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Derivatives of Carbamic Acid and Urea. V [1]

New Alkyl Dicarbamates and *N,N*-Dialkyl Diureas of the Diphenylmethane and the Diphenylchloroethylene Series, and Their Herbicidal Activity

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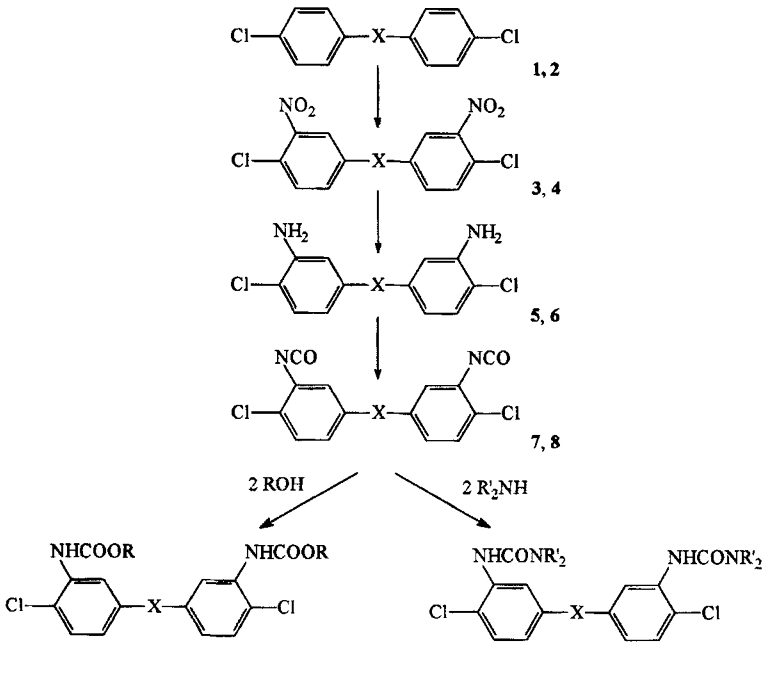
Dedicated to Prof. T. Lesiak on the Occasion of his 70th Birthday

Organic mono- and diisocyanates are valuable and versatile chemical intermediates in the syntheses of many commercially important products as e.g. polyurethanes, agrochemicals (herbicides, insecticides and fungicides), pharmaceutical drugs, etc. [2–4]. In a research program designed to develop derivatives of carbamic acid and urea with biological activity, some new alkyl dicarbamates and *N,N*-dialkyl diureas of benzophenone and diphenyldichloroethylene series with herbicidal, as well as insecticidal activity were prepared from corresponding aromatic diisocyanates [1, 5–8]. Since some of these derivatives recently described [6–8] showed satisfactory herbicidal and insecticidal action in screening and detailed tests, the further investigations of both classes of mentioned above compounds seemed desirable.

The starting compounds in the present work were bis(4-chlorophenyl)methane (**1**) and 2,2-dichloro-1,1-bis-(4-chlorophenyl)ethane (**2**), respectively. The nitration of **1** with fuming nitric acid below 20 °C [9] and of **2** by action of a mixture of glacial acetic and concentrated nitric acid [10] afforded the corresponding dinitro derivatives **3** and **4**. Condensation of *o*-nitrochlorobenzene with paraformaldehyde under strong acidic conditions also yielded the dinitro derivative **3**, cp. [11]. Compounds **3** and **4** were reduced with stannous chloride in ethanol / hydrochloric acid



9 ($X = CH_2$) **10** ($X = C{=}CHCl$) **11** ($X = CH_2$) **12** ($X = C{=}CHCl$)

	X
1,3,5,7	CH_2
2,4,6	$CHCHCl_2$
8	C=CHCl

9,10:	R	**11,12**: R'
a	Me	Et
b	Et	*n*-Pr
c	*n*-Pr	*n*-Bu
d	*i*-Pr	
e	*n*-Bu	
f	*i*-Bu	
g	2-Bu	

to yield the diamines **5** and **6**. According to [11], the diamine **5** may be prepared by pressure hydrogenation of dinitro derivative **3** in the presence of Raney nickel catalyst. Diamines **5** and **6** were subjected to phosgenation by trichloromethyl chloroformate (diphosgene) in toluene in the presence of active charcoal, resulting in bis(4-chloro-3-isocyanatophenyl) methane (**7**) and 2-chloro-1,1-bis(4-chloro-3-isocyanatophenyl)ethylene (**8**), respectively. On vacuum distillation of the reaction mixture containing the diisocyanate formed from the diamine **6** hydrogen chloride is evolved, and the chlorovinylidene compound **8** is formed.

6 and the diisocyanates **7** and **8** are so far not reported in the literature.

Treatment of diisocyanates **7** and **8** with aliphatic alcohols gave the appropriate alkyl dicarbamates **9** and **10**, while their reaction with aliphatic *N,N*-dialkylamines in toluene gave the corresponding *N,N*-dialkyl diureas **11** and **12**. Compounds **9a**, **10b**, **10d** and **11a** were obtained in crystalline, pure form. Repeated attempts to crystallize **10c**, **10e–g**, **11b,c** and **12a–c** were unsuccessful and resulted in thick, viscous liquids.

The obtained compound are summarized in Scheme 1

With the compounds prepared screening tests of the herbicidal activity were carried out against germinated seeds of sunflower, white mustard, wheat and corn. Among the alkyl dicarbamates **9**, **10** and *N,N*-dialkyl diureas **11**, **12** the greatest activity was found for the dicarbamate **9a** against white mustard. Dicarbamate **10g** showed medium activity against all investigated plants species, and the dicarbamates **10e,f** and diurea **11c** against sunflower, white mustard and corn. The other compounds (with the exception of **9c,d,f,g**, **10a**, and **12c**, which were inactive in these tests) exhibited medium activity against one or two investigated plants species (cp. Tables 1 and 2).

The comparison of these results with those described previously for carbamic acid and urea derivatives of the benzophenone series [6, 7] leads to the conclusion that a carbonyl group between the aromatic rings instead of the methylene or the chlorovinylidene group, increases the herbicidal activity of this type compounds considerably.

Experimental

Boiling and melting points are not corrected. – IR spectra were determined with a Specord M-80 (Carl Zeiss Jena) spectrophotometer. – ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer.

Bis(4-chloro-3-aminophenyl)methane (**5**)

To a boiling and stirred suspension of 35 g (0.107 mole) of bis(4-chloro-3-nitrophenyl)methane (**3**) in 300 ml of absolute ethanol, a solution of 172 g (0.9072 mole) of anhydrous stannous chloride in 180 ml of concentrated hydrochloric acid was added dropwise. The reaction mixture was refluxed for an additional hour, afterwards cooled and poured into 1.5 l of cold water. The solution obtained was treated with 20% solution of sodium hydroxide until a strong alkaline reaction resulted, and was allowed to stand for 12 hours. The precipitate was filtered off, washed with water, dried and extracted with diluted hydrochloric acid (3×500 ml; 1:20 dilution of concentrated hydrochloric acid). The combined extracts were alkalized with sodium hydrogen carbonate while stirring. The precipitate formed was filtered off, washed with water and crystallized from benzene–hexane. Yield 19.8 g (69.3%), m.p. 93–94 °C (Lit. [11] 91.5–93 °C).

2,2-Dichloro-1,1-bis(4-chloro-3-aminophenyl)ethane (**6**)

To a boiling and stirred suspension of 35 g (0.0854 mole) of 2,2-dichloro-1,1-bis(4-chloro-3-nitrophenyl)ethane (**4**) in 300 ml of absolute ethanol, a solution of 138 g (0.7279 mole) of anhydrous stannous chloride in 145 ml of concentrated hydrochloric acid was added dropwise. The further steps were carried out analogously as described for **5**. Crystallization from ethanol–water afforded 21.3 g (71.3%) of diamine **6**, m.p. 140–140.5 °C. – IR (KBr, cm^{-1}): 3463, 3346 (N-H), 2893 (C-H aliph.), 1611 (N-H), 1574, 1489 (C=C arom.). – ^{1}H NMR (TMS, $CDCl_3$, δ [ppm]): 4.06 (broad s, 4H, 2NH_2), 4.32 (d, 1H, >CH-), 6.24 (d, 1H, -$CHCl_2$), 6.62–6.69 (m, 4H arom. -2,2',6,6'), 7.19 (d, 2H arom. -5,5'). – ^{13}C NMR (TMS, $CDCl_3$, δ [ppm]): 129.61, 118.73, 115.78 (C-H arom.), 74.07 (-$CHCl_2$), 61.61 (>CH-). – $C_{14}H_{12}Cl_4N_2$ (350.1): calcd. C 48.03, H 3.45, N 8.00; found C 48.21, H 3.32, N 7.88.

Diacetyl derivative (crystallized from chlorobenzene): m.p. 100–101°C.

Bis(4-chloro-3-isocyanatophenyl)methane (**7**)

In a well ventilated hood to a stirred solution of 180 ml of anhydrous toluene and 15.7 g (0.0794 mole) of trichloromethyl chloroformate, a suspension of 13.3 g (0.0498 mole) of **5** and 0.5 g of active charcoal in 120 ml of anhydrous toluene was added dropwise at a temperature below 30 °C. The resultant mixture was then slowly heated to 55–60 °C and additional 7.9 g (0.0399 mole) of trichloromethyl chloroformate was added in portions. The temperature of the reaction system was raised gradually to 105–110 °C and maintained for 3 hours. Then the gases dissolved in the reaction mixture were removed with a stream of dry nitrogen and passed (together with gases escaping into the atmosphere during the course of the reaction) through a gas washing bottle containing sufficient solution of sodium hydroxide to react with phosgene and hydrogen chloride formed. The solvent was evaporated in a rotary vacuum evaporator, and the dry residue obtained was extracted with hexane in Soxhlet apparatus. Yield 14.2 g (89.4%), m.p. 128–129 °C. – IR (KBr, cm^{-1}): 2944 (C-H aliph.), 2264 (-N=C=O), 1596, 1516 (C=C arom.), 1050 (C-C-C arom.), 744 (C-Cl arom.). – ^{1}H NMR (TMS, $CDCl_3$, δ [ppm]): 3.85 (s, 2H, -CH_2-), 6.89–6.95 (m, 4H arom. -2,2',6,6'), 7.33 (d, 2H arom. -5,5'). – ^{13}C NMR (TMS, $CDCl_3$, δ [ppm]): 129.84, 127.04, 125.49 (C-H arom.), 40.14 (-CH_2-). – $C_{15}H_8Cl_2N_2O_2$ (319.2): calcd. C 56.45, H 2.53, N 8.78; found C 56.65, H 2.38, N 8.87.

2-Chloro-1,1-bis(4-chloro-3-isocyanatophenyl)ethylene (**8**)

In a well ventilated hood to a stirred solution of 180 ml of anhydrous toluene and 15.8 g (0.0799 mole) of trichloromethyl chloroformate, a suspension of 17.5 g (0.05 mole) of **6** and 0.5 g of active charcoal in 120 ml of anhydrous toluene was added dropwise at a temperature below 30 °C. Further synthesis was conducted analogously as described above for **7**. After the solvent was distilled off, the oily residue was distilled *in vacuo*, collecting **8** at 235–237 °C/0.7 mm Hg. The diisocyanate **8** obtained is a thick, light-yellow liquid which quickly solidifies, m.p. 88–90 °C. Yield 14.4 g (78.8%). – IR (KBr, cm^{-1}): 2924 (C-H aliph.), 2260 (-N=C=O), 1592, 1510 (C=C arom.), 1046 (C-C-C arom.), 760 (C-Cl arom.). – ^{1}H NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 6.63 (s, 1H, =CH-), 6.92–7.10 (m, 4H arom. -2,2',6,6'), 7.34-7.49 (m, 2H arom. -5,5'). – ^{13}C NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 129.92, 127.99, 126.49, 125.56, 124.21 (C-H arom.), 118.59 (=CH-). – $\mathrm{C_{16}H_7Cl_3N_2O_2}$ (365.6): calcd. C 52.56, H 1.93, N 7.66; found C 52.73, H 1.76, N 7.74.

Bis(4-chloro-3-alkoxycarbamoylphenyl)methanes (**9a–g**) and *2-Chloro-1,1-bis(4-chloro-3-alkoxycarbamoylphenyl)ethylenes* (**10a–g**)

The appropriate freshly distilled aliphatic alcohol (30 ml) was added while stirring to 1.6 g (0.005 mole) of diisocyanate **7** or to 1.83 g (0.005 mole) of diisocyanate **8**, respectively. Then the reaction mixtures were refluxed for 2 hours in an atmosphere of dry nitrogen, the hot solutions were filtered off and allowed to crystallize. The precipitates obtained (compounds **9a–10b** and **10d**, respectively) were recrystallized from methanol to constant melting points. Alkyl dicarbamates **10c** and **10e–g** neither crystallized from the reaction mixtures nor from methanol or hexane. After the low-boiling components of the reaction mixtures were distilled off in a rotary vacuum evaporator, dicarbamates **10c** and **10e–g** formed thick, viscous liquids.

9a: m.p. 137.5–139 °C. – IR (KBr, cm^{-1}): 3288 (N-H), 2992, 2944 (C-H aliph.), 1698 (C=O), 1578, 1518 (C=C arom.), 1228 (C-N), 1074 (C-O). – ^{1}H NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 3.92 (s, 2H, -CH$_2$-), 6.80 (dd, 2H arom. -6,6'), 7.12 (broad, 2H, 2N-H), 7.24 (d, 2H arom. -5,5'), 8.05 (broad, 2H arom. -2,2'). – ^{13}C NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 129.09, 124.25, 120.38 (C-H arom.), 41.50 (-CH$_2$-). – $\mathrm{C_{17}H_{16}Cl_2N_2O_4}$ (383.2): calcd. C 53.28, H 4.21, N 7.31; found C 53.11, H 4.14, N 7.43.

9b: m.p. 140–141°C. – IR (KBr, cm^{-1}): 3290 (N-H), 2984, 2932 (C-H aliph.), 1700 (C=O), 1588, 1532 (C=C arom.), 1246 (C-N), 1086 (C-O). – ^{1}H NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 3.91 (s, 2H, -CH$_2$-), 6.79 (dd, 2H arom. -6,6'), 7.09 (broad, 2H, 2N-H), 7.24 (d, 2H arom. -5,5'), 8.06 (broad, 2H arom. -2,2'). – ^{13}C NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 129.08, 124.13, 120.31 (C-H arom.), 41.53 (-CH$_2$-). – $\mathrm{C_{19}H_{20}Cl_2N_2O_4}$ (411.3): calcd. C 55.49, H 4.90, N 6.81; found C 55.65, H 4.96, N 6.89.

9c: m.p. 123.5–124 °C. – IR (KBr, cm^{-1}): 3304 (N-H), 2968, 2934 (C-H aliph.), 1700 (C=O), 1584, 1528 (C=C arom.), 1238 (C-N), 1084 (C-O). – ^{1}H NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 3.92 (s, 2H, -CH$_2$-), 6.79 (dd, 2H arom. -6,6'), 7.10 (broad , 2H, 2N-H), 7.24 (d, 2H arom. -5,5'), 8.06 (broad, 2H arom. -2,2'). – ^{13}C NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 129.08, 124.13, 120.33 (C-H arom.), 41.54 (-CH$_2$-). – $\mathrm{C_{21}H_{24}Cl_2N_2O_4}$ (439.3): calcd. C 57.41, H 5.51, N 6.38; found C 57.20, H 5.37, N 6.47.

9d: m.p. 153–153.5 °C. – IR (KBr, cm^{-1}): 3276 (N-H), 2960, 2912 (C-H aliph.), 1690 (C=O), 1566, 1510 (C=C arom.), 1234 (C-N), 1094 (C-O). – ^{1}H NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 3.91 (s, 2H, -CH$_2$-), 6.79 (dd, 2H arom. -6,6'), 7.05 (broad, 2H, 2N-H), 7.24 (d, 2H arom. -5,5'), 8.07 (broad, 2H arom. -2,2'). – ^{13}C NMR (TMS, $\mathrm{CDCl_3}$, d [ppm]): 129.04, 124.01, 120.28 (C-H arom.), 41.56 (-CH$_2$-). – $\mathrm{C_{21}H_{24}Cl_2N_2O_4}$ (439.3): calcd. C 57.41, H 5.51, N 6.38; found C 57.23, H 5.66, N 6.29.

9e: m.p. 107–108 °C. – IR (KBr, cm^{-1}): 3268 (N-H), 2956, 2924 (C-H aliph.), 1704 (C=O), 1578, 1524 (C=C arom.), 1244 (C-N), 1082 (C-O). – ^{1}H NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 3.92 (s, 2H, -CH$_2$-), 6.79 (dd, 2H arom. -6,6'), 7.09 (broad, 2H, 2N-H), 7.24 (d, 2H arom. -5,5'), 8.06 (broad, 2H arom. -2,2'). – ^{13}C NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 129.07, 124.11, 120.32 (C-H arom.), 41.54 (-CH$_2$-). – $\mathrm{C_{23}H_{28}Cl_2N_2O_4}$ (467.4): calcd. C 59.11, H 6.04, N 5.99; found C 59.29, H 6.16, N 5.84.

9f: m.p. 142–143.5 °C. – IR (KBr, cm^{-1}): 3304 (N-H), 2952, 2928 (C-H aliph.), 1706 (C=O), 1586, 1528 (C=C arom.), 1236 (C-N), 1086 (C-O). – ^{1}H NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 3.92 (s, 2H, -CH$_2$-), 6.80 (dd, 2H arom. -6,6'), 7.10 (broad, 2H, 2N-H), 7.24 (d, 2H arom. -5,5'), 8.05 (broad, 2H arom. -2,2'). – ^{13}C NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 129.08, 124.15, 120.38 (C-H arom.), 41.54 (-CH$_2$-). – $\mathrm{C_{23}H_{28}Cl_2N_2O_4}$ (467.4): calcd. C 59.11, H 6.04, N 5.99; found C 59.07, H 6.14, N 6.15.

9g: m.p. 84.5–86 °C. – IR (KBr, cm^{-1}): 3292 (N-H), 2976, 2936 (C-H aliph.), 1708 (C=O), 1588, 1532 (C=C arom.), 1252 (C-N), 1080 (C-O). – ^{1}H NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 3.92 (s, 2H, -CH$_2$-), 6.79 (dd, 2H arom. -6,6'), 7.06 (broad , 2H, 2N-H), 7.24 (d, 2H arom. -5,5'), 8.08 (broad, 2H arom. -2,2'). – ^{13}C NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 129.05, 124.01, 120.25 (C-H arom.), 41.57 (-CH$_2$-). – $\mathrm{C_{23}H_{28}Cl_2N_2O_4}$ (467.4): calcd. C 59.11, H 6.04, N 5.99; found C 59.30, H 5.95, N 5.86.

10a: m.p. 142.5–143 °C. – IR (KBr, cm^{-1}): 3300 (N-H), 2992, 2952 (C-H aliph.), 1716 (C=O), 1582, 1528 (C=C arom.), 1226 (C-N), 1080 (C-O). – ^{1}H NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 6.66 (s, 1H, =CH-), 6.74 and 6.94 (2dd, 2H arom. -6,6'), 7.13 and 7.17 (2 broad bands, 2H, 2N-H), 7.25 and 7.38 (2d, 2H arom. -5,5'), 8.16 (broad, 2H arom. -2,2'). – ^{13}C NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 129.05, 125.25, 123.29, 121.23, 118.64 (C-H arom.), 117.94 (=CH-). – $\mathrm{C_{18}H_{15}Cl_3N_2O_4}$ (429.7): calcd. C 50.32, H 3.52, N 6.52; found C 50.42, H 3.44, N 6.64.

10b: m.p. 130–131.5 °C. – IR (KBr, cm^{-1}): 3336 (N-H), 2996, 2944 (C-H aliph.), 1732 (C=O), 1582, 1532 (C=C arom.), 1226 (C-N), 1084 (C-O). – ^{1}H NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 6.65 (s, 1H, =CH-), 6.73 and 6.93 (2dd, 2H arom. -6,6'), 7.11 and 7.15 (2 broad bands, 2H, 2N-H), 7.25 and 7.38 (2d, 2H arom. -5,5'), 8.17 (broad, 2H arom. -2,2'). – ^{13}C NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 129.02, 125.12, 123.18, 121.20, 118.59 (C-H arom.), 117.87 (=CH-). – $\mathrm{C_{20}H_{19}Cl_3N_2O_4}$ (457.7): calcd. C 52.48, H 4.18, N 6.12; found C 52.64, H 4.32, N 6.18.

10c: IR (film, cm^{-1}): 3338 (N-H), 2968, 2936 (C-H aliph.), 1736 (C=O), 1580, 1526 (C=C arom.), 1206 (C-N), 1078 (C-O).

10d: m.p. 110–111°C. – IR (KBr, cm^{-1}): 3332 (N-H), 2984, 2940 (C-H aliph.), 1726 (C=O), 1584, 1528 (C=C arom.), 1228 (C-N), 1074 (C-O). – ^{1}H NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 6.65 (s, 1H, =CH-), 6.72 and 6.92 (2dd, 2H arom. -6,6'), 7.07 and 7.10 (2 broad bands, 2H, 2N-H), 7.24 and 7.38 (2d, 2H arom. -5,5'), 8.18 (broad, 2H arom. -2,2'). – ^{13}C NMR (TMS, $\mathrm{CDCl_3}$, δ [ppm]): 129.00, 124.99, 123.08, 121.12, 118.51

(C-H arom.), 117.82 (=CH-). – $C_{22}H_{23}Cl_3N_2O_4$ (485.8): calcd. C 54.39, H 4.77, N 5.77; found C 54.50, H 4.68, N 5.69.

10e: IR (film, cm^{-1}): 3340 (N-H), 2960, 2935 (C-H aliph.), 1736 (C=O), 1580, 1526 (C=C arom.), 1210 (C-N), 1078 (C-O).

10f: IR (film, cm^{-1}): 3342 (N-H), 2964, 2934 (C-H aliph.), 1744 (C=O), 1580, 1526 (C=C arom.), 1206 (C-N), 1076 (C-0).

10g: IR (film, cm^{-1}): 3344 (N-H), 2976, 2936 (C-H aliph.), 1736 (C=O), 1580, 1526 (C=C arom.), 1212 (C-N), 1070 (C-O).

Bis(4-chloro-3-N,N-dialkylureidophenyl)methanes (**11a–c**) and *2-Chloro-1,1-bis(4-chloro-3-N,N-dialkylureidophenyl)ethylenes* (**12a–c**)

The appropriate freshly distilled aliphatic *N,N*-dialkylamine (0.02 mole) was added while stirring to 1.6 g (0.005 mole) of diisocyanate **7** or to 1.83 g (0.005 mole) of diisocyanate **8** in 30 ml of anhydrous toluene, respectively. Then the reaction mixtures were refluxed for 2 hours in an atmosphere of dry nitrogen, the hot solutions were filtered off and allowed to crystallize. With the exception of derivative **11a** which was recrystallized from hexane to constant melting point, the *N,N*-dialkyl diureas **11b,c** and **12a–c** neither crystallized from the reaction mixtures nor from methanol or hexane. After the low-boiling components of the reaction mixtures were distilled off in a rotary vacuum evaporator, these diureas formed thick, viscous liquids.

11a: m.p. 103–104 °C. – IR (KBr, cm^{-1}): 3330 (N-H), 2984, 2940 (C-H aliph.), 1666 (C=O), 1588, 1538 (C=C arom.), 1262 (C-N). – ^{1}H NMR (TMS, $CDCl_3$, δ[ppm]): 3.89 (s, 2H, $-CH_2-$), 6.74 (dd, 2H arom. -6,6'), 6.96 (broad, 2H, 2N-H), 7.20 (d, 2H arom. -5,5'), 8.18 (d, 2H arom. -2,2'). – ^{13}C NMR (TMS, $CDCl_3$, δ[ppm]): 128.65, 123.35, 121.13 (C-H arom.), 41.89 ($-CH_2-$). – $C_{23}H_{30}Cl_2N_4O_2$ (465.4): calcd. C 59.36, H 6.50, N 12.04; found C 59.51, H 6.39, N 12.09.

11b: IR (film, cm^{-1}): 3336 (N-H), 2964, 2932 (C-H aliph.), 1678 (C=O), 1584, 1528 (C=C arom.), 1228 (C-O).

11c: IR (film, cm^{-1}): 3338 (N-H), 2956, 2936 (C-H aliph.), 1676 (C=O), 1586, 1536 (C=C arom.), 1216 (C-N).

12a: IR (film, cm^{-1}): 3328 (N-H), 2976, 2932 (C-H aliph.), 1672 (C=O), 1576, 1528 (C=C arom.), 1276 (C-N).

12b: IR (film, cm^{-1}): 3340 (N-H), 2964, 2932 (C-H aliph.), 1678 (C=O), 1580, 1526 (C=C arom.), 1228 (C-N).

12c: IR (film, cm^{-1}): 3342 (N-H), 2956, 2932 (C-H aliph.), 1674 (C=O), 1578, 1526 (C=C arom.), 1214 (C-N).

Table 1 Estimation of herbicidal activity of alkyl dicarbamates **9**, **10**

Cpd.	kg/ha	Activity (scale 1–3)			
		mustard	sunflower	wheat	corn
9a	1	3	3	3	3
	2	3	3	3	3
	4	1	3	3	2
9b	1	3	3	3	3
	2	3	3	3	3
	4	2	3	3	3
9c	1	3	3	3	3
	2	3	3	3	3
	4	3	3	3	3
9d	1	3	3	3	3
	2	3	3	3	3
	4	3	3	3	3
9e	1	3	3	3	3
	2	3	3	3	3
	4	2	3	3	2
9f	1	3	3	3	3
	2	3	3	3	3
	4	3	3	3	3
9g	1	3	3	3	3
	2	3	3	3	3
	4	3	3	3	3
10a	1	3	3	3	3
	2	3	3	3	3
	4	3	3	3	3
10b	1	3	3	3	3
	2	3	3	3	3
	4	3	2	3	2
10c	1	3	3	3	3
	2	3	3	3	3
	4	3	2	3	3
10d	1	3	3	3	3
	2	2	2	3	3
	4	2	2	3	3
10e	1	3	3	3	3
	2	3	3	3	3
	4	2	2	3	2
10f	1	3	3	3	3
	2	2	3	3	3
	4	2	2	3	2
10g	1	3	3	3	3
	2	3	3	3	3
	4	2	2	2	2
Check	–	3	3	3	3

Estimation of the herbicidal activity (General procedure)

The experiments were carried out under laboratory conditions using the seeds of *Sinapis alba* L. (white mustard), *Helianthus annuus* L. (sunflower), *Triticum aestivum* L. (wheat) and *Zea mays* L. (corn) as bioassay species for herbicidal activity of alkyl dicarbamates **9**, **10** and *N,N*-dialkyl diureas **11**, **12**. The seeds were placed in Petri dishes (100 cm^2 area) on filter paper wetted by 4 ml of the test solution. The solutions were prepared by dissolving of 40 mg of each compound in 40 ml of acetone (basic solutions). The test solutions were prepared as follows:

4 kg per ha: 20 ml of the basic solution are used;
2 kg per ha: 10 ml of basic solution + 10 ml of acetone;
1 kg per ha: 5 ml of basic solution + 15 ml of acetone.

After evaporation of acetone the filter papers were wetted by distillate water and the seeds were placed (5 seeds of *Helianthus* and *Zea*; 10 seeds of *Sinapis* and *Triticum* per each dish). Used seeds were dipped for 5 seconds in mercuric chloride ($HgCl_2$, concentration 0.1%) before the preparation for germination. Then the Petri dishes with the seeds were placed in a thermostat in darkness at 25°C. The herbicidal activity of the tested compounds was visually assessed after 6 days using the following scale: 1 – excellent activity (no germination of seeds), 2 – moderate activity, 3 – no activity (good germination and growth of cotyledons). Each treatment was compared with check (seeds placed on filter paper wetted

Table 2 Estimation of herbicidal activity of *N*,*N*-dialkyl-diureas **11**, **12**

Cpd.	kg/ha	Activity (scale 1–3)			
		mustard	sunflower	wheat	corn
11a	1	3	3	3	3
	2	3	3	3	3
	4	2	3	3	2
11b	1	3	3	3	3
	2	3	3	3	3
	4	3	2	3	2
11c	1	3	3	3	3
	2	2	3	3	3
	4	2	2	3	2
12a	1	3	3	3	3
	2	3	3	3	3
	4	2	3	3	3
12b	1	3	3	3	3
	2	3	3	3	3
	4	3	2	3	2
12c	1	3	3	3	3
	2	3	3	3	3
	4	3	3	3	3
Check	–	3	3	3	3

only by acetone) and was three times repeated. Results of estimation of herbicidal activity of alkyl dicarbamates **9**, **10** and *N*,*N*-dialkyl diureas **11**, **12** are presented in the Tables 1 and 2.

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