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A NEWER ROUTE FOR THE SYNTHESIS OF β-PHENYLTHIO, β-PHENYLSULFINYL AND β-PHENYLSULFONYL NITROETHYLENES

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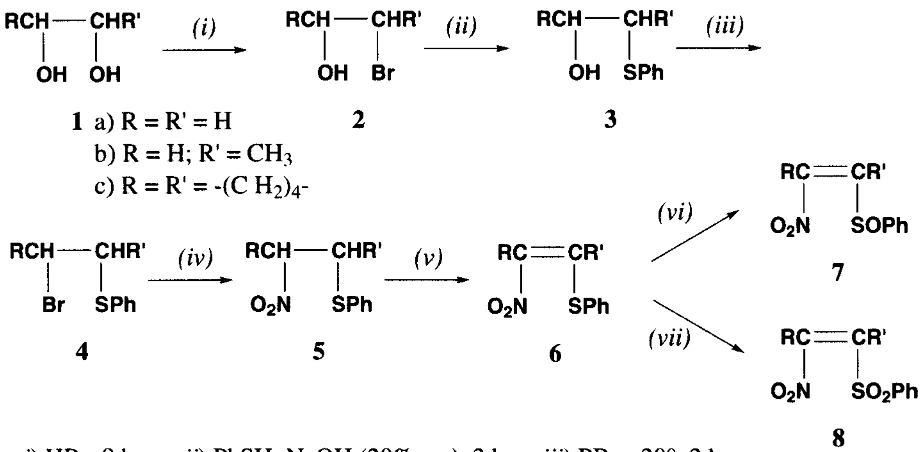
Olefins substituted with either nitro or sulfur functions have been shown to behave as excellent dienophiles in Diels-Alder reactions and as acceptors in Michael addition reactions.[1] Thus olefins substituted with both nitro and sulfur functions at each end of the double bond might be very useful synthons in organic synthesis. They should be reactive as Michael acceptors and/or dienophiles[2a] and the nitro and sulfur functions can be transformed into different functionalities.[3] However, there are only two reports for the preparation of this type of olefins.[2] Ono's method[2a] uses 2-nitroethanol as the starting material; however its preparation and handling requires utmost care and attention,[4] and it is very expensive. On the other hand, Node's[2b] method cannot be generalized for ß-alkylthionitroethylenes. This paper reports a new and simple route for the synthesis of these olefins as shown below.

Reaction of the 1,2-diols (**1**) with HBr gave the bromohydrins (**2**) and displacement of bromide by phenylmercaptide gave 2-phenylthio substituted alcohol (**3**). The second hydroxy group was then converted to the bromo derivative (**4**) employing PBr_3. The nitro group was then introduced by modification of the Kornblum's procedure.[5] In this step, both the nitro and the nitrite were formed. The use of ether as the main solvent reduced the yield of nitrite and the nitro compound was separated by elution through a short column of silica (eluent 3:1 hexane-chloroform). The purification *must* be carried out *immediately* in order to avoid a side- reaction involving the nitrite, the nitro compound and sodium nitrite.[6] The sulfide (**5**) was then converted to the olefin (**6**) by treatment with sulfuryl chloride/Et_3N in CH_2Cl_2 at 0° for 30 min. The sulfoxide (**7**) was obtained at 0° with one equivalent of *m*-chloroperbenzoic acid while the sulfone (**8**) was obtained at 20° using two equivalents of the oxidant. Thus this method which employs simple reaction steps and purification procedures, constitutes a facile and a more convenient method than previous routes. It has been applied with three diols (**1a-c**) to produce the olefins in reasonably good yields.



i) HBr, 8 hrs *ii*) PhSH, NaOH (20%, aq), 2 hrs *iii*) PBr_3, 20°, 2 hrs
iv) $NaNO_2$, DMSO, Ether, 20°, 3 hrs *v*) SO_2Cl_2, Et_3N, 0°, 30 min
vi) MCPBA, 1 eq, 0°, 2 hrs *vii*) MCPBA, 2 eq, 20°, 38 hrs

EXPERIMENTAL SECTION

Bps and mps are uncorrected. ^1H nmr spectra were recorded on a 90MHz Perkin-Elmer R32 spectrometer in $CDCl_3$ with TMS as the internal standard. All the reagents used were of laboratory grade and were purified according to standard procedures. DMSO used was dried over calcium hydride and fractionally distilled and stored over Type 4Å molecular sieves.

Nitroethylenes. Typical Procedure.- A mixture of conc. HBr (48%) (50 mL) and the diol (960 mmol) was refluxed for 8 hrs and then poured onto crushed ice, neutralized with solid Na_2CO_3 and saturated with Na_2SO_4. Extraction with ether, followed by drying over anhydrous $MgSO_4$ and distillation *in vacuo* yielded pure bromohydrin (**2**).

Then 500 mmol of (**2**) and 500 mmol of thiophenol were refluxed in the presence of 120 mL of 20% aqueous NaOH for 2 hrs; then the reaction mixture was added to 300 mL of cold water and extracted successively with 2 x 150 mL portions of chloroform. Removal of volatile products followed by distillation under reduced pressure yielded pure 2-phenylthio substituted alcohol (**3**).

To this alcohol (**3**) (30 mmol) was added 10 mmol of PBr_3 and the flask was cooled with ice water and stirred for 2 hrs. Crushed ice (50g) was added and the organic layer extracted with ether and dried over anhydrous $MgSO_4$. Distillation under reduced pressure gave pure 2-phenylthio substituted bromide (**4**).

To stirred dry $NaNO_2$ (20 mmol) in 5 mL of dry DMSO was added 10 mmol of (**4**) in 25 mL of dry ether and the heterogenous reaction mixture was stirred for 3 hrs under a dry nitrogen atmosphere. The contents were added to 50g of crushed ice and extracted with 2 x 50 mL portions of ether, dried over anhydrous Na_2SO_4 and chromatographed on a short silica column (3.5cm, 100-200 mesh) and elution with a hexane-chloroform mixture (3:1) gave pure nitro compound (**5**).

Table. Yields mp (bp). ^{1}H nmr and Combustion Analyses of Compounds

Cmpd	Yield	mp (°C)	lit.mp	^{1}H NMR	Analyses (Found)		
	(%)	(bp)	(bp)	δ	C	H	N
2a	49	(149-150)	(149-150)[6]	———	–	–	–
2b	63	(146)	(149)[7]	———	–	–	–
2c	69	(76/4mm)	(73-75/5mm)[8]	———	–	–	–
3a	87	(126/2mm)	(135/0.08torr)[6]	3.10 (t, 2H), 3.50 (b, 1H), 3.75 (t, 2H), 7.16-7.35 (m, 5H)	–	–	–
3b	88	(143/2mm)	—	1.20 (d, 2H), 3.10 (m, 3H), 3.90 (sextet, 1H), 7.30-7.60 (m, 5H)	64.26 (64.38)	7.20 (7.40)	–
3c	87	(143/2mm)	—	1.10-2.20 (m, 8H), 2.90 (dt, 1H), 4.50 (b, 1H), 7.30-7.70 (m, 5H)	69.19 (69.39)	7.74 (7.92)	–
4a	88	(149/2mm)	(120-122/ 0.05 torr.)[6]	3.50 (m, 4H), 7.50-7.80 (m, 5H)	-	-	–
4b	89	(171/2mm)		1.76 (d, J = 7Hz, 3H), 3.00 (dd, J = 14, 10Hz, 1H), 3.35 (dd, J = 14, 6Hz, 1H), 3.95 (m, 1H), 7.15-7.50 (m, 5H)	46.77 (46.91)	4.80 (4.86)	– –
4c	91	(187/2mm)		———	53.33 (53.46)	5.60 (5.80)	– –
5a	71	(156/2mm)	(130/0.3torr.)[6]	3.65 (t, 2H), 4.70 (t, 2H), 7.50-7.90 (m, 5H)	– –	– –	– –
5b	87	oil		1.85 (d, J = 7Hz, 3H), 3.20 (dd, J = 14, 10Hz,1H), 3.60 (dd, J = 14, 7Hz,1H), 4.15 (m, 1H), 7.10-7.50 (m, 5H)	54.81 (54.85)	5.63 (5.53)	7.11 (7.19)
5c	78	oil		0.90-2.50 (m, 8H), 2.80 (td, J = 10, 4Hz, 1H), 3.35 (td, J = 10, 4Hz, 1H), 7.10-7.50 (m, 5H)	60.74 (60.90)	6.38 (6.57)	5.91 (6.07)
6a	87[a]	oil		6.80 (d, J = 11Hz, 1H), 7.20-7.60 (m, 5H), 8.00 (d, J = 11Hz, 1H)	53.03 (52.85)	3.90 (3.85)	7.74 (7.63)
6b	88[b]	oil		2.10 (s,3H), 6.8 (s, (Z)-6b), 7.30-7.70 (m, 5H), 8.00 (s, (E)-6b)	55.37 (55.48)	4.65 (4.73)	7.18 (7.11)
6c	81	oil		0.90-3.90 (m, 8H), 7.30-7.80 (m, 5H),	61.26 (61.46)	5.57 (5.71)	5.96 (5.80)
7a	65	107-121	100-115[6]	7.10-7.80 (m, 7H)	–	–	–
8a	58	149-150	148-150[6]	7.40-7.90 (m, 7H)	–	–	–
8b	87	43-49	44-47[c],72-76[6]	2.30 (s,3H), 6.40 (s, (Z)-8b), 7.50-8.10 (m, 5H) 8.00 (s, (E)-8b)	–	–	–
8c	69	oil		1.20-4.10 (m, 8H), 7.40-7.90 (m, 5H)	53.92 (54.09)	4.91 (4.72)	5.24 (5.41)

a) E-isomer was obtained as the major product (95%); b) Obtained as a mixture E & Z isomers and the separation was not attempted; c) E,Z respectively.

Then 15 mmol of (**5**) in 50 mL of CH_2Cl_2 was stirred with 20 mmol of sulfuryl chloride at 0° for 10min and the volatile products were evaporated and the residue obtained was dissolved in 75 mL of CH_2Cl_2. 20 mmol of Et_3N was then added and stirred at 0° for 30 min and the contents were poured into 100 mL of cold water. The organic layer was washed with brine and water, dried and chromatographed on silica gel and eluted with hexane to afford the pure olefin (**6**).

The sulfoxide (**7**) was obtained by treatment of the olefin (**6**) (2.5 mmol) with one equivalent of *m*-CPBA (2.5 mmol) in 25 mL of CH_2Cl_2 at 0° for 1hr followed by washing with water, dilute sodium acetate solution and brine and evaporation of solvent, while the sulfone (**8**) was obtained by the use of two equivalents of the oxidant (5 mmol) at 20° for 38 hrs followed by a similar workup. The yields of the individual steps are furnished in table.

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