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Synthesis of bisalkenyl ethers by the reaction of 1,1,2,2-tetracyanoethane with α-alkylacroleins in isopropyl alcohol

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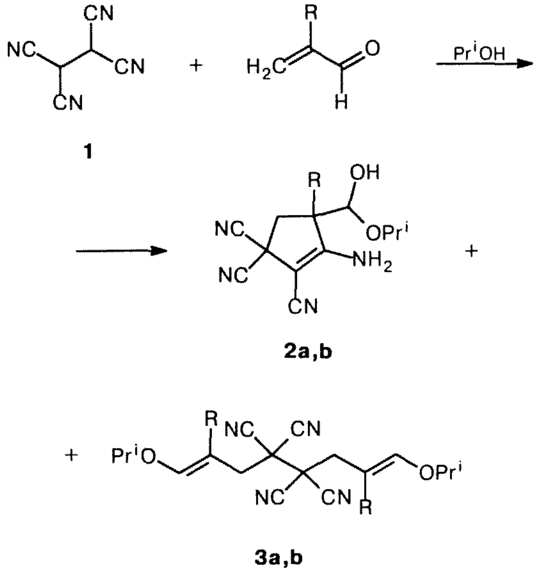
The reaction of 1,1,2,2-tetracyanoethane (**1**) with α–alkylacroleins in isopropyl alcohol affords 3-alkyl-2-amino-3-(isopropoxy)hydroxymethyl-1,5,5-tricyanocyclopentenes (**2a,b**) and 2,7-dialkyl-1,8-diisopropoxy-4,4,5,5-tetracyanoocta-1,7-dienes (**3a,b**). The structure of molecule **3b** has been established by X-ray structural analysis.

Key words: 1,1,2,2-tetracyanoethane, α–alkylacroleins, reaction; bisalkenyl ethers.

Previously[1] we have demonstrated that reactions of 1,1,2,2-tetracyanoethane (**1**) with α-alkylacroleins in alcohols afford stable hemiacetals, 3-alkyl-2-amino-3-(alkoxyhydroxymethyl)-1,5,5-tricyanocyclopentenes (in yields of up to 40 %). According to the regioselectivity of condensation of 1,1,2,2-tetracyanoethane with α,β-unsaturated carbonyl compounds, which we proposed,[2] the formation of adducts of composition 1 : 2 would be expected. Actually, 2,7-dialkyl-1,8-diisopropoxy-4,4,5,5-tetracyanoocta-1,7-dienes (**3a,b**) were isolated from the mixture of products of the reaction of cyanide **1** with 2-methyl- and 2-ethylacrolein in isopropyl alcohol in low yields and in addition to the known[1] 3-alkyl-2-amino-3-(isopropoxy)hydroxymethyl-1,5,5-tricyanocyclopentenes (**2a,b**) (the yield was 30—35 %). The structure of molecule **3b** has been established by X-ray structural analysis (Fig. 1).



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

Apparently, the formation of bisalkenyl ethers **3** is associated with the possibility of additional stabilization of the alkoxyalkenyl fragments. Apparently, the main stabilizing factor is the coordination of the nucleophilic C(2) and C(2a) atoms to the electrophilic C(42) and C(42a) atoms (see Fig. 1), as evidenced by the data of X-ray structural analysis (the C(2) · · · C(42) distance is 2.927(7) Å).

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† Deceased in 1995.

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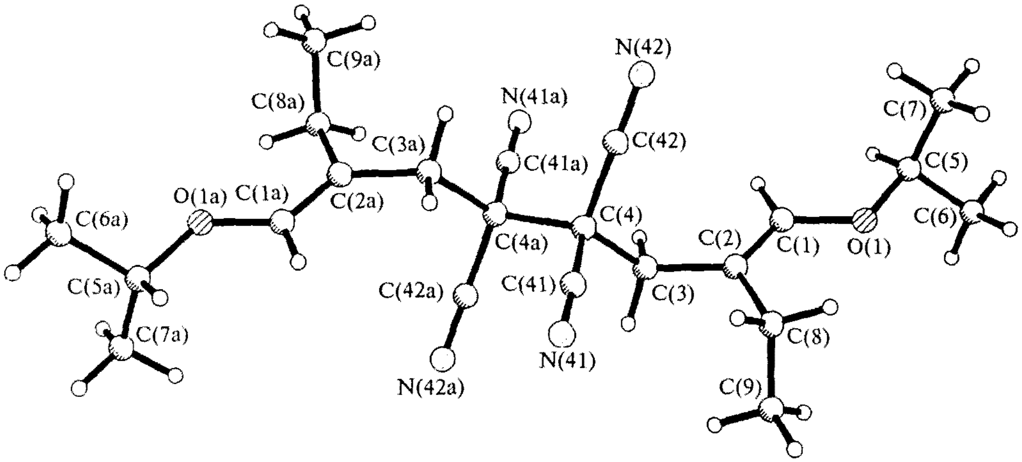

Fig. 1. Molecular structure of compound **3b**.

Experimental

IR spectra were recorded on a UR-20 instrument in Nujol mulls.

Reactions of compound 1 with α-alkylacroleins (general procedure). A mixture of cyanide **1** (0.1 mol) and the corresponding α-alkylacrolein (0.2 mol) in 50 mL of isopropyl alcohol was heated for 15—20 min to 70 °C. After ~24 h, the precipitate was filtered off, washed with isopropyl alcohol, and recrystallized from Pr^{i}OH. Compounds **3a,b** were obtained. After 3—4 days, the newly formed precipitate was isolated from the filtrate, and then the precipitate was washed with isopropyl alcohol and recrystallized from Pr^{i}OH. Compounds **2a,b** were obtained.

Compound 3a: the yield was 10 %, m.p. 141—142 °C. Found (%): C, 67.72; H, 7.45; N, 15.76. $C_{20}H_{26}N_4O_2$. Calculated (%): C, 67.77; H, 7.39; N, 15.81. IR, ν/cm^{-1}: 2270 (C≡N); 1680 (C=C); 1200, 1130 (C—O—C).

Compound 3b: the yield was 8 %, m.p. 94—95 °C. Found (%): C, 69.05; H, 7.96; N, 14.61. $C_{22}H_{30}N_4O_2$. Calculated (%): C, 69.08; H, 7.91; N, 14.65. IR, ν/cm^{-1}: 2265 (C≡N); 1670 (C=C); 1200, 1125 (C—O—C).

Compound 2a: the yield was 30 %, m.p. 150—151 °C. Found (%): C, 60.18; H, 5.89; N, 21.55. $C_{13}H_{16}N_4O_2$. Calculated (%): C, 59.98; H, 6.20; N, 21.52.

Compound 2b: the yield was 35 %, m.p. 154—155 °C. Found (%): C, 61.15; H, 6.47; N, 20.31. $C_{14}H_{18}N_4O_2$. Calculated (%): C, 61.30; H, 6.61; N, 20.42. Spectroscopic parameters of compounds **2a,b** were reported previously.[1]

X-ray structural analysis of compound 3b. Crystals **3b** are monoclinic, space group $P2_1/c$, at 20 °C a = 14.366(3) Å, b = 10.613(3) Å, c = 7.852(2) Å, β = 100.97(2)°, V = 1175.3(5) Å^3, Z = 2 (the molecule is located at the inversion center), d_{calc} = 1.075 g cm^{-3}. $C_{22}H_{28}N_4O_2$, M = 380.48. The unit-cell parameters and intensities of 2158 reflections were measured on an automated four-circle Siemens P3/PC diffractometer (20 °C, Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, θ_{max} = 25°). The structure was solved by the direct method and refined by the full-matrix least-squares method with anisotropic temperature factors for nonhydrogen atoms. Positions of hydrogen atoms were calculated from geometrical considerations and were included in the refinement with fixed positional (the riding model) and thermal (U_{iso} = 0.08 Å^2) parameters. The final values of the discrepancy factors are as follows: R_1 = 0.098 for 2032 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.250 for all independent reflections. All calculations were performed on an IBM PC/AT-386 computer using the SHELXTL PLUS program package; the final refinement was carried out with the use of the SHELXTL-93 program.

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