Tetrahedron Letters, Vol. 33, No. 46, pp. 7047-7048, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

Synthetic Exploitation of the Ring-Opening of 3,4-Dinitrothiophene. Part 3. Access to 1,4-Diaryl- and 1,4-Dialkyl-2-nitrobutanes

Carlo Dell'Erba, Marino Novi,* Giovanni Petrillo and Paola Stagnaro
Istituto di Chimica Organica dell'Università, C.N.R. Centro di Studio sui Diariloidi e loro Applicazioni,
Corso Europa 26, I-16132 Genova, Italy

Abstract *: 1,4-Diaryl- and 1,4-dialkyl-2,3-dinitro-1,3-butadienes* ***1a-i*** *are smoothly converted, in MeOH or MeOH-dioxane, to the corresponding 1,4-disubstituted 2-nitrobutanes* ***4a-i*** *by borohydride supported on ion-exchange resins.*

In the frame of a research project aimed at the exploitation of 3,4-dinitrothiophene as a synthetic tool via the ring-opening product 1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene, we recently reported on a useful route to 1,4-diaryl- or 1,4-dialkyl-2,3-dinitro-1,3-butadienes **1**.[1,2] In continuation of such studies, we have investigated the reactions of **1** with polymer-supported borohydride reagents; such reduction method, successfully applied to the transformation of 1-nitroalkenes into the corresponding nitroalkanes,[3] appeared particularly convenient because of the mild reaction conditions and of the simple operative procedures. A point of interest in this research was to ascertain whether the analogies in reactivity between dinitrobutadienes **1** and 1-nitroalkenes could be extended to the selective reduction of the two activated carbon-carbon double bonds of **1**: actually any formed 2,3-dinitrobutane **2** was expected to hardly survive experimental conditions and the outcome of the present reactions[4] consistently has been an efficient formation of nitroalkanes **4** most likely via nitrous acid elimination from **2** to 2-nitro-2-butenes **3** and eventual reduction of the latter.[6]

Examination of the results collected in Table 1 shows that the yields of **4** are generally good but for **4g**: actually, in spite of various attempts to optimize the procedure, the yield remained moderate, possibly due to

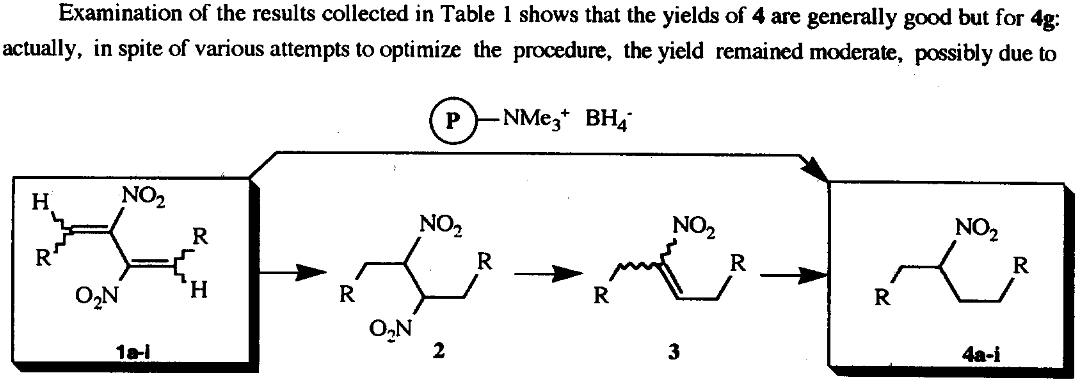

Table 1. Synthesis of 1,4-Diaryl- or 1,4-Dialkyl-2-nitrobutanes **4a-i** from of Dinitrobutadienes **1a-i**.

R =	Product	m.p. (°C)	Yield (%) ^{a}	Conditions ^{b}
phenyl	**4a**	48.4-48.7	76	M, 10 mM, IRA400, 1.0h
1-naphthyl	**4b**	83.6-84.5	66	M-D, 6 mM, IRA400, 3.0h
1-naphthyl	**4b**		79	M-D, 6 mM, A26, 1.5h
2-thienyl	**4c**	34.8-35.2	75	M, 15 mM, IRA400, 1.5h
2-MeC$_6$H$_4$	**4d**	86.8-88.4	75	M-D, 10 mM, IRA400, 2.5h
4-MeC$_6$H$_4$	**4e**	79.1-80.6	89 ^{c}	M-D, 15 mM, IRA400, 3.5h
4-MeC$_6$H$_4$	**4e**		99 ^{c}	M-D, 15 mM, A26, 2.0h
4-MeOC$_6$H$_4$	**4f**	100.3-101.7	93 ^{c}	M, 12 mM, IRA400, 3.0h
Et	**4g**	oil[8]	45 ^{c}	M, 20 mM, IRA400, 1.0h
Et	**4g**		53 ^{c}	M, 20 mM, A26, 1.0h
Bu^n	**4h**	oil	72	M, 20 mM, A26, 1.0h
c-C$_6$H$_{11}$	**4i**	40.9-41.4	91 ^{c}	M, 15 mM, A26, 2.5h

a) Yields of isolated products purified, unless otherwise stated, by chromatography on silica-gel column. Satisfactory analytical data and consistent ^{1}H NMR spectra were obtained for all compounds 4.[7] b) Solvent (M: methanol, M-D: methanol-dioxane), concentration of the substrate, kind of ion-exchange resin (Amberlite® IRA 400 or Amberlyst® A26, borohydride forms) and reaction times are reported. c) Yield of crude reaction product essentially pure by ^{1}H NMR.

some volatility of the nitroalkane. Under equivalent conditions, the polymer-supported borohydride reagent prepared with Amberlyst® A26 gives better results (more satisfactory yields with shorter reaction times) than that prepared with Amberlite® IRA400: the higher reactivity of the former reagent has already been observed in selective reductions of α,β-unsaturated carbonyl compounds.[9]

In conclusion the obtained results indicate that the approach herein constitutes an attractive route to nitroalkanes **4**, a class of compounds whose potentiality in synthesis is well documented.[10] Researches are in progress in order to extend the synthetic scope of the selective reductions of 2,3-dinitro-1,3-butadienes.

Acknowledgments. Financial support by M.U.R.S.T. (Roma) is gratefully acknowledged. We thank Miss A.M. Canuti for her skilful contribution.

REFERENCES AND NOTES

1. Part 1: Dell'Erba, C.; Mele, A.; Novi, M.; Petrillo, G.; Stagnaro, P. *Tetrahedron Lett.* **1990**, *31*, 4933.
2. Part 2: Dell'Erba, C.; Mele, A.; Novi, M.; Petrillo, G.; Stagnaro, P. *Tetrahedron* **1992**, *48*, 4407.
3. Goudgaon, N.M.; Wadgaonkar, P.P.; Kabalka, G.W. *Synth. Commun.* **1989**, *19*, 805.
4. In a typical procedure the dinitrobutadienes **1** (2 mmol) and MeOH (100 ml) were magnetically stirred in an Erlenmeyer flask and at room temperature; depending on the solubility of the substrate more MeOH (or dioxane) was added in order to obtain a homogeneous solution whose final concentration is reported in Table 1. Borohydride exchange resin[5] (3 g) was added, the flask stoppered, and stirring continued at room temperature following the disappearance of the starting material by TLC. A simple filtration followed by rinsing of the resin with methanol and evaporation of the filtrate under reduced pressure gave essentially pure 1,4-diaryl- and 1,4-dialkyl-2-nitrobutanes **4**.
5. Borohydride forms of Amberlite ® IRA400[3] and of Amberlyst ® A26[5a] were prepared according to literature. (a) Weber, J.V.; Faller, P.; Kirsch, G.; Schneider, M. *Synthesis* **1984**, 1044.
6. Signals attributable to vinyl hydrogens of possible intermediates **3** have been detected in the ^{1}H NMR spectra of crude mixtures of reactions stopped before completion.
7. With the obvious exception of the aromatic hydrogen absorptions, the ^{1}H NMR pattern of **4a** is typical of 1,4-diaryl-substituted **4**: δ(CDCl$_3$) 2.05 (1H, m), 2.54 (1H, m), 2.65 (2H, m), 3.03 and 3.27 (1H each, AB of ABX, J_{AB} 14.1 Hz, J_{AX} 8.5 Hz, J_{BX} 6.0 Hz), 4.70 (1H, m), 7.12 (4H, m) and 7.26 (6H, m).
8. Asinger, F.; Geiseler, G.; Hoppe, M. *Chem. Ber.* **1957**, *90*, 114.
9. Sande, A.R.; Jagadale, M.H.; Mane, R.B.; Salunkhe, M.M. *Tetrahedron Lett.* **1984**, *25*, 3501.
10. Rosini, G.; Ballini, R. *Synthesis* **1988**, 833.

(Received in UK 8 June 1992)