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REGARDING THE REACTION OF S-TRICHLOROTRINITROBENZENE WITH HYDRAZINE

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ABSTRACT: The reaction of S-trichlorotrinitrobenzene with hydrazine is shown to give 1,3-dihydrazino-4,6-dinitrobenzene (4), not S-trihydrazinotrinitrobenzene as previously reported.

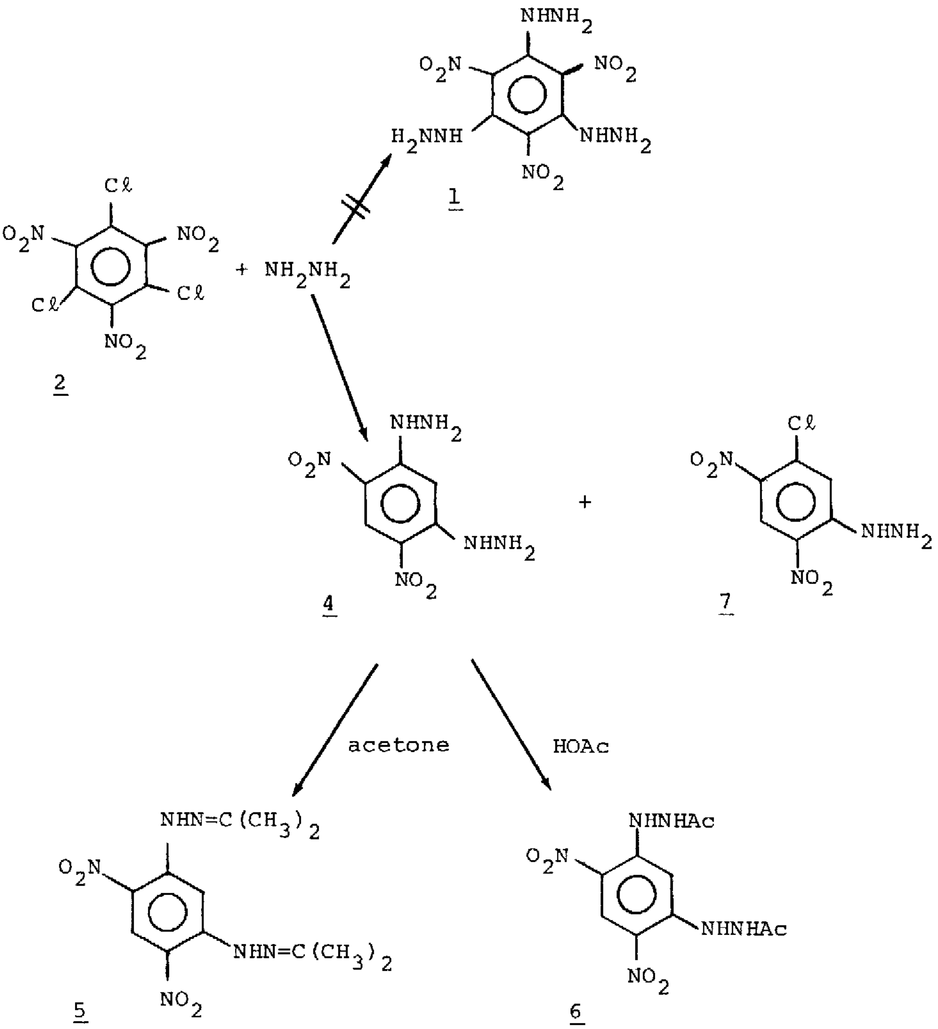
Many simple hexasubstituted benzene derivatives have been synthesized for the first time or become available in substantial quantities relatively recently, and interest in the often unusual chemistry and properties of this class of compounds is continuing to this day. Examples include hexafluorobenzene[1], hexaisopropylbenzene[2], hexacyanobenzene[3], s-trifluorotrinitrobenzene[4], and hexanitrobenzene[5].

In conjunction with structure-property relationship studies of fully substituted s-trinitrobenzene derivatives, we required a sample of trihydrazinotrinitrobenzene (1), whose preparation from s-trichlorotrinitrobenzene (2) and hydrazine hydrate (3) in 95% ethanol had been described by Civera and Giuliano in 1959[6]. We now wish to report that the material prepared by these authors is not 1, and that 1 is, in fact, unknown.

We repeated the procedure given by Civera and Giuliano as closely as possible and in addition conducted a number of reactions between 2 and 3 in methanol under varying conditions of temperature, reaction time, and order of addition. In all cases the same alcohol-insoluble product was obtained in yields ranging from 10 - 36%. The properties of this material are those reported for 1, in that a hydrazone and an acetyl derivative were formed under the conditions given by Civera and Giuliano (see below).

However, the compounds prepared by these workers are actually 1,3-dihydrazino-4,6-dinitrobenzene (4) and its diisopropylidene (5) and diacetyl

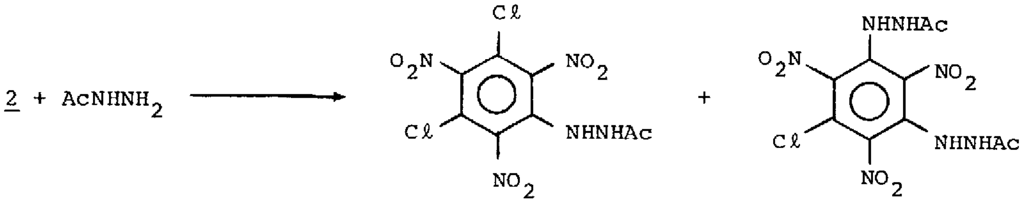
(6) derivatives based on the following data: the mp of "1" after recrystallization from DMF or nitrobenzene is 241-242° (dec) which is near that reported for 4 (246° dec)[8]. The NMR clearly shows the presence of 2 aromatic protons and is otherwise in agreement with structure 4 also: NMR (DMSO-d_6) δ 9.25 (s, 2, broad, NH), 8.85 (s, 1, sharp, aromatic H-5), 7.15 (s, 1, sharp, aromatic H-2), and 4.73 (s, 4, broad, NH$_2$) ppm. The mass spectrum showed a parent ion for 4 at m/e 228. The hydrazone obtained by refluxing "1" in acetone had mp 263-4° (acetone) as compared to 269-270° given by Civera and Giuliano. Analytical data supportive of its structure 1,3-diisopropylidene-



hydrazino-4,6-dinitrobenzene (5) are as follows: NMR (DMSO-d_6) δ 10.64 (s, 2, NH), 8.93 (s, 1, aromatic H-5), 7.60 (s, 1, aromatic H-2), 2.08 (s, 6, CCH_3), and 2.00 (s, 6, CCH_3) ppm; MS m/e 308 (parent). Anal. Calcd for $C_{12}H_{16}N_6O_4$: C, 46.75; H, 5.23; N, 27.26; M.W. 308. Found: C, 46.66; H, 5.18; N, 26.98; M.W. (DMF) 290. "1" on treatment with aqueous acetic acid as described by Civera and Giuliano gave an acetyl derivative which did not melt clearly but decomposed above 300°C. The mass spectrum is again in agreement with the structure 1,3-diacetylhydrazino-4,6-trinitrobenzene (6): NMR (DMSO-d_6) δ 10.25 (s, 2, $NHNHCOCH_3$), 9.61 (s, 2, $NHNHCOCH_3$), 8.90 (s, 1, aromatic H-5), 6.26 (s, 1, aromatic H-2), and 1.95 (s, 6, $NHCOCH_3$) ppm Also, we have prepared 1,3,5-triacetylhydrazino-2,4,6-trinitrobenzene from s-trifluorotrinitrobenzene and found that it melts much lower (185° dec.) than 6.[7]

In several of the experiments conducted in methanol, 1-chloro-3-hydrazino-4,6-dinitrobenzene (7) was isolated in up to 25% yield by evaporating the methanol and washing the residue with water. The crude product was purified by absorbing a filtered ethyl acetate solution onto silica gel and eluting with dichloromethane to give tan crystals of mp 198°, lit.[8] mp 198°. NMR (DMSO-d_6) δ 9.92 (s, 1, NH), 8.81 (s, 1, aromatic H-5), 7.67 (s, 1, aromatic H-2), and 4.95 (s, 2, NH_2) ppm; MS m/e 232 (parent).

A similar 1,4-reduction was not observed when 2 was reacted with acetylhydrazine in acetonitrile solution for 20 h at room temperature. The yellow solid obtained after evaporating the acetonitrile layer and triturating the residue with water was separated chromatographically into unreacted 2 and 1-acetylhydrazino-3,5-dichloro-2,4,6-trinitrobenzene (8), mp 220° (dec); NMR (DMSO-d_6) δ 10.21 (s, 1, $NHNHCOCH_3$), 9.54 (s, 1, $NHNHCOCH_3$), and 1.80 (s, 3, CH_3) ppm; MS m/e 353, 355 (parent), and a small amount of 1,3-diacetylhydrazino-5-chloro-2,4,6-trinitrobenzene (9), mp 195° (dec.); NMR (DMSO-d_6) δ 9.99 (s, 2, $NHNHCOCH_3$), 8.78 (s, 2, $NHNHCOCH_3$), and 1.71 (s, 3, CH_3) ppm; MS m/e 391, 393 (parent), 345 347 (M - NO_2). No triacetylhydrazinotrinitrobenzene was formed under these conditions, and when run at 60°, the reaction yielded unidentified brown solids.



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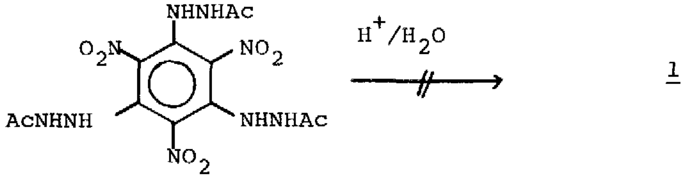
Efforts to remove the acetyl groups in triacetylhydrazinotrinitrobenzene by hydrolysis did not result in the formation of 4. Although treatment of 10 with 12 N $HC\ell$ at ambient temperature gave a solid product essentially free of amide bands in the ir, this was not 4. It exhibited a strong band in the ir at ca. 2100 cm^{-1}, and was surprisingly sensitive to a mild hammer blow. These features could be indicative of the formation of a diazo structure via intra-molecular oxydation-reduction.



The lack of similarity between the products from the hydrolysis of 10 and the reaction of 2 with hydrazine suggests that in the latter case 1 is not an intermediate. The formation of 4 probably proceeds via 1,3-dichloro-4,6-dinitrobenzene as indicated by the detection of 7 as a by - or alternative product. There appears to be no precedence for this type of a 1,4-reduction of nitroaromatics, and no data was obtained in the present work which would permit a possible mechanism to be delineated.

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