Reactions of isocyanates with compounds containing active methylene groups in the presence of triethylamine

Yu. G. Gololobov, O. A. Linchenko, I. R. Golding, M. A. Galkina, I. Yu. Krasnova, I. A. Garbuzova, and P. V. Petrovskii*

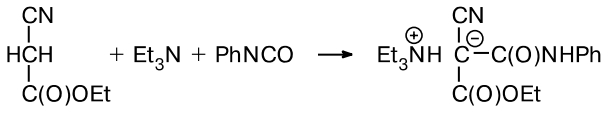
A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5085. E-mail: Yugol@ineos.ac.ru

Compounds containing active methylene groups react with isocyanates of different structures in the presence of triethylamine to form functionally substituted amides.

Key words: compounds with active methylene groups, isocyanates, triethylammonium salts of CH-acids, carboxamides, phosphorylamides.

Most of the transformations of compounds containing active methylene groups with isocyanates in the presence of bases, which afford monosubstituted carboxamides, involve sodium derivatives of compounds containing active methylene groups.[1] At the same time, these reactions were also carried out using organic bases as deprotonating agents.[2—4] The latter variant is convenient because simplifies the process and allows one, in some cases, to obtain salts of the corresponding amines, which are stable on storage and can be used in subsequent syntheses as functionally substituted carbanions. For instances, in the presence of triethylamine, ethyl cyanoacetate and phenyl isocyanate react to form triethylammonium salt **1** [2] (Scheme 1).

Scheme 1



1

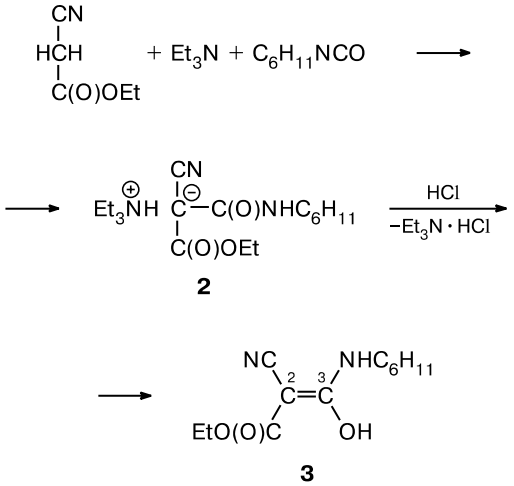
The first representatives of polymers with carbanions in the main backbone were obtained by the reaction of glycol cyanoacetates with 1,4-phenylenediisocyanate in the presence of triethylamine. Polymeric CH-acids that formed exist as stable salts with triethylamine.[5]

To synthesize new potentially biologically active monosubstituted amides of carboxylic and organoelement acids, organic and organoelement compounds with active methylene groups were introduced into the reactions with aliphatic and aromatic isocyanates and with isocyanate of diphenylthiophosphinic acid in the presence of triethylamine.

Published data on the use of alkyl(cycloalkyl) isocyanates and isocyanates of phosphorus acids in these transformations are lacking.

It is known that alkyl isocyanates have a much lower reactivity than aryl isocyanates. The latter can react *via* the above-presented scheme, while alkyl isocyanates form the corresponding amides only upon many-day storage of the reactants at ~20 °C under solvent-free conditions. For instance, cyclohexyl isocyanate reacts with ethyl cyanoacetate in the presence of triethylamine at ~20 °C for several days to form triethylammonium salt **2** in 92% yield. The treatment of salt **2** with dilute hydrochloric acid produces enol **3** (Scheme 2).

Scheme 2



2

3

The characteristic signals in the ^{1}H NMR spectrum of compound **3** are the signal of the enolic proton with the

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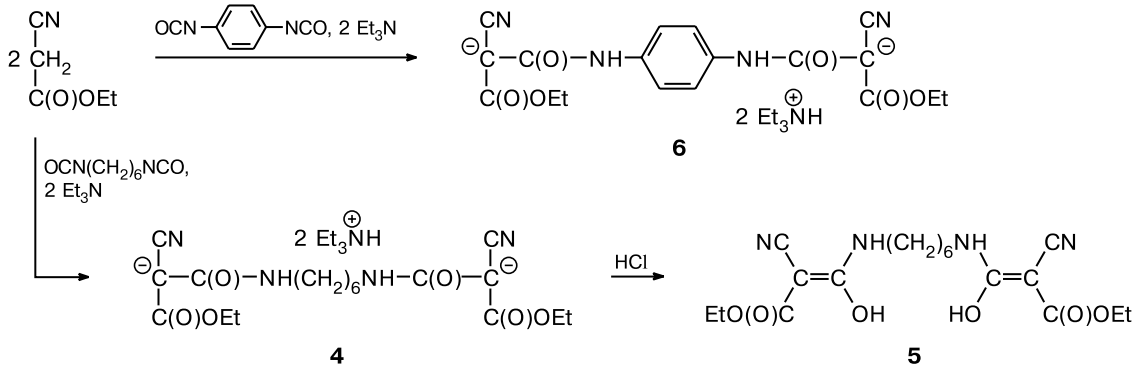
Scheme 3

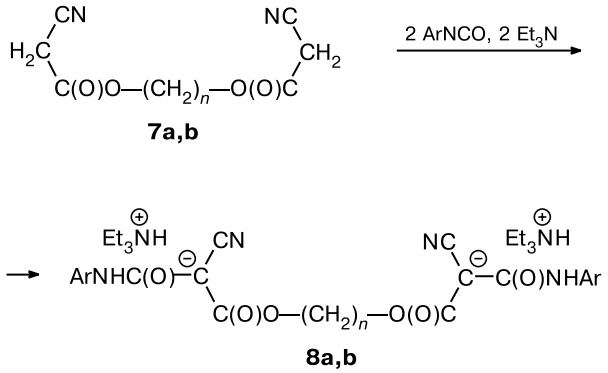


chemical shift δ_H = 15.01 and that of the proton of the NH fragment with δ_H = 5.72 ($J_{H,H}$ = 6.4 Hz). The position of signals of the vinylic protons of the C(2) and C(3) carbon atoms in the ^{13}C NMR spectrum are of substantial interest. Due to a high total electron-withdrawing effect of the ester and cyano groups and the electron-releasing influence of the amino and hydroxy groups, the polarization of the C=C multiple bond is directed from the C(3) carbon atom to the C(2) carbon atom, which reflects the position of signals of the C(2) and C(3) carbon atoms: $\delta_{C(2)}$ = 55.1 and $\delta_{C(3)}$ = 171.3.

1,6-Hexamethylenediisocyanate interacts with two moles of ethyl cyanoacetate in the presence of triethylamine without a solvent to form binary triethylammonium salt **4**, which on treatment with hydrochloric acid in an acetone solution is transformed into bisamide **5**. At the same time, 1,4-phenylenediisocyanate readily forms salt **6** in diethyl ether (Scheme 3).

Functionally substituted bisamides **8a,b** of different type were obtained by the reactions of monoisocyanates with diol dicyanoacetate under similar conditions (Scheme 4).

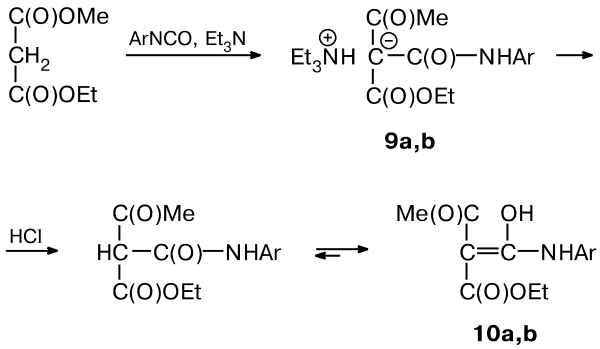
Scheme 4



Ar = 3,4-$Cl_2C_6H_3$; n = 2 (**a**), 6 (**b**)

The reactions of sodium salts of acetylacetone and acetoacetic ester with aryl isocyanates were patented,[6,7] and biological activity of the amides synthesized in these reactions was mentioned. We carried out the reactions of acetoacetic ester with phenyl and 3,4-dichlorophenyl isocyanates in the presence of triethylamine in ethereal solutions and obtained free derivatives **10a,b**. Salts **9a,b** that are formed in the first step were unstable and decomposed during attempts of their isolation (Scheme 5).

Scheme 5



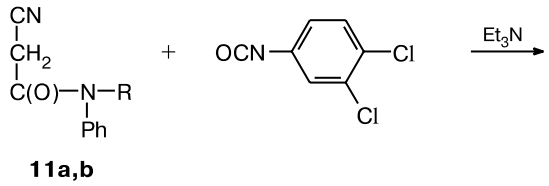
Ar = Ph (**a**), 3,4-$Cl_2C_6H_3$ (**b**)

Cyanoacetic amides **11a** and **11b** react readily with 3,4-dichlorophenyl isocyanate in the presence of diethylamine or benzene at ~20 °C to form salts of bisamides **12a** and **12b** in high yields (Scheme 6).

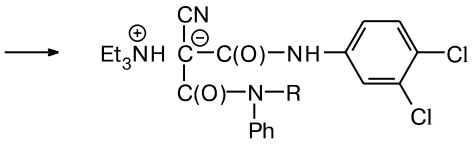
Diphenylphosphoryl- and phenylsulfoacetonitriles also have sufficient CH-acidity of the methylene group to interact successfully with aryl- and phosphorus-containing isocyanates. For instance, a mixture of diphenylphosphinylacetonitrile and 3,4-dichlorophenyl isocyanate reacts readily with triethylamine in methylene chloride to form triethylammonium salt **13** (Scheme 7).

Phenylcyanomethylsulfone reacts similarly with aryl isocyanates. Several minutes after the reactants were

Scheme 6



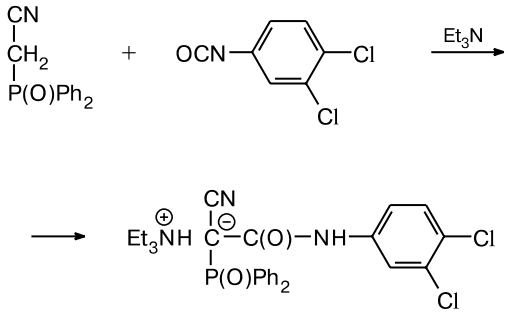
11a,b



12a,b

R = Me (**a**), Et (**b**)

Scheme 7

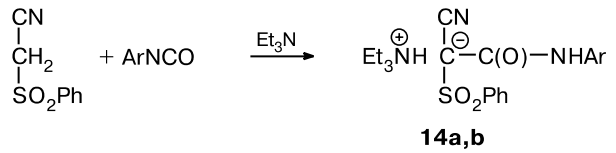


13

mixed in ether, crystalline salt **14a** (or **14b**) precipitated (Scheme 8).

The reactions of compounds containing active methylene groups with isocyanates of phosphorus acids are of special interest, because they can afford compounds with fragments of monosubstituted amides of phosphorus acids. In fact, when triethylamine was added to a solution of ethyl cyanoacetate and diphenylthiophosphinic isocyanate **15** in diethyl ether, a crystalline precipitate of salt **16** was formed after several minutes (Scheme 9). Compound **16** is characterized by the spin-spin coupling constant of the proton with the phosphorus through the nitrogen atom $^2J_{H,P} = 14$ Hz.

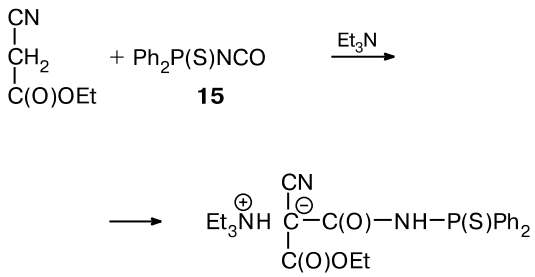
Scheme 8



14a,b

Ar = 3,4-$Cl_2C_6H_3$ (**a**), 4-O_2N-C_6H_4 (**b**)

Scheme 9



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The synthesized salts of functionally substituted amides were characterized by the data of elemental analysis (Table 1) and IR and NMR spectroscopy (Table 2).

Table 1. Characteristics of triethylammonium salts of functionally substituted amides **12a,b**, **13**, **14a,b**, and **16**

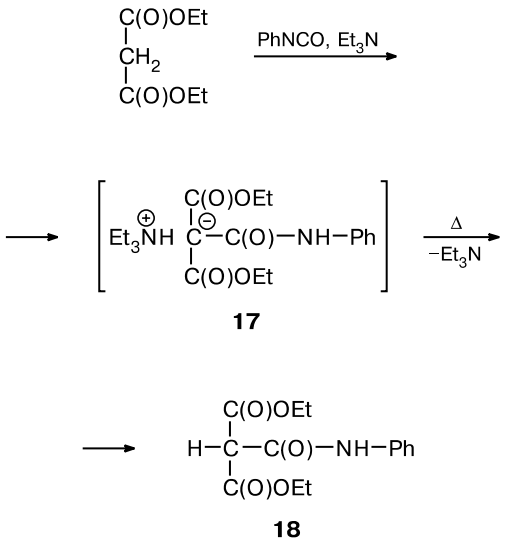
Compound	Yield (%)	M.p. /°C	Found / Calculated (%)			Molecular formula
			C	H	N	
12a	70	97—99	59.64	6.02	12.17	$C_{17}H_{12}Cl_2N_3O_2 \cdot C_6H_{16}N$
			59.61	6.05	12.09	
12b	79	104—107	60.51	6.37	11.76	$C_{18}H_{14}Cl_2N_3O_2 \cdot C_6H_{16}N$
			60.38	6.29	11.74	
13	50	119—121	61.21	5.71	7.84	$C_{21}H_{14}Cl_2N_2O_2P \cdot C_6H_{16}N$
			61.13	5.66	7.92	
14a	79	142—143	53.78	5.36	9.03	$C_{15}H_9Cl_2N_2O_3S \cdot C_6H_{16}N$
			53.62	5.32	8.94	
14b	57	112—114	56.37	5.81	12.46	$C_{15}H_{10}N_3O_5S \cdot C_6H_{16}N$
			56.50	5.83	12.56	
16	90	143—145	60.89	6.71	8.81	$C_{18}H_{16}N_2O_3PS \cdot C_6H_{16}N$
			60.89	6.76	8.88	

Table 2. IR and NMR spectra of compounds **12a,b**, **13**, **14a,b**, and **16**

Com-зщгтв	IR, ν/cm^{-1}	NMR ($CDCl_3$), δ	
		^{1}H	^{31}P
12a	1551 (C(O)NMe), 1597 (C(O)), 2170 (CN), 2636 ($^+$NH)	1.23 (t, 9 H, C<u>H</u>$_3$CH$_2$N, ^3J = 7.2); 3.06 (q, 6 H, CH$_3$C<u>H</u>$_2$N, ^3J = 7.2); 3.31 (s, 3 H, CH$_3$N); 7.09 (dd, 1 H, H$_\alpha$, ^3J = 7.2, ^4J = 2.0); 7.19 (t, 1 H, H$_p$, ^3J = 7.2); 7.22—7.26 (m, 3 H, 2 H$_o$, H$_\beta$); 7.33 (t, 2 H, H$_m$, ^3J = 7.2); 7.99 (d, 1 H, H$_{\alpha'}$, ^4J = 2.0); 10.72 (br.s, 1 H, NHC(O)); 12.00 (s, 1 H, $^+$NH)	
12b	1553 (CONEt), 1612 (C(O)NH), 2163 (CN), 2644 ($^+$NH), 3452 (NHC(O))	1.15 (t, 3 H, C<u>H</u>$_3$CH$_2$NPh, ^3J = 7.2); 1.22 (t, 9 H, C<u>H</u>$_3$CH$_2$N, ^3J = 7.2); 3.04 (q, 6 H, CH$_3$C<u>H</u>$_2$N, ^3J = 7.2); 3.78 (q, 2 H, CH$_3$C<u>H</u>$_2$NPh, ^3J = 7.2); 7.12 (dd, 1 H, H$_\alpha$, ^3J = 7.2, ^4J = 2.4); 7.19—7.25 (m, 4 H, 2 H$_o$, H$_p$, H$_\beta$); 7.34 (t, 2 H, H$_m$, ^3J = 7.2); 8.00 (s, 1 H, H$_{\alpha'}$); 10.80 (br.s, 1 H, NHC(O)); 12.08 (s, 1 H, $^+$NH)	—
13	1619 (C(O)N), 2158 (CN), 3196 ($^+$NH), 3272 (NHC(O))	1.28 (dt, 9 H, C<u>H</u>$_3$CH$_2$N, ^3J = 7.2, ^4J = 2.0); 3.12 (dq, 6 H, CH$_3$C<u>H</u>$_2$N, ^3J = 7.2, ^4J = 2.0); 7.08 (dd, 1 H, H$_\alpha$, ^3J = 7.2, ^4J = 2.0); 7.21 (d, 1 H, H$_\beta$, ^3J = 7.2); 7.41—7.45 (m, 6 H, H$_m$ + H$_p$); 7.78 (d, 2 H, H$_o$, ^3J = 7.2); 7.80 (d, 2 H, H$_o$, ^3J = 7.2); 7.91(s, 1 H, H$_{\alpha'}$); 10.45 (s, 1 H, $^+$NH); 11.13 (br.s, 1 H, NHC(O))	32.90
14a	1614 (C(O)N), 2170 (CN), 2714 ($^+$NH), 3314 (NHC(O))	1.25 (t, 9 H, C<u>H</u>$_3$CH$_2$N, ^3J = 7.2); 3.15 (q, 6 H, CH$_3$C<u>H</u>$_2$N, ^3J = 7.2); 7.06 (dd, 1 H, H$_\alpha$, ^3J = 7.2, ^4J = 2.0); 7.27 (d, 1 H, H$_\beta$, ^3J = 7.2); 7.40—7.48 (m, 3 H, 2 H$_m$+ H$_p$); 7.80 (d, 1 H, H$_{\alpha'}$, ^4J = 2.0); 7.88 (dd, 2 H, H$_o$, ^3J = 7.2, ^4J = 2.0); 9.35 (br.s, 1 H, NHC(O)); 9.66 (s, 1 H, $^+$NH)	—
14b	1135 (SO_2Ph), 1501 (NO_2), 1590 (C(O)N), 2187 (CN), 2704 ($^+$NH), 3304 (NHC(O))	1.28 (t, 9 H, C<u>H</u>$_3$CH$_2$N, ^3J = 7.2); 3.18 (q, 6 H, CH$_3$C<u>H</u>$_2$N, ^3J = 7.2); 7.41—7.47 (m, 3 H, 2 H$_m$ + H$_p$); 7.56 (d, 2 H, H$_o$, ^3J = 7.2); 7.88 (dd, 2 H, H$_\alpha$(NO_2); ^3J = 7.2, ^4J = 1.6); 8.09—8.11 (d, 2 H, H$_\beta$(NO_2), ^3J = 7.2); 9.36 (s, 1 H, $^+$NH); 9.75 (br.s, 1 H, NHC(O))	—
16	1593 (C(O)OEt), 1628 (C(O)N), 2193 (CN), 2696 ($^+$NH), 3440 (NHC(O))	1.07 (t, 9 H, C<u>H</u>$_3$CH$_2$N, ^3J = 7.2); 1.26 (t, 3 H, C<u>H</u>$_3$CH$_2$O, ^3J = 7.2); 2.99 (q, 6 H, CH$_3$C<u>H</u>$_2$N, ^3J = 7.2); 4.12 (q, 2 H, CH$_3$C<u>H</u>$_2$O, ^3J = 7.2); 7.38—7.42 (m, 6 H, H$_m$ + H$_p$); 7.90—7.96 (m, 4 H, H$_o$); 9.98 (s, 1 H, $^+$NH); 10.30 (d, 1 H, NHP, $^2J_{H,P}$ = 14)	48.81

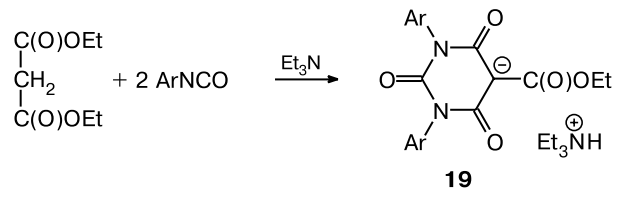
Similarly to acetoacetic ester, malonic ester reacts with aryl isocyanates in the presence of triethylamine to form unstable triethylammonium salt **17**, whose crystallization from acetone affords free acid **18** (Scheme 10).[4]

Scheme 10



At the same time, the reaction of 3,4-dichlorophenyl isocyanate with malonic ester and triethylamine in a molar ratio of 2 : 1 : 1 (similarly to unsubstituted phenyl isocyanate[2]) affords stable salt **19**,[1] since the CH-acidity of the corresponding barbiturate is sufficient for the formation of a salt with triethylamine (Scheme 11).

Scheme 11

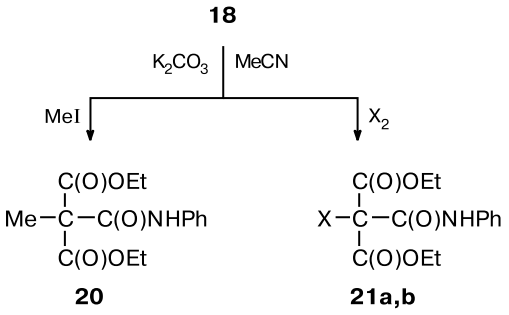


Ar = 3,4-$Cl_2C_6H_3$

In the presence of K_2CO_3, CH-acid **18** in acetonitrile is methylated with methyl iodide at the carbon atom to form monosubstituted amide **20**. It is of interest that

CH-acid **18** is easily brominated and iodinated, under the same conditions, to form the corresponding halide-substituted esters **21a,b** (Scheme 12).

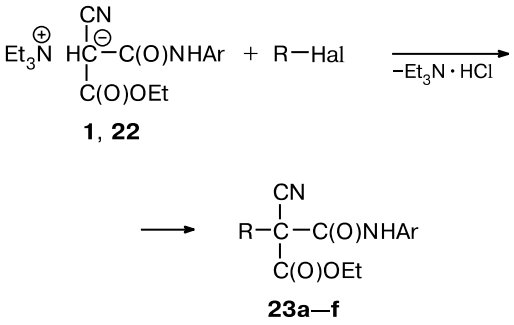
Scheme 12



X = Br (**a**), I (**b**)

Triethylammonium salts of ethyl cyanoacetate, such as phenylamide **1** and 3,4-dichlorophenylamide **22**, in a solution of benzene or acetonitrile are rather readily alkylated at the carbon atom with methyl iodide, allyl bromide, benzyl chloride, 4-nitrobenzyl bromide, or 2,4-dinitrobenzyl bromide to form crystalline derivatives **23a—f** (Scheme 13).

Scheme 13



1: Ar = Ph
22: Ar = 3,4-$Cl_2C_6H_3$
23: R = Allyl, Ar = Ph (**a**); R = 4-$O_2NC_6H_4CH_2$, Ar = Ph (**b**); R = 2,4-$(O_2N)_2C_6H_3CH_2$, Ar = Ph (**c**); R = Me, Ar = 3,4-$Cl_2C_6H_3$ (**d**); R = Allyl, Ar = 3,4-$Cl_2C_6H_3$ (**e**); R = Bn, Ar = 3,4-$Cl_2C_6H_3$ (**f**)

The synthesized compounds were characterized by the data of elemental analysis (Table 3) and IR and NMR spectroscopy (Table 4).

Thus, the method for syntheses of functionally substituted carboxamides by the reactions of compounds containing active methylene groups with aryl isocyanates in the presence of organic bases was extended to aliphatic mono-, bisisocyanates, and isocyanates of phosphorus acids. This method can provide new functionally substituted amides using not only compounds of new types with one active methylene group (cyanoacetamides, phosphine oxides with the cyanomethylene group at phosphorus) but also compounds containing two active methylene groups .

Table 3. Characteristics of amides **23a—f**

Compound	Yield (%)	M.p. /°C	Found / Calculated (%) C	H	N	Molecular formula
23a	88	31—32	66.24 / 66.18	5.89 / 5.92	10.28 / 10.28	$C_{15}H_{16}N_2O_3$
23b	45	129—131	62.04 / 62.12	4.71 / 4.66	11.37 / 11.44	$C_{19}H_{17}N_3O_5$
23c	49	128—129	55.41 / 55.34	3.87 / 3.91	13.60 / 13.59	$C_{19}H_{16}N_4O_7$
23d	55	86—87	49.54 / 49.52	3.85 / 3.81	8.91 / 8.89	$C_{13}H_{12}Cl_2N_2O_3$
23e	71	76—77	52.81 / 52.79	4.04 / 4.10	8.17 / 8.21	$C_{15}H_{14}Cl_2N_2O_3$
23f	3	135—137	58.37 / 58.31	4.09 / 4.09	7.14 / 7.16	$C_{19}H_{16}Cl_2N_2O_3$

Experimental

NMR spectra were obtained on a Bruker AMX-400 spectrometer with working frequencies of 400.1 (^{1}H), 100.6 (^{13}C), and 162.0 MHz (^{31}P) using $CDCl_3$ as the solvent. IR spectra were recorded on a Magna-IR-750 FTIR spectrometer (Nicolet) in KBr pellets.

Ethyl 2-cyano-3-hydroxy-3-*N*-cyclohexylaminoacrylate (3). A mixture of ethyl cyanoacetate (1.13 g, 10 mmol) and cyclohexyl isocyanate (1.44 g, 10 mmol), and triethylamine (1.15 g, 10 mmol) was stored for 6 days at 20 °C. Diethyl ether was added to the mixture, and the resulting solution was filtered. After the solvent was distilled off *in vacuo*, a residue was dissolved in benzene, and 2.5% hydrochloric acid (35 mL) was added. A white precipitate that formed was filtered off and doubly crystallized from a petroleum ether—acetone (3 : 4) mixture. Colorless crystals were obtained in 56.0% yield (1.33 g), m.p. 136—138 °C. Found (%): C, 60.68; H, 7.67; N, 11.72. $C_{12}H_{18}N_2O_3$. Calculated (%): C, 60.50; H, 7.56; N, 11.76. ^{1}H NMR, δ: 1.11—1.40 (m, 8 H, CH_3CH_2 + 2 $CH_{2,cyclo\text{-}Hex}$ + + 1 $CH_{cyclo\text{-}Hex}$); 1.62—1.64 (m, 1 H, $CH_{cyclo\text{-}Hex}$); 1.74—1.76 (m, 2 H, $CH_{2,cyclo\text{-}Hex}$); 1.92—1.95 (m, 2 H, $CH_{2,cyclo\text{-}Hex}$); 3.68—3.77 (m, 1 H, $CH_{cyclo\text{-}Hex}$); 4.24 (q, 2 H, CH_3CH_2O, ^3J = 7.2 Hz); 5.72 (d, 1 H, NH, ^3J = 6.4 Hz); 15.01 (s, 1 H, OH). ^{13}C NMR, δ: 14.2 (CH_3), 25.0 ($CH_{2,cyclo\text{-}Hex}$), 32.8 ($CH_{2,cyclo\text{-}Hex}$), 50.3 (CHNH), 55.1 (CCN), 61.3 (CH_2O), 116.9 (CN), 171.3 (COH), 173.2 (C=O). IR, ν/cm^{-1}: 1615 (C(O)N), 1647 (C(O)OEt), 2201 (CN), 2937 ($^+$NH), 3408 (NHC(O)).

Bis(triethylammonium) 1,12-dicyano-1,12-diethoxycarbonyl-2,11-dioxo-3,10-diazadodecane-1,12-diide (4). A mixture of ethyl cyanoacetate (3.25 g, 26 mmol), 1,6-hexylenediisocyanate (2.18 g, 13 mmol), and triethylamine (2.63 g, 26 mmol) was stored for 12 h at ~20 °C, and then the mixture was triply washed with diethyl ether. A powder that formed was dissolved in hot acetone (50 mL), and the solution was cooled down. After diethyl ether was added until the medium grew turbid, the solu-

Table 4. Data of IR and ^{1}H NMR spectroscopy for compounds **23a—f**

Compound	IR, ν/cm^{-1}	^{1}H NMR ($CDCl_3$), δ
23a	1677 (C(O)N), 1754 (COOEt), 2246 (CN), 3294 (NH)	1.30 (t, 3 H, C<u>H</u>$_3$CH$_2$, ^3J = 7.2); 2.99, 3.02 (both dd, H$_A$, H$_B$, CCH$_2$C, ^3J = 7.2, ^2J(H$_A$H$_B$) = 3.2); 4.30 (q, 2 H, CH$_3$C<u>H</u>$_2$O, ^3J = 7.2); 5.30 (m, 2 H, C<u>H</u>$_2$=CH); 5.83 (m, 1 H, CH$_2$=C<u>H</u>); 7.15 (t, 1 H, H$_p$, ^3J = 7.2); 7.31 (t, 2 H, H$_m$, ^3J = 7.2); 7.50 (d, 2 H, H$_o$, ^3J = 7.2); 8.50 (s, 1 H, HN)
23b	1523 (NO_2), 1709 (C(O)N), 1733 (COOEt), 2245 (CN), 3346 (NH)	1.31 (t, 3 H, C<u>H</u>$_3$CH$_2$, ^3J = 7.2); 3.60, 3.75 (both dd, H$_A$, H$_B$, CCH$_2$C, ^3J = 7.2, J(H$_A$H$_B$) = 14.0); 4.38 (q, 2 H, CH$_3$C<u>H</u>$_2$O, ^3J = 7.2); 7.20 (t, 1 H, H$_p$, Ph, ^3J = 7.2); 7.35 (t, 2 H, H$_m$, Ph, ^3J = 7.2); 7.43 (d, 2 H, H$_o$, Ph, ^3J = 7.2); 7.45 (d, 2 H, H$_o$(Ar), ^3J = 7.2); 8.09 (s, 1 H, HN); 8.18 (d, 2 H, H$_m$(Ar), ^3J = 7.2)
23c	1531 (NO_2), 1712 (C(O)N), 1738 (COOEt), 2252 (CN), 3341 (NH)	1.34 (t, 3 H, C<u>H</u>$_3$CH$_2$, ^3J = 7.2); 4.17, 4.22 (both dd, H$_A$, H$_B$, CCH$_2$C, ^3J = 7.2, J(H$_A$H$_B$) = 14.0); 4.38 (q, 2 H, CH$_3$C<u>H</u>$_2$O, ^3J = 7.2); 7.22 (t, 1 H, H$_p$, ^3J = 7.2); 7.36 (t, 2 H, H$_m$, ^3J = 7.2); 7.46 (d, 2 H, H$_o$, ^3J = 7.2); 7.84 (d, 1 H, C<u>H</u>CHC(NO$_2$), ^3J = 7.2); 8.21 (s, 1 H, HN); 8.40 (d, 1 H, CHC<u>H</u>C(NO$_2$), ^3J = 7.2); 8.92 (s, 1 H, (NO$_2$)CC<u>H</u>C(NO$_2$))
23d	1696 (C(O)N), 1743 (COOEt), 2251 (CN), 3396 (NH)	1.34 (t, 3 H, C<u>H</u>$_3$CH$_2$, ^3J = 7.2); 1.96 (s, 3 H, CH$_3$C); 4.36 (q, 2 H, CH$_3$C<u>H</u>$_2$O, ^3J = 7.2); 7.34 (dd, 1 H, H$_\alpha$, ^4J = 2.4, ^3J = 7.2); 7.39 (d, 1 H, H$_\beta$, ^3J = 7.2); 7.75 (d, 1 H, H$_{\alpha'}$, ^4J = 2.4); 8.48 (s, 1 H, HN)
23e	1102 (CCl), 1649 (C(O)N), 1734 (COOEt), 2215 (CN).	1.34 (t, 3 H, C<u>H</u>$_3$CH$_2$, ^3J = 8.4); 3.02 (m, 2 H, C<u>H</u>$_2$CHCH$_2$); 4.38 (m, 2 H, CH$_3$C<u>H</u>$_2$O); 5.34 (dt, 2 H, CH$_2$CHC<u>H</u>$_2$, ^2J = 1.2, ^3J = 8.4); 5.81 (tt, 1 H, CH$_2$C<u>H</u>CH$_2$, ^3J = 8.4); 7.34 (dd, 1 H, H$_\alpha$, ^4J = 2.4, ^3J = 8.4); 7.40 (d, 1 H, H$_\beta$, ^3J = 8.4); 7.76 (d, 1 H, H$_{\alpha'}$, ^4J = 2.4); 8.20 (s, 1 H, HN)
23f	1696 (C(O)N), 1761 (COOEt), 2251 (CN), 3396 (NH)	1.26 (t, 3 H, C<u>H</u>$_3$CH$_2$, ^3J = 7.2); 3.50 (d, 1 H, PhC<u>H</u>$_A$H$_B$, $^2J_{HA,HB}$ = 13.8); 3.62 (d, 1 H, PhCH$_A$<u>H</u>$_B$, $^2J_{HA,HB}$ = 13.8); 4.30 (q, 2 H, CH$_3$C<u>H</u>$_2$O, ^3J = 7.2); 7.22—7.40 (m, 7 H, H$_\alpha$, H$_\beta$, H$_{Ph}$); 7.67 (s, 1 H, H$_{\alpha'}$); 8.32 (s, 1 H, NH)

tion was left to stand at ~–4 °C. Compound **4** was obtained in 12.0% yield (0.99 g), m.p. 91—94 °C. Found (%): C, 60.45; H, 9.52; N, 14.21. $C_{18}H_{24}N_4O_6 \cdot 2C_6H_{16}N$. Calculated (%): C, 60.40; H, 9.40; N, 14.09. ^{1}H NMR, δ: 1.20 (t, 6 H, C<u>H</u>$_3$CH$_2$O, ^3J = 7.2 Hz); 1.27 (t, 18 H, C<u>H</u>$_3$CH$_2$N, ^3J = 7.2 Hz); 1.40—1.42 (m, 4 H, NCH$_2$CH$_2$C<u>H</u>$_2$C<u>H</u>$_2$); 3.11—3.13 (m, 14 H, CH$_3$C<u>H</u>$_2$N, NC<u>H</u>$_2$C<u>H</u>$_2$CH$_2$); 4.06 (q, 4 H, CH$_3$C<u>H</u>$_2$O, ^3J = 7.2 Hz); 8.49 (s, 2 H, NHC(O)); 11.50 (br.s, 2 H, $^+$NH). IR, ν/cm^{-1}: 1534, 1592 (C(O)N), 1620 (C(O)), 2179 (CN), 2622 ($^+$NH), 3303 (NH).

Diethyl (2,13-dicyano-3,12-dihydroxy-4,11-diazatetradeca-2,12-dienedioate) (5). Dilute hydrochloric acid was added to a solution of salt **4** (0.40 g, 0.63 mmol) in acetone to acidic pH. A precipitate that formed was crystallized from acetone to obtain compound **5** (0.25 g, 95.0%), m.p. 166—168 °C. Found (%): C, 54.81; H, 6.68; N, 14.20. $C_{18}H_{26}N_4O_6$. Calculated (%): C, 54.82; H, 6.59; N, 14.21. ^{1}H NMR, δ: 1.31 (t, 6 H, C<u>H</u>$_3$CH$_2$O, ^3J = 6.8 Hz); 1.35—1.37 (m, 4 H, NCH$_2$CH$_2$C<u>H</u>$_2$C<u>H</u>$_2$); 1.57—1.60 (m, 4 H, NCH$_2$C<u>H</u>$_2$CH$_2$); 3.36 (dt, 4 H, NHC<u>H</u>$_2$); 4.26 (q, 4 H, CH$_3$C<u>H</u>$_2$O, ^3J = 6.8 Hz); 6.04 (t, 2 H, NH, ^3J = 6.8 Hz); 15.10 (br.s, 2 H, OH). IR, ν/cm^{-1}: 1660 (C(O)N), 2200 (CN), 2622 ($^+$NH), 3311 (NH).

Synthesis of compounds 6, 8a,b, 10a,b, 12a,b, 13, 14a,b, 16, 18, and 19 (general procedure). Triethylamine was added dropwise in a small excess to a solution of a compound with an active methylene group and aryl isocyanate in a diethyl ether—toluene—THF (1 : 1 : 2) mixture (**6**), in C_6H_6 (**8a**, **12b**, **14b**), in CH_2Cl_2 (**8b**, **13**), in diethyl ether (**10a,b**, **12a**, **14a**, **16**, **18**), or without a solvent (**19**). The solution was filtered, and a precipitate that formed was washed with a petroleum ether—diethyl ether (1 : 1) mixture (**10a,b**, **14a**, **16**), dried, and crystallized from a $CHCl_3$—acetone (1 : 1) mixture (**6**), a $CHCl_3$—EtOH—acetone (1 : 2 : 2) mixture (**8a**), MeCN (**8b**, **16**), a petroleum ether—acetone (1 : 1) mixture (**12a**), a petroleum ether—C_6H_6 (1 : 1) mixture (**12b**, **13**), C_6H_6 (**14b**), or a petroleum ether—C_6H_6—$CHCl_3$ (2 : 3 : 1) mixture (**19**).

Bis(triethylammonium)-1,4-bis(1-cyano-1-ethoxycarbonyl-2-oxo-1-azapropanid-3-yl)benzene (6). Compound **6** was obtained according to a general procedure in 83.0% yield (2.0 g, m.p. 179—181 °C) from ethyl cyanoacetate (ECA) (0.83 g, 7.30 mmol), 1,4-phenylenediisocyanate (0.80 g, 5.31 mmol), and triethylamine (0.54 mL, 7.30 mmol). Found (%): C, 61.31; H, 8.27; N, 14.08. $C_{18}H_{16}N_4O_6 \cdot 2C_6H_{16}N$. Calculated (%): C, 61.22; H, 8.16; N, 14.29. ^{1}H NMR, δ: 1.25—1.30 (m, 24 H, C<u>H</u>$_3$CH$_2$N + C<u>H</u>$_3$CH$_2$O); 3.10—3.15 (q, 12 H, CH$_3$C<u>H</u>$_2$N, ^3J = 6.8 Hz); 4.12—4.17 (q, 4 H, CH$_3$C<u>H</u>$_2$O, ^3J = 6.8 Hz); 7.32 (s, 4 H, H$_{Ph}$); 10.67 (br.s, 2 H, NHC(O)); 10.91 (s, 2 H, $^+$NH). ^{13}C NMR, δ: 8.5 (<u>C</u>H$_3$CH$_2$N), 14.7 (<u>C</u>H$_3$CH$_2$O), 45.9 (CH$_3$<u>C</u>H$_2$N), 58.8 (CH$_3$<u>C</u>H$_2$O), 59.7 (C$^-$), 120.2 (CH$_{Ar}$), 124.6 (C$_{Ar}$), 169.5 (C=O), 171.0 (COOEt). IR, ν/cm^{-1}: 1597 (C(O)), 2184 (CN), 2686 ($^+$NH), 3194 (NHC(O)).

Bis(triethylammonium) 1,8-dicyano-2,7-dioxo-1,8-di-[*N*,*N*′-(3,4-dichlorophenylcarbamoyl)]-3,6-dioxaoctane-1,8-diide (8a).

Compound **8a** was obtained according to a general procedure in 68.2% yield (1.32 g, m.p. 184—186 °C) from compound **7a** (0.49 g, 2.50 mmol), 3,4-dichlorophenyl isocyanate (0.94 g, 5.0 mmol), and triethylamine (0.69 mL, 5.0 mmol). Found (%): C, 52.71; H, 5.74; N, 10.74. $C_{22}H_{12}Cl_4N_4O_6 \cdot 2C_6H_{16}N$. Calculated (%): C, 52.71; H, 5.68; N, 10.85. ^{1}H NMR, δ: 0.46 (t, 18 H, C$\underline{H}_3$CH$_2$N, ^3J = 7.2 Hz, ^4J = 2.0 Hz); 2.35 (q, 12 H, CH$_3$C$\underline{H}_2$N, ^3J = 7.2 Hz, ^4J = 2.0 Hz); 3.35 (s, 4 H, O(CH$_2$)$_2$O); 7.06—7.09 (m, 4 H, H$_\alpha$, H$_\beta$); 7.27 (s, 2 H, H$_{\alpha'}$); 8.30 (br.s, 1 H, NHC(O)); 10.01 (s, 1 H, $^+$NH). ^{13}C NMR, δ: 7.0 (C$\underline{H}_3$CH$_2$N), 44.3 (CH$_3$C$\underline{H}_2$N), 59.1 (C$\underline{H}_2$O), 59.7 (C$^-$), 116.1 (C$_\alpha$), 117.7 (C$_\beta$), 120.6 (CCl), 121.0 (C$'$Cl), 128.1 (C$_{\alpha'}$), 129.4 (NC$_{Ar}$), 138.7 (CN), 165.8 (NC(O)), 168.5 (C(O)). IR, ν/cm^{-1}: 1614 (C(O)N), 2170 (CN), 2714 ($^+$NH), 3314 (NHC(O)).

Bis(triethylammonium) 1,12-dicyano-1,12-di-[*N*,*N*′-(3,4-dichlorophenylcarbomoyl)]-2,11-dioxo-3,10-dioxadodecane-1,12-diide (8b). Compound **8b** was obtained according to an above-presented general procedure from compound **7b** (0.62 g, 2.50 mmol), 3,4-dichlorophenyl isocyanate (0.94 g, 5.00 mmol), and triethylamine (0.70 mL, 5.00 mmol) in a yield of 1.75 g (84.5%), m.p. 166—168 °C. Found (%): C, 54.97; H, 6.31; N, 10.16. $C_{26}H_{20}Cl_4N_4O_6 \cdot 2C_6H_{16}N$. Calculated (%): C, 54.94; H, 6.26; N, 10.12. ^{1}H NMR, δ: 1.34 (t, 18 H, C$\underline{H}_3$CH$_2$N, ^3J = 7.2 Hz, ^4J = 2.0 Hz); 1.40—1.44 (m, 4 H, CH$_2$CH$_2$(C$\underline{H}_2$)$_2$CH$_2$CH$_2$); 1.67—1.70 (m, 4 H, CH$_2$C$\underline{H}_2$(CH$_2$)$_2$C$\underline{H}_2$CH$_2$); 3.21—3.23 (m, 12 H, CH$_3$C$\underline{H}_2$N); 4.09 (t, 4 H, C$\underline{H}_2$(CH$_2$)$_4$C$\underline{H}_2$, ^3J = 7.2 Hz); 7.07 (dd, 2 H, H$_o$, ^3J = 7.2 Hz, ^4J = 2.0 Hz); 7.24 (d, 2 H, H$_m$, ^3J = 7.2 Hz); 7.97 (d, 1 H, H$_{o'}$, ^4J = 2.0 Hz); 10.76 (br.s, 1 H, NHC(O)); 10.94 (s, 1 H, $^+$NH). IR, ν/cm^{-1}: 1601 (C(O)N), 1634 (C(O)); 2185 (CN), 2659 ($^+$NH), 3170 (N$\underline{H}$C(O)).

Ethyl 2-acetyl-3-hydroxy-3-(*N*-phenylamino)acrylate (10a). Colorless compound **10a** was synthesized in a yield of 6.4 g (89%) from acetoacetic ester (3.76 g, 29 mmol), PhNCO (3.44 g, 29 mmol), and triethylamine (4.1 mL, 29 mmol), m.p. 56—58 °C (Ref. 8: 56—58 °C). ^{1}H NMR, δ: 1.37 (t, 3 H, C$\underline{H}_3$CH$_2$, ^3J = 7.2 Hz); 2.47 (s, 3 H, CH$_3$C(O)); 4.30 (q, 2 H, CH$_3$C$\underline{H}_2$, ^3J = 7.2 Hz); 7.11—7.53 (m, 5 H, Ar); 11.30 (s, 1 H, NH); 18.17 (s, 1 H, OH (enol); enol content >99%). IR (Nujol), ν/cm^{-1}: 1675 (C(O)).

Ethyl 2-acetyl-3-*N*-(3,4-dichlorophenylamino)-3-hydroxyacrylate (10b). Compound **10b** (m.p. 106—108 °C) was synthesized from acetoacetic ester (3.9 g, 30 mmol), 3,4-dichlorophenyl isocyanate (5.86 g, 31 mmol), and triethylamine (4.5 mL, 32 mmol) in a yield of 5.8 g (60%). Found (%): C, 49.06; H, 4.00; N, 4.24; Cl, 22.26. $C_{13}H_{13}Cl_2NO_4$. Calculated (%): C, 49.08; H, 4.12; N, 4.40; Cl, 22.28. ^{1}H NMR, δ: 1.37 (t, 3 H, C$\underline{H}_3$CH$_2$, ^3J = 7.2 Hz); 2.47 (s, 3 H, CH$_3$CO); 4.30 (q, 2 H, CH$_3$C$\underline{H}_2$, ^3J = 7.2 Hz); 7.30—7.78 (m, 3 H, Ar); 11.43 (s, 1 H, NH); 17.75 (s, 1 H, OH (enol); enol content >99%). IR (Nujol), ν/cm^{-1}: 1671 (C(O)).

Triethylammonium cyano[*N*-(3,4-dichlorophenylcarbamoyl)](*N*′-methyl-*N*′-phenylcarbamoyl)methanide (12a). Compound **12a** was obtained in a yield of 0.81 g according to an above-presented procedure from cyanoacetic methylphenylamide **11a** (0.43 g, 2.5 mmol), 3,4-dichlorophenyl isocyanate (0.47 g, 2.5 mmol), and triethylamine (0.25 mL, 2.5 mmol).

Triethylammonium cyano[*N*-(3,4-dichlorophenylcarbamoyl)](*N*′-ethyl-*N*′-phenylcarbamoyl)methanide (12b). Compound **12b** was obtained in a yield of 1.0 g according to a general procedure from cyanoacetic ethylphenylamide **11b** (0.50 g, 2.66 mmol), 3,4-dichlorophenyl isocyanate (0.50 g, 2.66 mmol), and triethylamine (0.54 mL, 3.96 mmol).

Triethylammonium cyano(diphenylphosphoryl)[*N*-(3,4-dichlorophenylcarbamoyl)]methanide (13). Compound **13** was obtained according to a general procedure from diphenylphosphinylacetonitrile (0.40 g, 1.66 mmol), 3,4-dichlorophenyl isocyanate (0.39 g, 2.07 mmol), and triethylamine (0.23 mL, 1.66 mmol).

Triethylammonium cyano[*N*-(3,4-dichlorophenylcarbamoyl)](phenylsulfonyl)methanide (14a). Compound **14a** was synthesized in a yield of 1.83 g according to a general procedure from phenylcyanomethylsulfone (0.90 g, 5.0 mmol), 3,4-dichlorophenyl isocyanate (0.93 g, 5.0 mmol), and triethylamine (0.7 mL, 5.05 mmol).

Triethylammonium cyano[*N*-(4-nitrophenylcarbamoyl)](phenylsulfonyl)methanide (14b). Compound **14b** was synthesized in a yield of 0.7 g according to a general procedure from phenylcyanomethylsulfone (0.50 g, 2.76 mmol), *p*-nitrophenyl isocyanate (0.45 g, 2.76 mmol), and triethylamine (0.5 mL, 3.61 mmol).

Triethylammonium cyano(diphenylthiophosphorylcarbamoyl)(ethoxycarbonyl)methanide (16). Compound **16** was synthesized in a yield of 0.88 g from ECA (0.22 g, 1.93 mmol), diphenyl thiophosphinatoisocyanate **15** (0.5 g, 1.93 mmol), and triethylamine (0.3 mL, 2.16 mmol).

Diethyl (*N*-phenylaminocarbonyl)malonate (18). Compound **18** was obtained in 76.2% yield (31.90 g) as a colorless powder with m.p. 123—125 °C (Ref. 2: m.p. 125 °C) from malonic ester (24.00 g, 0.15 mol), phenyl isocyanate (18.00 g, 0.15 mol), and triethylamine (20 mL, 0.15 mol) according to a general procedure. ^{1}H NMR, δ: 1.30 (t, 6 H, C$\underline{H}_3$CH$_2$, ^3J = 7.2 Hz); 4.28 (dq, 4 H, CH$_2$, ^3J = 7.2 Hz); 4.44 (s, 1 H, CH); 7.12 (t, 1 H, H$_p$, ^3J = 7.2 Hz); 7.32 (t, 2 H, H$_m$, ^3J = 7.2 Hz); 7.55 (d, 2 H, H$_o$, ^3J = 7.2 Hz); 9.31 (s, 1 H, NH). IR, ν/cm^{-1}: 1667 (C(O)N), 1748 (C(O)), 3211 (N$\underline{H}$C(O)).

Triethylammonium 3,5-*N*,*N*′-di-(3,4-dichlorophenyl)-1-ethoxycarbonyl-2,4,6-trioxo-3,5-diazacyclohexanide (19) was synthesized from malonic ester (1.00 g, 6.2 mmol), 3,4-dichlorophenyl isocyanate (2.56 g, 13.6 mmol), and triethylamine (1 mL, 7.2 mmol). The reaction occurred with heat release, after 2 h volatiles were distilled off *in vacuo*, and a glassy product that formed was treated according to a general procedure. Compound **19** was obtained in 5.5% yield (0.2 g), m.p. 180 °C (with decomposition). Found (%): C, 50.68; H, 4.61; N, 7.14. $C_{19}H_{11}Cl_4N_2O_5 \cdot C_6H_{16}N$. Calculated (%): C, 50.76; H, 4.57; N, 7.11. ^{1}H NMR, δ: 1.17 (t, 9 H, C$\underline{H}_3$CH$_2$N, ^3J = 7.2 Hz); 1.30 (t, 9 H, C$\underline{H}_3$CH$_2$O, ^3J = 7.2 Hz); 3.00 (t, 6 H, C$\underline{H}_3$CH$_2$N, ^3J = 7.2 Hz); 4.17 (q, 2 H, CH$_3$C$\underline{H}_2$O, ^3J = 7.2 Hz); 7.12 (dd, 1 H, H$_\alpha$, ^3J = 7.2 Hz, ^4J = 2.0 Hz); 7.38 (d, 1 H, H$_{\alpha'}$, ^3J = 2.0 Hz); 7.45 (d, 1 H, H$_\beta$, ^3J = 7.2 Hz); 10.20 (s, 1 H, Et$_3$NH). IR, ν/cm^{-1}: 1650 (CO), 1671 (COOEt).

Diethyl methyl(*N*-phenylaminocarbonyl)malonate (20). Methyl iodide (1.56 g, 10 mol) was added dropwise with stirring to a mixture of amide **18** (2.79 g, 10 mmol) and K_2CO_3 (2.76 g, 20 mmol) in MeCN (40 mL). The mixture was stirred for 6 h and filtered off after a petroleum ether—benzene (1 : 1) mixture (50 mL) was added. The solvent was distilled off *in vacuo* from the filtrate, and an oil that formed was dissolved on heating in petroleum ether. The solution was cooled to ~20 °C, stored at 0 °C for 1 h, and filtered. A powder of compound **20** was obtained in a yield of 0.75 g (25.6%), m.p. 40—43 °C.

Found (%): C, 61.47; H, 6.56; N, 4.82. $C_{15}H_{19}NO_5$. Calculated (%): C, 61.43; H, 6.48, N, 4.78. ^{1}H NMR, δ: 1.27 (t, 6 H, $C\underline{H}_3CH_2$, ^3J = 7.2 Hz); 1.80 (s, 3 H, CH_3C); 4.27 (q, 4 H, $CH_3C\underline{H}_2O$, ^3J = 7.2 Hz); 7.11 (t, 1 H, H_p, ^3J = 7.2 Hz); 7.32 (t, 2 H, H_m, ^3J = 7.2 Hz); 7.56 (d, 2 H, H_o, ^3J = 7.2 Hz); 9.82 (s, 1 H, NH). IR, ν/cm^{-1}: 1667 (C(O)N), 1760 (COOEt), 3281 (NH).

Synthesis of compounds 21a,b (general procedure). A solution of Br_2 or I_2 in CH_2Cl_2 was added dropwise to a stirred mixture of phenylamide **18** and dry K_2CO_3 in CH_2Cl_2 or $CHCl_3$. The solution was filtered off, the solvent was distilled off from the filtrate, and a residue was crystallized from a diethyl ether—petroleum ether (1 : 1) mixture.

Diethyl bromo(*N*-phenylcarbamoyl)malonate (21a). Compound **21a** was synthesized according to an above-presented general procedure from phenylamide **18** (1.00 g, 3.6 mmol), K_2CO_3 (0.50 g, 3.6 mmol), and Br_2 (0.57 g, 3.6 mmol) in a yield of 0.90 g (70.6%), m.p. 44—45 °C. Found (%): C, 46.88; H, 4.47; N, 3.91; Br, 22.23. $C_{14}H_{16}BrNO_5$. Calculated (%): C, 46.93; H, 4.47; N, 3.91; Br, 22.35. ^{1}H NMR, δ: 1.30 (t, 6 H, $C\underline{H}_3CH_2$, ^3J = 7.2 Hz); 4.35 (dq, 4 H, $CH_3C\underline{H}_2O$, ^3J = 7.2 Hz, ^4J = 2.0 Hz); 7.14 (t, 1 H, H_p, ^3J = 7.2 Hz); 7.33 (t, 2 H, H_m, ^3J = 7.2 Hz); 7.56 (d, 2 H, H_o, ^3J = 7.2 Hz); 9.74 (s, 1 H, HN). IR, ν/cm^{-1}: 1684 (C(O)N), 1776 (COOEt), 3260 (NH).

Diethyl iodo(*N*-phenylcarbamoyl)malonate (21b). A crystalline product with m.p. 59—61 °C was obtained in a yield of 0.44 g (20%) according to a general procedure from phenylamide **18** (1.53 g, 5.5 mmol), K_2CO_3 (0.75 g, 5.5 mmol), and I_2 (1.39 g, 5.5 mmol). Found (%): C, 41.58; H, 4.01; N, 3.42. $C_{14}H_{16}INO_5$. Calculated (%): C, 41.48; H, 3.95; N, 3.46. ^{1}H NMR, δ: 1.30 (t, 6 H, $C\underline{H}_3CH_2$, ^3J = 7.2 Hz); 4.34 (dq, 4 H, $CH_3C\underline{H}_2O$, ^3J = 7.2 Hz, ^4J = 1.6 Hz); 7.14 (t, 1 H, H_p, ^3J = 7.2 Hz); 7.34 (t, 2 H, H_m, ^3J = 7.2 Hz); 7.57 (dd, 2 H, H_o, ^3J = 7.2 Hz, ^4J = 1.0 Hz); 10.01 (s, 1 H, HN). IR, ν/cm^{-1}: 1677 (C(O)N), 1760 (COOEt), 3326 (NH).

Synthesis of compounds 23a—f (general procedure). A solution of triethylammonium salt **1** and, correspondingly, allyl bromide, 4-nitrobenzyl bromide, or 2,4-dinitrobenzyl chloride was stirred at ~20 °C in benzene for several hours. The mixture was filtered, and the filtrate was evaporated *in vacuo*. After the solvent was removed *in vacuo*, a residue was washed with petroleum ether and crystallized from petroleum ether (**23a**), from a petroleum ether—$CHCl_3$ (1 : 1) mixture (**23b**), or from a petroleum ether—$CHCl_3$ (1 : 2) mixture (**23c**).

A solution of triethylammonium salt **22** and methyl iodide, allyl bromide, or benzyl chloride was stirred on heating in MeCN or benzene. A precipitate that formed was filtered off, and the filtrate was evaporated. A residue was crystallized from a diethyl ether—acetone (2 : 1) mixture (**23d**), a petroleum ether—benzene (1 : 1) mixture (**23e**), or a petroleum ether—CH_2Cl_2 (1 : 1) mixture (**23f**).

***N*-Phenyl-2-cyano-2-ethoxycarbonylpent-4-enamide (23a)** was synthesized from phenylamide **1** (1.67 g, 5.0 mmol) and allyl bromide (1.30 g, 10.0 mmol) according to a procedure presented above. The yield was 1.2 g.

2-Cyano-2-ethoxycarbonyl-2-(4-nitrobenzyl)-*N*-phenylacetamide (23b) was synthesized from phenylamide triethylammonium salt **1** (0.5 g, 1.5 mmol) and 4-nitrobenzyl bromide (0.32 g, 1.5 mmol) according to a general procedure. The yield was 0.25 g.

2-Cyano-2-ethoxycarbonyl-2-(2,4-dinitrobenzene)-*N*-phenylacetamide (23c) was synthesized from phenylamide triethylammonium salt **1** (0.5 g, 1.5 mmol) and 2,4-dinitrobenzyl chloride (0.32 g, 1.5 mmol) according to a general procedure. The yield was 0.3 g.

***N*-(3,4-Dichlorophenyl)-2-cyano-2-ethoxycarbonylpropioamide (23d)** was synthesized from triethylammonium salt **22** (2.0 g, 0.005 mol) and MeI (1.42 g, 0.01 mol) according to a general procedure. The yield was 0.86 g. ^{13}C NMR, δ: 13.7 ($\underline{C}H_3CH_2O$); 21.4 ($\underline{C}H_3C$); 50.7 ($\underline{C}CN$); 64.4 ($CH_3\underline{C}H_2O$); 116.6 (CN); 119.5, 122.1, 122.9, 130.5, 132.8, 139.1 (Ar); 160.5 (CO); 165.2 (COOEt).

***N*-(3,4-Dichlorophenyl)-2-cyano-2-ethoxycarbonylpent-4-enamide (23e)** was synthesized from triethylammonium salt **22** (5.0 g, 0.012 mol) and allyl bromide (3.0 g, 0.024 mol) according to a general procedure. The yield was 3.0 g.

2-Benzyl-*N*-(3,4-dichlorophenyl)-2-cyano-2-ethoxycarbonylacetamide (23f) was synthesized from triethylammonium salt **22** (3.0 g, 0.075 mol) and benzyl chloride (1.89 g, 0.15 mol) according to a general procedure. The yield was 0.09 g.

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