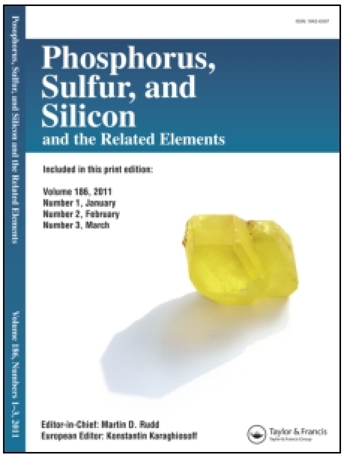
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A NON CLASSICAL REACTION OF 2(3)- BROMOMETHYL-3(2)-NITROTHIOPHENES TOWARDS BASES

Adam Daich[a]; Yann Prigent[b]; Bernard Decroix[a]
[a] Laboratoire de Chimie, UER des Sciences et Techniques de l'université du Havre, Lp Havre, France [b] Laboratoire de RMN, URA 464 CNRS, UER des Sciences et Techniques et IRCOF Université de Rouen, Mt St Aignan Cedex, France

To cite this Article Daich, Adam , Prigent, Yann and Decroix, Bernard(1997) 'A NON CLASSICAL REACTION OF 2(3)-BROMOMETHYL-3(2)-NITROTHIOPHENES TOWARDS BASES', Phosphorus, Sulfur, and Silicon and the Related Elements, 127: 1, 91 — 95

To link to this Article: DOI: 10.1080/10426509708040499

URL: http://dx.doi.org/10.1080/10426509708040499

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulphur, and Silicon, 1997, Vol. 127, pp. 91–95
Reprints available directly from the publisher
Photocopying permitted by license only

© 1997 OPA (Overseas Publishers Association) N.V.
Published by license under
the Gordon and Breach Publishers imprint.
Printed in Malaysia.

A NON CLASSICAL REACTION OF 2(3)-BROMOMETHYL-3(2)-NITROTHIOPHENES TOWARDS BASES

ADAM DAICH[a], YANN PRIGENT[b] and BERNARD DECROIX[a*]

[a]Laboratoire de Chimie, UER des Sciences et Techniques de l'Université du Havre, 30 rue Gabriel Péri, 76600 Le Havre, France; [b]Laboratoire de RMN, URA 464 CNRS, UER des Sciences et Techniques et IRCOF, Université de Rouen, 76821 Mt St Aignan Cedex, France

(Received 21 January 1997; In final form 4 March 1997)

Treatment of 3-bromomethyl-2-nitrothiophene with base led to the dimerized product **3** while the 2-bromomethyl-3-nitrothiophene under the same conditions provided the dithienylethene **5**.

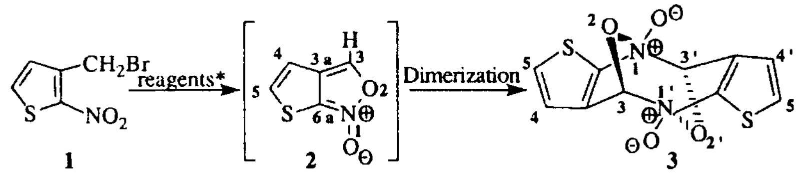
Keywords: C-substitution; o-bromomethylnitrothiophenes; thieno[2,3-c]isoxazole-1-oxide; dimerization

Downloaded At: 17:19 28 January 2011

In the course of our research on new precursors to polyheterocycles containing a nitrogen atom we investigated the reactivity of o-halogenomethylnitrothiophenes.[1] o-Nitrobenzylbromide[2,3] or o-nitrobenzylchloride[4] gave with a nucleophile the corresponding C-substitution product. Furthermore, the 2-chloromethyl-3-nitroimidazo[1,2-a]pyridine reacted *via* an $S_{RN}1$ with the 2-nitropropane anion[5] to give the C-alkyl product. On the other hand, o-substituted nitrothiophenes with various nucleophiles gave Meisenheimer-type adducts.[6,7] To our surprise, when 3-bromomethyl-2-nitrothiophene **1** was treated with the potassium salt of pyrrole substituted at position 2 or not in dry tetrahydrofuran we observed none of these preceding reactions. A yellow product immediately precipitated.[8] The ^{1}H NMR spectrum[9] of this solid did not reveal the protons of the pyrrole ring consecutively to a C-alkylation product, but only three protons: two doublets at δ = 7.95 and 7.10 ppm respectively with a coupling constant J = 5.5 Hz characteristic of an α,β substituted thiophene and a singulet with a chemical shift of 4.65 ppm. This value assigned to the -CH-

---

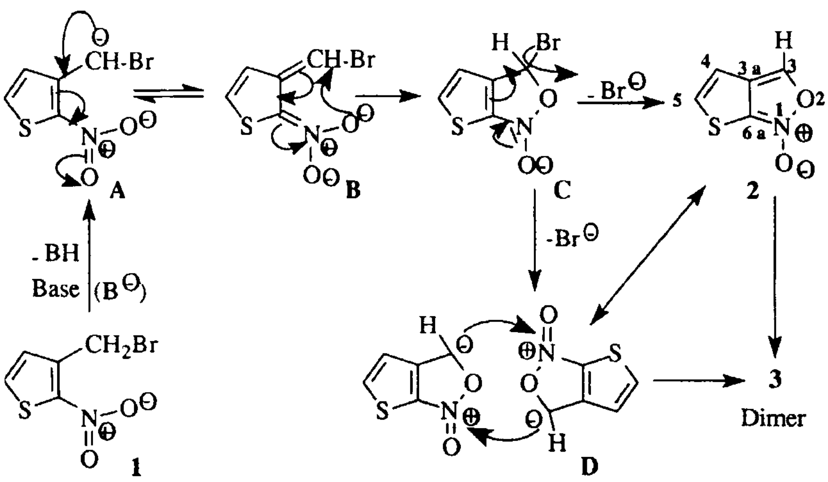
*Corresponding author.



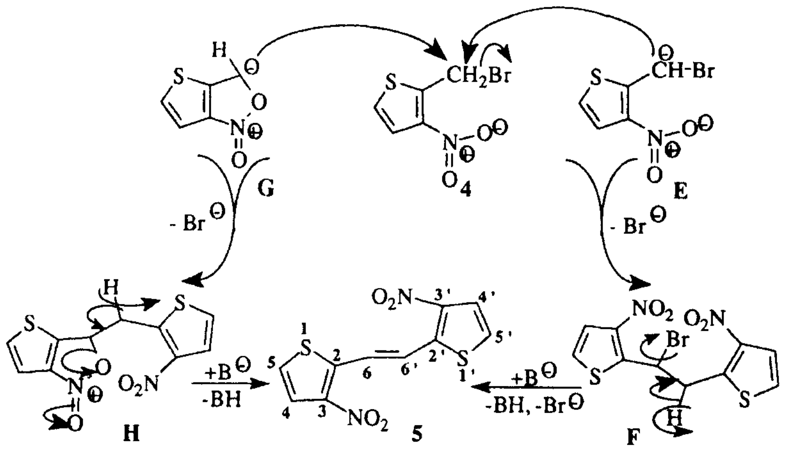
* Sodium methoxide or potassium salt of 2-substituted pyrroles.

O- proton of compound **3**, the chemical shift of -CH-O- carbon (δ = 56.7 ppm) in the ^{13}C NMR spectrum[9] of **3** and the microanalysis data suggested a dimer structure as **3** (Scheme 1). This structure was supported by its electronic impact mass spectrum which revealed a molecular ion of 282 (10%) and a strong ion of 141 (90%) corresponding to the thienoisoxazole form **2**.[9] It is interesting to note that when this reaction was tried with another solvent (methanol, ethanol, DMF or dioxane) at variable temperature (0 to 60°C), the same product was collected with moderate yields (35 to 45%).

Recently, Rigo[10] observed the degradation of the halide when o-nitrobenzylhalides were treated with N-trimethylsilylpyroglutamate. That reaction was due to a thermal degradation as mentioned during hydrolysis of o-nitrobenzhydrylbromide.[11] Probably in our case the reaction passes through the intermediate **2** (Scheme 2). Actually, the potassium salts reacts as base and eliminates one hydrogen of the bromomethyl group of **1** to form **A**. Electron redistribution in **A** leads to an active nitronate ion **B**, which by nucleophilic attack facilitates the formation of 3-bromothienoisoxazole-1-oxide **C**. An electron redistribution in **C** followed by displacement of bromide ion leads to the thieno[2,3-



Downloaded At: 17:19 28 January 2011



Downloaded At: 17:19 28 January 2011

c]isoxazole-1-oxide **2** analogous to 2,1-benzisoxazole-1-oxide (anthranil-1-oxide) which immediately dimerize into the structure **3** or to the intermediate **D** which dimerized equally to the stable dimer compound **3**.

The formation of anthranils is well known[12,13] and many reactions involve an acidic medium[14] nevertheless 3-(2′,4′-dibromophenylazo)anthranil-1-oxide has been prepared from o-nitro-ω-bromobenzaldehyde-2,4-dibromophenylhydrazone in the presence of bases.[15] To our knowledge, it is the first example of an intramolecular cyclization of an o-bromomethylnitroaromatic compound in basic medium.

The same reaction using sodium methoxide as the base gave the N-oxide compound **3** with an equivalent yield of 75%. So it appeared interesting to study the reactivity of the position isomer **4**, namely 2-bromomethyl-3-nitrothiophene (Scheme 3). This isomer[16] treated with a base (sodium methoxide or the potassium salt of 2-substituted pyrroles)[8] gave a different reaction since it afforded the unknown *trans* dithienylethene **5** in a satisfactory yield (67%).[17]

The probable intermediate **E**[18,19] similar to **A** reacts as a nucleophile and substitute the bromine atom of another molecule of **4** leading to the intermediate **F**. The elimination of an hydrobromid acid molecule in **F** leads to the dithienylethene **5**. On the other hand, the ion **G** similar to **D** can react as a nucleophile in similar manner as described above for **E** and give the intermediate **H**. Abstraction of a proton in **H** by the base followed by an electron redistribution gave the dithienylethene **5**. The structure of this olefin **5** was supported by the IR, ^{1}H, ^{13}C NMR spectra as well as by the microanalysis data.[17] Actually, it is interesting to observe that the vinyl protons H_6, H_6' are shifted downfield at $\delta = 8.12$ ppm according to the related carboxy derivatives reported elsewhere.[20]

This assignment is supported by the chemical shift of C_6, C_6' carbons (δ = 124.3 ppm) and the electronic impact mass spectra confirmed the proposed structure **5** by a strong molecular ion of 282 (100%).

In summary, o-bromomethylnitrothiophenes can give a non-classical reaction with basic nucleophilic reagents such as sodium methoxide and potassium salts of 2-substituted pyrroles to furnish a dithienylethene or a dimer of thieno[2,3-c]isoxazole-1-oxide.

Acknowledgements

The NMR facilities used in this study were funded by the Région Haute-Normandie, France.

References

[1] A. Daïch, J. Morel, B. Decroix, *J. Heterocyclic Chem.*, **30**, 675–678 (1993).

[2] L. Cecchi, G. Filacchioni, *J. Heterocyclic Chem.*, **20**, 871–873 (1983).

[3] F. Melani, L. Cecchi, G. Filacchioni, *J. Heterocyclic Chem.*, **21**, 813–815 (1984).

[4] J. S. Duceppe, G. Gauthier, *J. Heterocyclic Chem.*, **22**, 305–310 (1985).

[5] P. Vanelle, J. Maldonado, N. Madadi, A. Gueiffier, J. C. Teulade, J. P. Chapat, M.P. Crozet, *Tetrahedron Lett.*, **31**, 3013–3016 (1990).

[6] C. Dell'Erba, F. Sancassan, M. Novi, D. Spinelli, G. Consiglio, *J. Chem. Soc. Perkin Trans. II*, 1631–1636 (1991).

[7] E. Buncel, M. R. Crampton, M. J. Strauss, F. Terrier, *Electron Deficient Aromatic and Heteroaromatic Base Interactions. The Chemistry of Anionic Sigma Complexes*, Elsevier, Amsterdam, pp. 161–166 (1984) and Refs therein.

[8] **Typical procedure**: To a well stirred solution of o-bromomethylnitrothiophene **1** or **4** (2.22 g; 10 mmol) in 50 ml of dry THF at room temperature was added in three portions sodium methoxide (0.6 g; 11.1 mmol) or potassium salt of pyrrole (1.17 g; 11.1 mmol) (prepared by reaction of potassium metal and pyrrole in dry THF). After 15 minutes of reaction, the yellow precipitate formed was collected by filtration, washed with diethyl ether and recrystallized from anhydrous methanol to yield compound **3** or **5** in 75 and 67% respectively.

[9] Selected data for compound **3**: mp 226°C (decomp); ^1H NMR (DMSO-d_6) δ: 4.65 (s, 1H, H_3), 7.10 (d, J = 5.3 Hz, 1H, H_4), 7.95 (d, J = 5.3 Hz, 1H, H_5); ^{13}C NMR (DMSO-d_6) δ: 56.7, 126.2, 134.2, 140.4, 148.3; MS (EI) m/z 282 (10), 141 (90), 113 (70), 85 (100), 70 (70). *Anal.* Calcd. for $C_{10}H_6N_2O_4S_2$: C, 42.55; H, 2.14; N, 9.92. Found: C, 42.18; H, 1.85; N, 9.67.

[10] B. Rigo, R. Dolaine, S. El Ghammarti, D. Couturier, *J. Heterocyclic Chem.*, **33**, 1063–1066 (1996).

[11] A. D. Mease, M. J. Strauss, I. Horman, L. J. Andrews, R. M. Keefer, *J. Am. Chem. Soc.*, **90**, 1797–1800 (1968).

[12] J. D. Loudon, G. Tennant, *Quart. Rev.*, **18**, 389–413 (1964).

[13] A. Katritzky, J. M. Lagowski, *Chemistry of the Heterocyclic N-Oxides*, Academic Press, London, Ch. 2 (1971).

[14] P. L. Coe, A. E. Jukes, J. C. Tatlow, *J. Chem. Soc. C.*, 2020–2025 (1966).

[15] M. S. Gibson, *Tetrahedron*, **18**, 1377–1380 (1962).

[16] H. R. Snyder, L. A. Carpino, J. F. Jr. Zack, J. F. Mills, *J. Am. Chem. Soc.*, **79**, 2556–2559 (1957).

[17] Selected data for product **5**: mp 247–250°C (decomp); IR(KBr): ν 950 cm^{-1} (CH = CH trans);

Downloaded At: 17:19 28 January 2011

^{1}H NMR (DMSO-d_6) δ: 7.75 (d, J = 5.5 Hz, 1H, H_4), 7.82 (d, J = 5.5 Hz, 1H, H_5), 8.12 (s, 1H, H_6); ^{13}C NMR (DMSO-d_6) δ: 124.3, 125.1, 126.7, 141.4, 144.1; MS (EI) m/z 282 (100), 191(20), 177 (20), 157 (30), 140 (40), 110 (50), 98 (50), 70 (30). *Anal.* Calcd. for $C_{10}H_6N_2O_4S_2$: C, 42.55; H, 2.14; N, 9.92. Found: C, 42.31; H, 2.36; N, 10.09.

[18] P. Caubère, B. Loubinoux, *Bull. Soc. Chim. Fr*, 2483–2489 (1969).

[19] P. Caubère, J. Moreau, *Bull. Soc. Chim. Fr*, 1986–1991 (1970).

[20] B. Yom-Tov, S. Gronowitz, *Chemica Scripta*, **3**, 37–47 (1973).

Downloaded At: 17:19 28 January 2011