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SYNTHETIC EXPLOITATION OF THE RING-OPENING OF 3,4-DINITROTHIOPHENE. A NOVEL ACCESS TO 1,4-DIALKYL- AND 1,4-DIARYL-2,3-DINITRO-1,3-BUTADIENES

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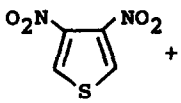
Summary: (E,E)-1,4-Bis(diethylamino)-2,3-dinitro-1,3-butadiene (2a), obtained from the ring-opening of 3,4-dinitrothiophene, reacts with Grignard reagents in THF to give good yields of 1,4-disubstituted (Et, cy-Hex, Ph) 2,3-dinitro-1,3-butadienes (3a-c) having almost exclusively (E,E) configuration.

In previous short communications from our laboratories[1] we reported on the isolation of some 1,4-diamino-2,3-dinitro-1,3-butadienes (2) from the ring-opening reaction which 3,4-dinitrothiophene (1) undergoes by treatment with primary and secondary amines (eq. 1).



(1) + 2 R^1R^2NH ⟶ $R^1R^2NCH{=}C(NO_2){-}C(NO_2){=}CHNR^1R^2$ + H_2S (1)

(1)

(2) R^1 = alkyl, aryl
R^2 = R^1 or H
(2a) R^1 = R^2 = Et

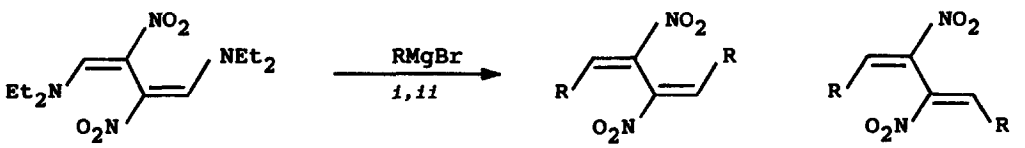
The presence in (2) of nitroenaminic functionalities, whose synthetic potentialities are well known,[2] has prompted us to undertake a research project eventually aimed to the utilization of the four-carbon skeleton of (1) as a synthetic building block.

Accordingly, while studies are still in progress on reaction (1) in order to both better define scope and limitation and optimize yields of the ring-opening products (2), we report herein preliminary results on the reaction of 1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene (2a) with some Grignard reagents.

Results and Discussion

Compound (2a) was obtained through a very simple procedure[3] and in good yield by treatment of 3,4-dinitrothiophene in EtOH at 0°. In the ^1H NMR spectrum of (2a) the resonance of the olefinic protons (δ 8.58 with respect to Me_4Si) indicated for (2a) an (E,E) configuration, by analogy with similar nitroenaminic systems[2] and in good agreement with the chemical shifts calculated on the basis of substituent-effect additivity.

As shown in the Scheme below, when (2a) was reacted[5] for 30 min with Grignard reagents in THF at 0°, the acidic (3% HCl) work-up of the reaction mixture gave almost quantitative yields of 2,3-dinitro-1,3-butadienes (3a-c) stemming from the substitution of both diethylamino groups in (2a) with the hydrocarbon moiety of the Grignard. The ^1H NMR analysis of the crude products showed the presence of small amounts of the (E,Z)-stereoisomers beside the main components which invariably had (E,E)



(E,E)-(2a) (E,E)-(3a-c) (E,Z)-(3a-c)

	ov. yield (%)	(E,E)/(E,Z)[iii]
a: R = Et	94	92/8
b: R = cy-Hex	90	85/15
c: R = Ph	88	*iv*

[i] THF, 0 °C, 30 min, 2.2 mol equiv of RMgBr; [ii] quenching into 3% HCl; [iii] determined by ^1H NMR spectroscopy of the crude reaction product; [iv] the (E,Z) isomer could not be detected.

configuration.[6] Unfortunately any attempt of separation of the two stereoisomers by chromatography proved fruitless. Crystallization from a proper solvent, however, allowed us to obtain pure crystalline forms of the (E,E) isomers[7] in yields ranging between 60 and 80%.

To our knowledge, while 1,4-dinitro and, to a minor extent, 1,3-dinitro-1,3-butadienes are compounds whose reactivity has been somehow investigated,[8] 2,3-dinitro-1,3-butadienes are unknown to date. The herein reported (1) → (2a) → (3) sequence represents therefore a novel, simple, and even highly stereospecific method to otherwise difficult-to-access 2,3-dinitrobutadiene derivatives.

References and Notes

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3 In an Enlermeyer flask, 3,4-dinitrothiophene[4] (1 g, 5.75 mmol) is suspended in 20 ml of EtOH and cooled at 0° by an external ice bath. Under magnetic stirring, diethylamine (2.4 ml, 23 mmol) is syringed into the reaction mixture which becomes in a short time a homogeneous red solution. After standing 2 h at 0° and 22 h at room temperature, compound (2a), which precipitates in almost quantitative yield, is filtered off, washed with little EtOH and then crystallized from the same solvent. Pure (E,E)-(2a) is thus obtained in 75% yield: m.p. 154 °C; δ ($CDCl_3$, 200 MHz) 8.58 (2H, s), 3.46 (2H, q, J = 7.3 Hz), 3.32 (2H, qq, AB of ABX_3 system, J_{AB} = 14.3 Hz, J_{AX} = 7.2 Hz), 1.34 (3H, t, J = 7.3 Hz), and 1.09 (3H, dd, X_3 of ABX_3 system, $J_{AX} = J_{BX}$ = 7.2 Hz)

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5 In a typical procedure a magnetically stirred 0.04M solution of (2a) in THF is cooled to 0° under argon and added of 2.2 mol equiv of a 1.2-1.4 M THF solution of the Grignard reagent. The reaction mixture is kept at the same temperature for ca. 30 min and then poured into ice/3% HCl. Extraction with ether, followed by drying (Na_2SO_4) and

evaporation of the solvent under reduced pressure, gives almost quantitative yields of crude derivatives (3).

6 Structure assignments are based on the high deshielding observed for the nitrovinylic protons in the (E,E) isomers and in the (E) portion of the (E,Z) isomers as compared to the chemical shifts of the same protons belonging to the (Z) portion of the molecules.

7 Compounds (3a-c) gave microanalytical data in full agreement with the proposed structure. (E,E)-3a : m.p. 57.5-58.5 °C (light petroleum b.p. 30-50°), δ ($CDCl_3$, 200 MHz) 7.65 (1H, t, J = 8.1 Hz), 2.21 (2H, quint, J = 7.7 Hz), and 1.16 (3H, t, J = 7.6 Hz); (E,E)-3b : m.p. 95.2-96.0 °C (MeOH/H_2O), δ ($CDCl_3$, 200 MHz) 7.48 (1H, d, J = 11.35 Hz), 2.06 (1H, m), 1.64 (5H, m), and 1.26 (5H, m); (E,E)-3c : m.p. 131.2-132.5 °C (light petroleum b.p. 80-100°), δ ($CDCl_3$, 200 MHz) 8.49 (1H, s) and 7.36 (5H, m).
^1H NMR absorptions ($CDCl_3$, 200 MHz) of the nitrovinylic protons in the (E,Z) stereoisomers: (3a) δ 7.53 and 6.27; (3b) δ 7.35 and 6.05; (3c) undetected.

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