Letters to the Editor

New convenient method for the synthesis of spiro[2.5]octane-1,1-dicarbonitriles

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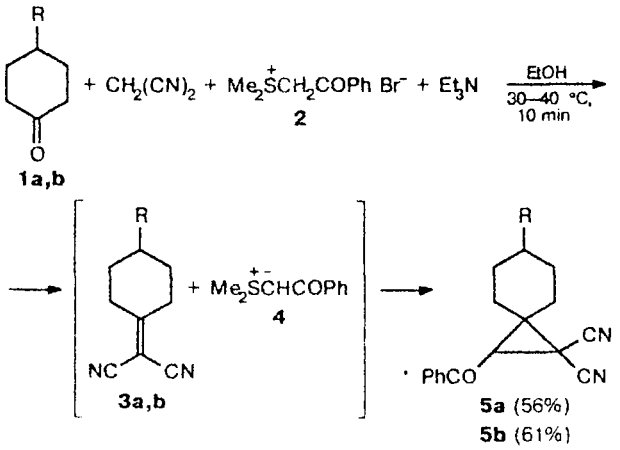
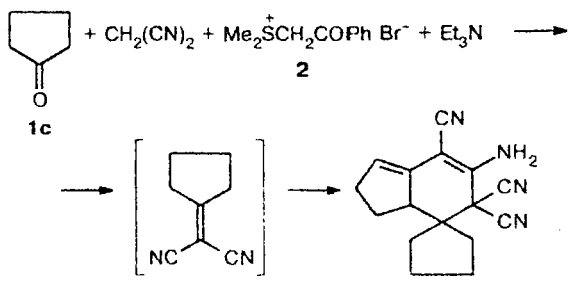
Reactions of stabilized sulfonium ylides $Me_2S^+C^-HCOR$ with electron-deficient alkenes can afford the corresponding substituted cyclopropanes.[1–3] Sometimes the synthesis and isolation of the initial ylides and alkenes are rather laborious procedures. In this connection, here we describe a method which involves generation of both initial compounds directly in the reaction mixture. Thus the reaction of cyclohexanones (**1a,b**) with malononitrile, dimethylphenacylsulfonium bromide (**2**), and triethylamine (a 10% excess of Et_3N was used and the other reagents were taken in equimolar amounts) yielded substituted spiro[2.5]octanes (**5a,b**). Apparently, the reaction occurred *via* intermediate cyclohexylidenemalononitriles (**3a,b**) and dimethylsulfonium phenacylide (**4**) that formed in the reaction mixture under the action of a base.

As can be seen, the products were rapidly formed in satisfactory yields and both could be readily isolated from the reaction mixture by filtration.

The scope and limitations of this synthetic method call for further investigation. For example, when the reaction was carried out with cyclopentanone **1c** under the same conditions, compound **6**, which is the product of dimerization of cyclopentylidenemalononitrile (**3c**),[4] was isolated instead of the corresponding spiro[2.4]heptane.





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The results of this work agree with the enhanced tendency of compound **3c** to undergo dimerization under the action of bases.[4]

The characteristics of the compounds synthesized are given below.

2-Benzoylspiro[2.5]octane-1,1-dicarbonitrile (5a). M.p. 114—115 °C (EtOH). IR (KBr), ν/cm^{-1}: 2255 (CN), 1680 (CO). ^{1}H NMR ((CD$_3$)$_2$CO), δ: 1.4—2.3 (m, 10 H); 4.00 (s, 1 H, H(2)); 7.62 (t, 2 H); 7.74 (t, 1 H); 8.11 (d, 2 H) (all H$_{Ph}$).

2-Benzoyl-6-(*tert*-butyl)spiro[2.5]octane-1,1-dicarbonitrile (5b). M.p. 134—135 °C (EtOH). ^{1}H NMR ((CD$_3$)$_2$CO), δ: 0.93 (s, 9 H; Bu^t); 1.2—2.1 (m, 8 H); 2.40 (m, 1 H, H(6)); 3.95 (s, 1 H; H(2)); 7.60 (t, 2 H); 7.73 (t, 1 H); 8.05 (d, 2 H) (all H$_{Ph}$).

6′-Amino-3′,3′a,4′,5′-tetrahydrospiro[cyclopentane-1,4′(2′*H*)-indene]-5′,5′,7′-tricarbonitrile (6). M.p. 182—184 °C (EtOH) (*cf.* Ref. 4: m.p. 184—186 °C). ^{1}H NMR ((CD$_3$)$_2$CO), δ: 1.4—2.2 (m, 10 H); 2.46 (m, 2 H, 2 H(2′)); 3.15 (m, 1 H; H(3′a)); 5.63 (m, 1 H; H(1′)); 6.7 (br.s, 2 H, NH$_2$).

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A new one-step method for the synthesis of 1-(alkoxy-*NNO*-azoxy)-2-phenylethenes from di(alkoxy-*NNO*-azoxy)methanes

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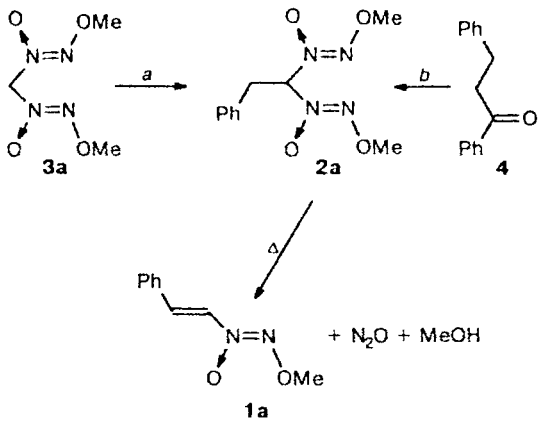
In a single publication,[1] where (alkoxy-*NNO*-azoxy)olefins have been mentioned, 1-(methoxy-*NNO*-azoxy)-2-phenylethene (**1a**) was obtained by the pyrolysis of compound **2a** synthesized in four steps from bisazoxymethane **3a** or ketone **4**. No reaction conditions, yields, and properties of the products were reported.[1]

We attempted to synthesize an intermediate product **2a** by the direct *C*-benzylation of compound **3a**. However, the reaction unexpectedly furnished the target olefin **1a** in 46% yield. The ethyl homologue **1b** was synthesized similarly in 42% yield. Compounds **2a** and **2b** are formed in the first step. They predominate, according to TLC, over **1a,b** and **3a,b** during the first 10 min and disappear completely in 1 h.

1-(Methoxy-*NNO*-azoxy)-2-phenylethene (1a). Aqueous 45% NaOH (2.6 mL, 0.06 mol) was added with stirring and cooling with tap water to a solution of compound **3a** [2] (3.28 g, 0.02 mol), $PhCH_2Cl$ (5.06 g, 0.04 mol), and Et_4NBr (0.42 g, 0.002 mol) in DMSO (10 mL). The reaction was monitored by TLC on Silufol (PhH—EtOAc, 3 : 1): R_f for **1a**, 0.09; for **2a**, 0.29; and for **3a**, 0.40. One hour later, the reaction mixture was diluted with water, acidified with HCl, and extracted with $CHCl_3$ (3×20 mL). The extract was washed with 10% Na_2CO_3 (10 mL), a saturated solution of NaCl (2×20 mL), and water (20 mL), and concentrated *in vacuo*. The residue (3.35 g) was



Reagents: *a.* 1) PhCHO, MeONa, 2) Ac_2O, 3) Et_3N, 4) [H]; *b.* 1) NO, MeONa, 2) H_2O/OH^-, 3) $AgNO_3$, 4) MeI.

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