PREPARATION OF 3-SUBSTITUTED 4,6-DINITROANTHRANILS BY THE OXIDATION OF ANIONIC 1,3,5-TRINITROBENZENE σ-COMPLEXES

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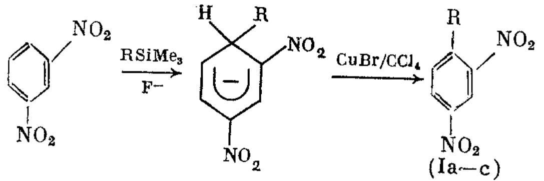
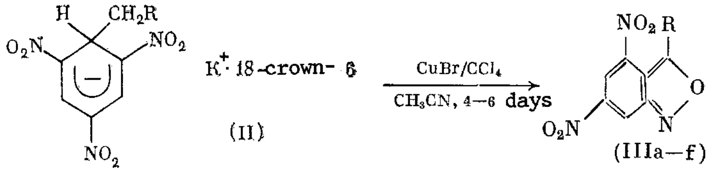
UDC 542.943.7:541.49:547.546-128.2

We have shown that the oxidation of the anionic σ-complexes of 1,3-dinitrobenzene by a system containing a catalytic amount of CuBr in CCl_4 leads to the formation of substitution products (Ia)-(Ic).



R = CH_2COOEt (a), CH_2Ph (b), $CH_2CH{=}CH_2$ (c).

In contrast, anionic σ-complexes of 1,3,5-trinitrobenzene are oxidized by the $CuBr/CCl_4$ system to give 3-acyl-, 3-carboethoxy-, or 3-phenyl-4,6-dinitroanthranils (IIIa)-(IIIf) in good yields.



R = COMe (a), COEt (b), COPh (c), CO—◁ (d), COOEt (e), Ph (f).

The structures of (IIIa)-(IIIf) were confirmed by elemental analysis, PMR and IR spectroscopy, and mass spectrometry.

A mixture of 0.002 mole complex (II) and 0.03 g (0.0002 mole) CuBr in 10 ml 1:1 CH_3CN–CCl_4 was stirred at 20°C for 96-144 h. The products were subjected to chromatography on silica gel and recrystallized from ethanol. Product (IIIa) was obtained in 62% yield, mp 143-144°C. Product (IIIb) was obtained in 70% yield, mp 120-121°C. Product (IIIc) was obtained in 65% yield, mp 163-164°C. Product (IIId) was obtained in 54% yield, mp 110-112°C. Product (IIIe) was obtained in 63% yield, mp 72-73°C. Product (IIIf) was obtained in 30% yield, mp 158-159°C.

M. V. Lomonosov Moscow State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2869-2870, December, 1987. Original article submitted July 2, 1987.

0568-5230/87/3612-2668$12.50