807.
20. Adams, D.B., *Analyst*, 1966, vol. 91, no. 1083, p. 397.
21. Mair, R.D. and Graupner, A.J., *Anal. Chem.*, 1964, vol. 36, no. 1, p. 194.
22. Roedig, A. and Kloss, R., *Chem. Ber.*, 1957, vol. 90, no. 12, p. 2902.