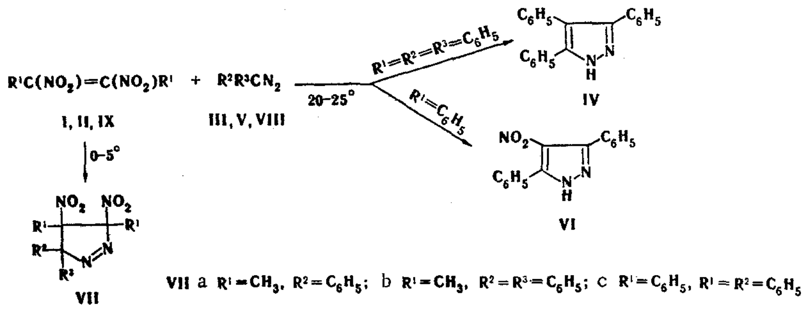
PECULIARITIES OF THE REACTION OF ALIPHATIC DIAZO COMPOUNDS WITH VICINAL DINITROALKENES

F. A. Gabitov, A. L. Fridman,
and O. B. Kremleva

UDC 547.778.2

The reaction of aliphatic diazo compounds with vicinal dinitroalkenes may, depending on the substituents and the reaction conditions, proceed in several directions. Thus cis- and trans-1,2-diphenyl-1,2-dinitroethylenes (I and II) react with phenyldiazomethane (III) at 20-25°C to give 3,4,5-triphenylpyrazole (IV) with splitting out of both nitro groups, whereas the reaction with diazomethane (V) is accompanied by splitting out of the elements of nitrous acid and migration of the phenyl group from C_4 to C_5 and leads to 3,5-diphenyl-4-nitropyrazole (VI).



VII a $R^1=CH_3$, $R^2=C_6H_5$; b $R^1=CH_3$, $R^2=R^3=C_6H_5$; c $R^1=C_6H_5$, $R^1=R^2=C_6H_5$

We succeeded in finding conditions under which the reaction proceeds with retention of both nitro groups to give stable substituted Δ'-3,4-dinitropyrazolines (VII) in quite high yields. Thus diazoalkane III and diphenyldiazomethane (VIII) react at 0-5° with 2,3-dinitro-2-butene (IX), as do III and V with dinitroalkene I.

3,4,5-Triphenylpyrazone (IV). A solution of 2 g of I or II in 50 ml of ether was mixed with a solution of 1 g of diazoalkane III in 50 ml of ether, and the mixture was allowed to stand at 20-25° for 3 days. The solvent was removed by vacuum distillation to give IV with mp 264-265° (from ethanol) in 72% yield.

3,5-Diphenyl-4-nitropyrazole (VI). A solution of 2 g of dinitroalkene I in 40 ml of ether was mixed with a solution of 1 g of diazoalkane V in 50 ml of ether, and the mixture was allowed to stand at 20-25° for 24 h. The solvent was then removed by vacuum distillation to give VI with mp 259-260° (from ethanol) in 67% yield. IR spectrum, cm^{-1}: 3285, 1520, 1350, 972, 844, 780, 734, and 700. UV spectrum, λ_{max}, nm (log ε): 227 (3.68) and 278 (3.14).

Δ'-3,4-Dinitropyrazolines (VIIa-d). Solutions of 0.01 mole of dinitroalkene I or IX and 0.01-0.015 mole of diazo compounds III, V, or VIII in 50-80 ml of ether or benzene were mixed at 0-5°, and the mixture was allowed to stand at the same temperature for 2-10 h. The solvent was then removed by vacuum distillation, and the residue was recrystallized from ethanol or ether to give the following compounds: VIIa, 69% yield, mp 120-121°, IR spectrum, cm^{-1}: 1550, 1352, 910, 894, 856, 750, and 708. UV spectrum: λ_{max}, 330 nm (log ε 2.38); VIIb, 68% yield, mp 109-110°, IR spectrum, cm^{-1}: 1598, 1558, 1354, and 854. UV spectrum, λ_{max}, nm (log ε): 272 (3.30) and 422 (3.63); VIIc, 71% yield, mp 104-105°, IR spectrum, cm^{-1}: 1535, 1355, 852, 740, and 706; VIId, 74% yield, mp 156-157°, IR spectrum, cm^{-1}: 1552, 1348, 852, 772, 750, and 728. UV spectrum: λ_{max}, 332 nm (log ε 2.52).

Perm State Pharmaceutical Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, p. 1577, November, 1975. Original article submitted March 21, 1975.