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

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Novel reactions of isocyanates with compounds containing active methylene groups in the presence of triethylamine are described. The reactions afford derivatives of pyrrolidine-2,3,5-trione and barbituric acid.

Key words: acyclic and heterocyclic compounds with active methylene groups, isocyanates, triethylammonium salts of CH acids, amides of carboxylic acids, thiophosphinicamides.

The reactions of compounds containing active methylene groups with isocyanates in the presence of bases[1,2] afford functionally substituted amides of acids, which can be considered as potential remedies for treatment of dangerous viral diseases. Their structures contain fragments of substances that behaved as active inhibitors of integrase of the AIDS virus.[3] Antibacterial activity of amides of carboxylic acids prepared by the reactions of isocyanates with sodium derivatives of compounds containing active methylene groups have been tested previously.[4,5] Continuing to study the reactions of the latter with isocyanates in the presence of organic bases and intending to synthesize novel physiologically active substances,[2] we studied the reactions of 3,4-dichlorophenyl and diphenylthiophosphinoyl isocyanates with compounds containing active methylene groups and the chlorine atom or methoxyl substituent as leaving groups in the presence of triethylamine.

Results and Discussion

We believed that under certain conditions the adducts formed in the first reaction step could transform into the corresponding heterocyclic systems through the intramolecular interactions. However, this requires several steric and electronic conditions. For instance, the first step of the reactions of cyanoacetates **1** with isocyanates affords adducts **2** (Scheme 1), whose cyclization due to the elimination of the alkoxy group is hindered, because this process would result in strained four-membered cycle **4**. Therefore, the reaction products in similar transformations are usually amides of type **3** or barbiturates **5**, depending on conditions of the process.[1] No published data for the formation of four-membered cyclic products of type **4** in the reactions of the compounds containing active methylene groups with isocyanates in the presence of triethylamine are available.

For the cyclization of intermediates **2**, which are formed in the reactions of isocyanates with the compounds containing active methylene groups, we used as reactant ester **6** containing the keto fragment between the ester and methylene groups (Scheme 2) to form a five-membered ring. This allows intermediate adduct **7** to transform into heterocycle **8** by the intramolecular elimination of the methanol molecule. The process is facilitated by the enhancement of CH-acidity of compound **6** containing the active methylene group due to the electron-withdrawing properties of the keto group. The treatment of unstable triethylammonium salt **7** with hydrochloric acid produces free cyclic CH acid **8**.

At the same time, diphenylthiophosphinoyl isocyanate reacts with keto ester **6** to form triethylammonium salt **9**, whose stability is caused, most likely, by rather acidic properties of the corresponding conjugated CH acid (Scheme 3).

Note that compound **10** containing no similar activated methoxycarbonyl group reacts with 3,4-dichlorophenyl isocyanate in the presence of triethylamine without loss of methanol to form stable salt **11** (Scheme 4).

However, when salt **11** is acidified, heterocyclization involves enolic form **12** and proceeds through the elimination of the mobile chlorine atom to form crystalline 2-amino-4,5-dihydrofuran-4-one **13** in high yield (*cf.* Ref. 4).

Since a molecule of pyrazolone **14** contains no good leaving groups and its CH-acidity is fairly low, its reaction with phenyl isocyanate in the presence of triethylamine affords unstable triethylammonium salt **15** (Scheme 5).

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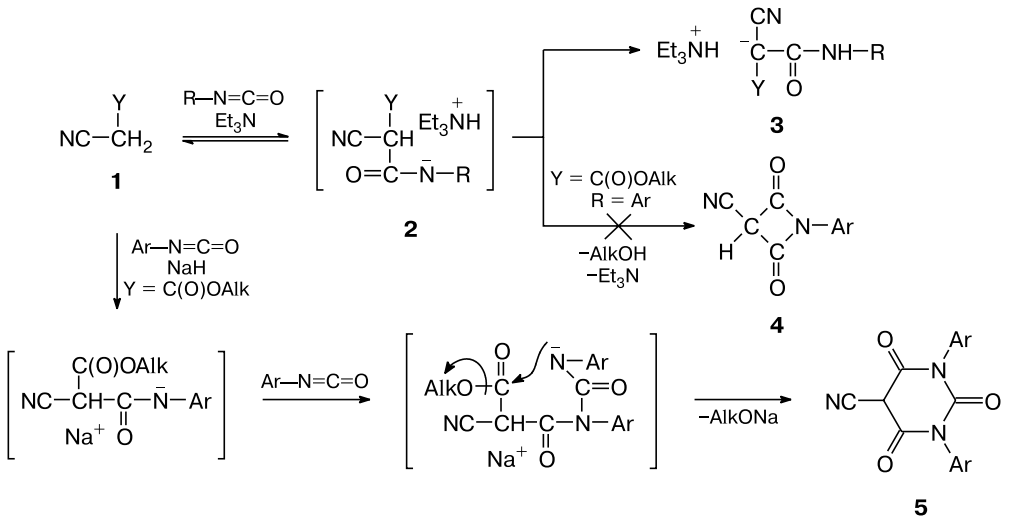
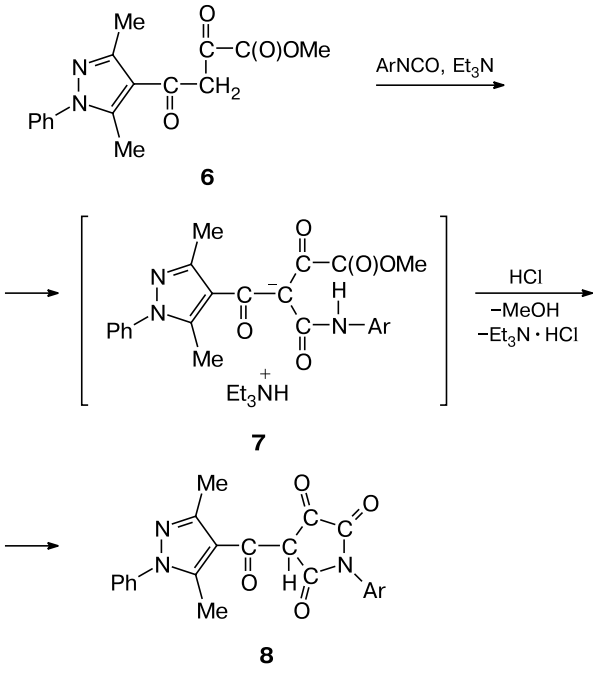
Scheme 1



3: Y = C(O)OEt; R = C_6H_{11}, 3,4-$Cl_2C_6H_3$, $Ph_2P(S)$
Y = C(O)NRPh; R = 3,4-$Cl_2C_6H_3$
Y = $P(O)Ph_2$; R = 3,4-$Cl_2C_6H_3$
Y = SO_2Ph; R = 3,4-$Cl_2C_6H_3$, 4-$NO_2C_6H_4$

Scheme 2



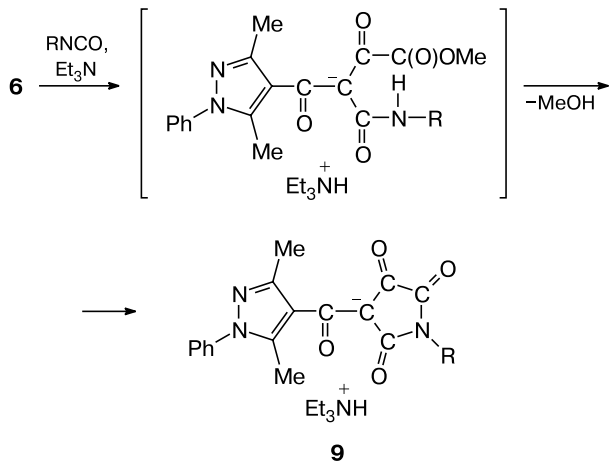
Ar = 3,4-$Cl_2C_6H_3$

Salt **15** was identified by ^{1}H NMR spectroscopy. The treatment of the reaction mixture with a solution of dilute hydrochloric acid gave crystalline CH acid **16**, which is equilibrated with the enolic form in a $CDCl_3$ solution.

It is important that the reactions of the compounds containing active methylene groups with isocyanates in the presence of triethylamine afford amides or their cyclization products only at fairly high CH-acidity of the former. For instance, thiobarbituric acid **17** reacts easily with phenyl isocyanate in the presence of triethylamine in solution to form triethylammonium salt **19** (Scheme 6). In the first step of the reaction, triethylammonium salt of thiobarbituric acid **18** is evidently formed and then transformed into amide salt **19**.

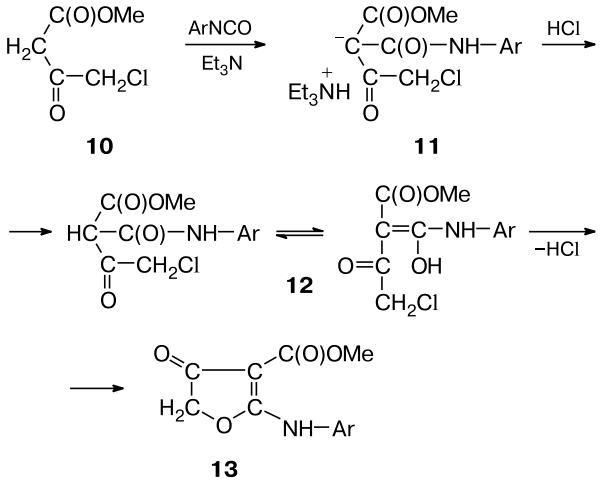
Low CH-acidity of the compounds with active methylene groups requires the use of stronger bases (usually metallic sodium or sodium hydride). For example, methyl 2-phenylcarboran-1-yl acetate **20** in the presence of

Scheme 3



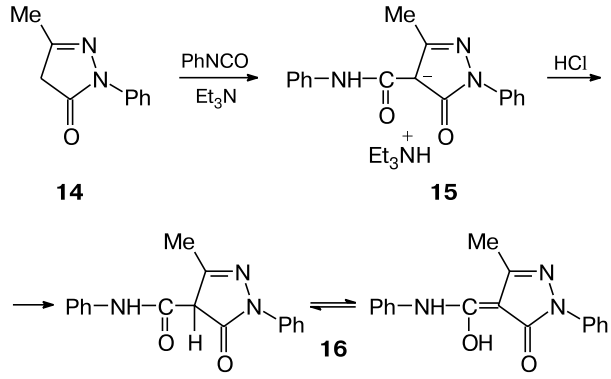
R = $P(S)Ph_2$

Scheme 4

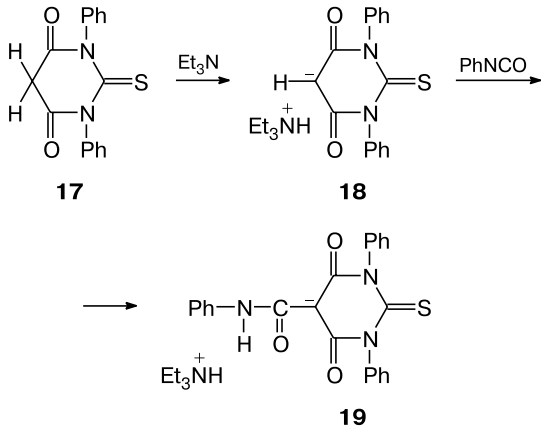


Ar = 3,4-$Cl_2C_6H_3$

Scheme 5

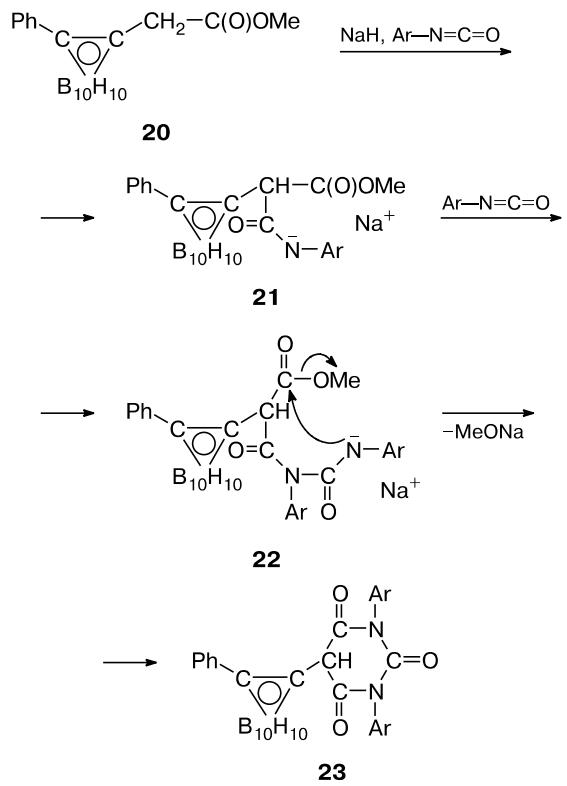


Scheme 6



triethylamine does not react with 3,4-dichlorophenyl isocyanate: only polymerization of the latter is observed. However, sodium derivative of ester **20** reacts with 3,4-dichlorophenyl isocyanate in a THF solution to form barbiturate **23** (Scheme 7), whose structure was determined by elemental analysis, NMR spectroscopy, IR spectroscopy, and X-ray diffraction analysis. The first step of the reaction results unambiguously in N-anion **21**, which is not protonated due to the C—N-migration of a proton because of its relatively low CH-acidity. The interaction of this anion with the second isocyanate molecule produces N-anion **22**, which undergoes intramolecular transformation into barbiturate **23** (*cf.* Ref. 6).

Scheme 7



Ar = 3,4-$Cl_2C_6H_3$

The spatial structure of carborane-containing barbiturate **23** was studied by X-ray diffraction analysis (Fig. 1). The structure of compound **23** contains two independent molecules with the same structure and bonded through the symmetry pseudo-center. The barbituric ring is nonplanar, the C(3) atom deviates from the plane of other atoms by 0.45 Å, and the angle of cycle bending along the C(4)...C(5) line is 26°. This structure is typical of derivatives of barbituric acid. The dichlorophenyl rings are unfolded relatively to the barbituric ring along the N(1)—C(Ph) and N(2)—C(Ph) bonds by 68 and 79°, respectively. The C—C bond in the carborane ring is strongly elongated (average value 1.73 Å) (Table 1) compared to unsubstituted *ortho*-carborane[7] (1.599 Å).

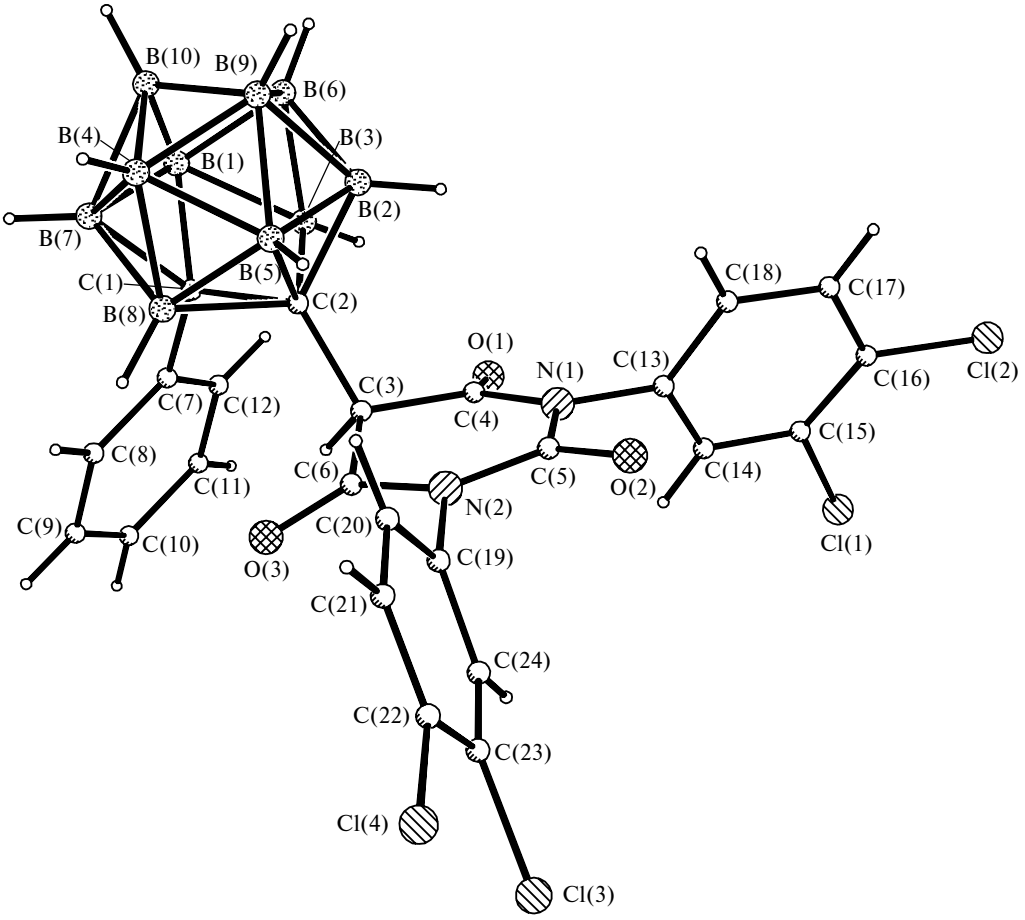


Fig. 1. Spatial structure of compound **23**.

Table 1. Selected bond lengths (*d*) in the structure of compound **23** (two independent molecules)

Bond	*d*/Å	
	Molecule 1	Molecule 2
C(1)—C(2)	1.72(1)	1.75(2)
C(1)—C(7)	1.49(1)	1.51(1)
C(2)—C(3)	1.55(1)	1.56(1)
C(3)—C(4)	1.51(1)	1.52(2)
C(4)—O(1)	1.19(1)	1.19(1)
C(4)—N(1)	1.39(1)	1.38(1)
N(1)—C(13)	1.42(1)	1.45(1)
N(1)—C(5)	1.39(1)	1.40(1)
C(5)—O(2)	1.20(1)	1.18(1)
C(5)—N(2)	1.37(1)	1.40(1)
N(2)—C(19)	1.44(1)	1.43(1)
N(2)—C(6)	1.42(1)	1.39(1)
C(6)—O(3)	1.23(1)	1.20(1)
C(6)—C(3)	1.49(1)	1.49(2)

In monosubstituted 1-phenyl-*ortho*-carborane, the C—C bond is[8] 1.640 and 1.671 Å, and in disubstituted 1,2-diphenyl-*ortho*-carborane this bond is even longer (1.720(3) and 1.733(3) Å).[9]

Thus, in the presence of triethylamine, stable triethylammonium salts of the reaction products of isocyanates with the compounds containing active methylene groups are formed only at fairly high CH-acidity of the latter. This made it possible to synthesize the heterocyclic systems including the pyrrolidine, barbituric, and furan rings.

Experimental

NMR spectra were obtained on a Bruker AMX-400 spectrometer (400.1 (^{1}H), 282.4 (^{19}F) and 162.0 MHz (^{31}P)) in $CDCl_3$. IR spectra were recorded on a Magna-IR-750 FTIR spectrometer (Nicolet) in Nujol. The reactions were carried out under dry nitrogen.

Starting compounds **6**, **10**, **14**, and **17** were provided by the Interbioskrin Company. Compound **20** was synthesized according to a known procedure.[10]

4-(3,5-Dimethyl-1-phenyl-1*H*-pyrazole-4-ylcarbonyl)-1-(3,4-dichlorophenyl)pyrrolidine-2,3,5-trione (8). Triethylamine (0.35 mL, 2.43 mmol) was poured to a solution of methyl 4-(3,5-dimethyl-1-phenylpyrazolyl) 2,4-dioxobutanoate (**6**) (0.5 g, 1.67 mmol) and 3,4-dichlorophenyl isocyanate (0.32 g, 1.67 mmol) in acetone (10 mL). The reaction solution instantly gained the yellow-green color. The solution was stored

for 3 days and concentrated by evaporation, Et_2O and a 5% solution of HCl were added to the residue, and the resulting mixture was stirred until a precipitate completely disappeared. The organic layer was separated, and a precipitate that formed was recrystallized from an ether—acetone (1 : 1) mixture. The yield was 0.30 g (40%), m.p. 155—156 °C. Found (%): C, 57.95; H, 3.34; N, 9.19. $C_{22}H_{15}Cl_2N_3O_4$. Calculated (%): C, 57.89; H, 3.29; N, 9.21. IR, ν/cm^{-1}: 1674 (C(O)N), 1733, 1782 (C(O) of cycle). ^{1}H NMR, δ: 2.32, 2.45 (both s, 3 H each, Me); 3.25 (br.s, 0.5 H, CH); 7.35—7.38 (m, 1 H, *o*-H arom.); 7.44—7.54 (m, 5 H, Ph); 7.58 (d, 1 H, *m*-H arom., $^3J_{H,H}$ = 8.0 Hz); 7.64 (s, 1 H, CH=CCl arom.); 12.86 (br.s, 0.5 H, OH).

Triethylammonium 4-(3,5-dimethyl-1-phenyl-1*H*-pyrazole-4-ylcarbonyl)-1-diphenylthiophosphinoyl-2,3,5-trioxopyrrolidin-4-ide (9). Triethylamine (0.35 mL, 2.43 mmol) was poured to a solution of methyl 4-(3,5-dimethyl-1-phenylpyrazolyl) 2,4-dioxobutanoate (**6**) (0.5 g, 1.67 mmol) in benzene (15 mL). The reaction solution instantly gained the yellow-green color. The reaction mixture was stored for 10 min, and a solution of diphenyl thiophosphoryl isocyanate (0.43 g, 1.67 mmol) in benzene (5 mL) and ether (15 mL) were added. A formed precipitate of unreacted compound **6** was separated, and the filtrate was concentrated by evaporation. The residue was multiply recrystallized from an ether—acetone (1 : 2) mixture. The yield was 0.05 g (5%), m.p. 111—113 °C. Found (%): C, 65.01; H, 6.01; N, 8.64. $C_{28}H_{21}N_3O_4PS \cdot C_6H_{16}N$. Calculated (%): C, 64.97; H, 5.89; N, 8.92. ^{1}H NMR, δ: 1.20 (t, 9 H, C<u>H</u>$_3$CH$_2$N, $^3J_{H,H}$ = 7.2 Hz); 2.22, 2.27 (both s, 3 H each, Me); 3.12 (q, 6 H, CH$_3$C<u>H</u>$_2$N, $^3J_{H,H}$ = 7.2 Hz); 7.29—7.49 (m, 11 H, Ph); 7.95 (dd, 4 H, *o*-H arom., $^3J_{H,H}$ = 7.2 Hz, $^4J_{H,H}$ = 1.2 Hz); 10.17 (br.s, 1 H, N$^+$H). ^{31}P NMR, δ: 50.07.

Triethylammonium 3,4-dichlorophenylcarbamoyl(methoxycarbonyl)chloroacetylmethide (11). Triethylamine (0.45 mL, 3.3 mmol) was added dropwise to a solution of methyl 4-chloro-3-oxobutanoate (**10**) (0.5 g, 3.3 mmol) and 3,4-dichlorophenyl isocyanate (0.62 g, 3.3 mmol). A white precipitate appeared upon vigorous stirring and was filtered off and dried. The yield was 1.35 g (93%), m.p. 226—227 °C. Found (%): C, 49.16; H, 5.58; Cl, 24.24; N, 6.41. $C_{12}H_9Cl_3NO_4 \cdot C_6H_{16}N$. Calculated (%): C, 49.15; H, 5.69; Cl, 24.23; N, 6.37. IR, ν/cm^{-1}: 1591 (C(O)N), 1624 (C(O)), 1663 (COOMe), 2576 (NH$^+$), 3256 (CO<u>NH</u>). ^{1}H NMR, δ: 1.39 (t, 9 H, C<u>H</u>$_3$CH$_2$N, $^3J_{H,H}$ = 7.2 Hz); 3.07—3.09 (m, 6 H, CH$_3$C<u>H</u>$_2$N); 3.88 (s, 3 H, OMe); 4.72 (s, 2 H, CH$_2$Cl); 7.19 (dd, 1 H, *o*-H arom., $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 2.4 Hz); 7.44 (d, 1 H, *m*-H arom., $^3J_{H,H}$ = 8.0 Hz); 7.55 (d, 1 H, *o*-H arom., $^3J_{H,H}$ = 2.4 Hz); 10.27 (s, 1 H, NH); 12.01 (s, 1 H, Et$_3$N<u>H</u>).

Methyl 2-(3,4-dichloroanilino)-4-oxo-4,5-dihydrofuran-3-carboxylate (13). A solution of 5% hydrochloric acid was poured with stirring to a suspension of salt **11** (0.5 g, 1.13 mmol) in acetone to an acidic pH value. A suspension was filtered off and washed with acetone, the solvent was distilled off, and the residue was dried. A white powder (360 mg) was obtained. The yield was 97%, m.p. 225—226 °C. Found (%): C, 47.68; H, 2.98; Cl, 23.51; N, 4.64. $C_{12}H_9Cl_2NO_4$. Calculated (%): C, 47.69; H, 2.98; Cl, 23.59; N, 4.65. ^{1}H NMR, δ: 3.89 (s, 3 H, OMe); 4.73 (s, 2 H, CH$_2$); 7.20 (dd, 1 H, *o*-H arom., $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 2.4 Hz); 7.45 (d, 1 H, *m*-H arom., $^3J_{H,H}$ = 8.0 Hz); 7.56 (d, 1 H, *o*-H arom., $^3J_{H,H}$ = 2.4 Hz); 10.28 (s, 1 H, NH). ^{13}C NMR, δ: 51.91 (Me); 75.60 (CH$_2$); 120.49, 123.03 (CH arom.); 129.89 (CCl arom.); 133.48 (C$_{Ar}$—N); 134.23 (CCl arom.); 165.78 (C=<u>C</u>N); 177.80 (C—<u>C</u>=C); 187.86 (<u>C</u>OOMe); 201.75 (CH$_2$<u>C</u>O).

3-Methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazole-4-carboxanilide (16). Triethylamine (0.40 mL, 2.87 mmol) was added to a mixture of 3-methyl-1-phenyl-2-pyrazolin-5-one (**14**) (0.5 g, 2.87 mmol) and phenyl isocyanate (0.34 g, 2.87 mmol). The reaction mixture turned dark rapidly. The mixture was stored for 3 days. The dark oil was separated, washed with petroleum ether, and dried *in vacuo*. A solution of 5% hydrochloric acid was poured to a solution of the oil in acetone to an acidic pH value, and a precipitate that formed was filtered off and recrystallized from acetone. The yield was 0.34 g (40%), m.p. 96—98 °C. Found (%): C, 65.39; H, 5.10; N, 13.30. $C_{17}H_{15}N_3O_2 \cdot H_2O$. Calculated (%): C, 65.59; H, 4.82; N, 13.50. IR, ν/cm^{-1}: 1674 (C(O)N), 3361 (CO<u>NH</u>). ^{1}H NMR, δ: 2.26 (s, 3 H, Me); 6.65—7.32 (m, 10 H, Ph); 10.31 (s, 1 H, NH); 12.30 (br.s, 1 H, OH).

Triethylammonium 1,3-diphenyl 2-thiobarbiturate (18). Triethylamine (0.23 mL, 1.68 mmol) in ether was added dropwise to a solution of 1,3-diphenyl-2-thiobarbituric acid (**17**) (0.5 g, 1.68 mmol) in acetone. A rapidly formed precipitate was filtered off in 3 h, washed with Et_2O, and dried. The yield was 0.44 g (66%), m.p. 138—140 °C. Found (%): C, 65.58; H, 6.82; N, 10.31. $C_6H_{11}N_2O_2S \cdot 0.5H_2O \cdot C_6H_{16}N$. Calculated (%): C, 65.02; H, 6.65; N, 10.34. ^{1}H NMR, δ: 1.09 (t, 9 H, C<u>H</u>$_3$CH$_2$N, $^3J_{H,H}$ = 7.2 Hz); 2.77 (q, 6 H, CH$_3$C<u>H</u>$_2$N, $^3J_{H,H}$ = 7.2 Hz); 4.96 (br.s, 1 H, C$^-$H); 7.25 (dd, 4 H, *o*-H arom., $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.2 Hz); 7.32 (dt, 2 H, *p*-H arom., $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.2 Hz); 7.41 (t, 4 H, *m*-H arom., $^3J_{H,H}$ = 7.7 Hz); 11.09 (br.s, 1 H, N$^+$H).

Triethylammonium 1,3-diphenyl-5-phenylcarbamoyl-2-thiobarbiturate (19). Triethylamine (0.23 mL, 1.68 mmol) was added dropwise to a solution of 1,3-diphenyl-2-thiobarbituric acid (**17**) (0.5 g, 1.68 mmol) and phenyl isocyanate (0.2 g, 1.68 mmol) in an acetone—ether (1 : 1) mixture (50 mL). A precipitate that formed dissolved upon the addition of acetone. The solvent was distilled off, and the residue was washed with ether and dried. The yield was 0.80 g (92%), m.p. 230 °C. Found (%): C, 67.42; H, 6.10; N, 10.78. $C_{23}H_{16}N_3O_3S \cdot C_6H_{16}N$. Calculated (%): C, 67.44; H, 6.20; N, 10.85. ^{1}H NMR, δ: 1.15 (t, 9 H, C<u>H</u>$_3$CH$_2$N, $^3J_{H,H}$ = 7.2 Hz); 2.95 (q, 6 H, CH$_3$C<u>H</u>$_2$N, $^3J_{H,H}$ = 7.2 Hz); 6.98 (t, 1 H, *p*-H arom., $^3J_{H,H}$ = 7.3 Hz); 7.22 (t, 2 H, *p*-H arom., $^3J_{H,H}$ = 7.8 Hz); 7.28 (d, 4 H, *o*-H arom., $^3J_{H,H}$ = 7.8 Hz); 7.37 (t, 2 H, *m*-H arom., $^3J_{H,H}$ = 7.3 Hz); 7.46 (t, 4 H, *m*-H arom., $^3J_{H,H}$ = 7.8 Hz); 7.54 (d, 2 H, *o*-H arom., $^3J_{H,H}$ = 7.3 Hz); 10.79 (br.s, 1 H, N$^+$H); 11.78 (s, 1 H, CONH).

1,3-Bis(3,4-dichlorophenyl)-5-(2-phenylcarboran-1-yl)barbituric acid (23). Sodium hydride (0.046 g, 1.9 mmol) was added to a solution of methyl 2-phenylcarboranyl-1 acetate (**20**) (0.44 g, 1.5 mmol) in THF (20 mL). The reaction solution instantly turned yellow (with gas evolution). The mixture was stirred for 20 min, and 3,4-dichlorophenyl isocyanate (0.31 g, 1.65 mmol) was added. The reaction mixture was stored for 12 h, the solvent was distilled off, and ether was poured to the residue. A white precipitate that formed was filtered off, dissolved in benzene, treated with TFA to a weakly acidic pH value, and filtered. The filtrate was concentrated by evaporation, and the residue was recrystallized from a hexane—acetone (1 : 1) mixture (50 mL). The yield was 0.3 g (31%), m.p. >260 °C.

Found (%): C, 46.86; H, 3.99; B, 15.83; N, 3.91. $C_{24}H_{22}B_{10}Cl_4N_2O_3 \cdot 0.5Et_2O$. Calculated (%): C, 46.22; H, 4.00; B, 16.30; N, 4.15. IR ($CDCl_3$), ν/cm^{-1}: 1713 (C(O)), 2593 (BH), 2927 (CH). ^1H NMR, δ: 1.50—3.20 (br.s, 10 H, CH); 3.59 (s, 1 H, CH); 7.10 (dd, 2 H, *o*-H arom., $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 2.4 Hz); 7.33 (d, 2 H, *m*-H arom., $^4J_{H,H}$ = 2.4 Hz); 7.42 (t, 2 H, *m*-H_{Ph}, $^3J_{H,H}$ = 8.0 Hz); 7.51 (t, 1 H, *p*-H_{Ph}, $^3J_{H,H}$ = 8.0 Hz); 7.58 (d, 2 H, *o*-H arom., $^3J_{H,H}$ = 8.0 Hz); 7.58 (d, 2 H, *o*-H_{Ph}, $^3J_{H,H}$ = 8.0 Hz).

X-ray diffraction analysis of compound 23. Colorless plate-like crystals, $C_{24}H_{22}B_{10}Cl_4N_2O_3 \cdot 0.5Et_2O$ (M = 673.40), monoclinic, at 293 K a = 7.996(4) Å, b = 26.356(9) Å, c = 30.76(1) Å, β = 96.54(1)°, V = 6440(6) Å^3, space group Cc, Z = 8, d_{calc} = 1.389 g cm^{-3}. The experimental set of 6470 reflections was obtained on an Enraf-Nonius CAD4 diffractometer at 293 K (Mo-Kα radiation, $2\theta_{max}$ = 49.94°) from a single crystal 0.25×0.20×0.15 mm in size. After equivalent reflections were averaged, 6033 independent reflections (R_{int} = 0.0473) were obtained and used to solve and refine the structure. The structure was solved by a direct method. All atoms were localized in difference electron density syntheses and refined against F^2_{hkl} in the anisotropic approximation (positions of hydrogen atoms were calculated and refined in the isotropic approximation using the riding model). The final R factors were R_1 = 0.0656 (calculated by F_{hkl} for 2923 reflections with $I > 2\sigma(I)$), wR_2 = 0.1527 (calculated by F^2_{hkl} for all reflections involved in refinement), GOOF = 1.169, and 771 refined parameters. All calculations were performed by the SHELXTL PLUS 5 program package.[11]

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