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 ($(CD_3)_2CO$), 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 ($(CD_3)_2CO$), 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 ($(CD_3)_2CO$), 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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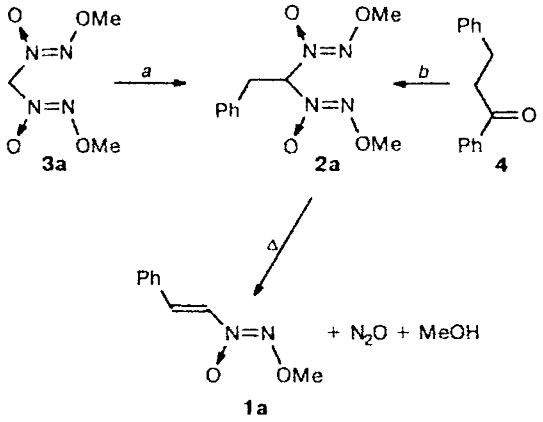
In a single publication,[1] where (alkoxy-*NNO*-azoxy)olefins have been mentioned, 1-(methoxy-*NNO*-azoxy)-2-phenylethene (**1a**) was obtained by the pyrolysis of compound **2a** synthesized in four steps from bisazoxymethane **3a** or ketone **4**. No reaction conditions, yields, and properties of 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.



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.

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

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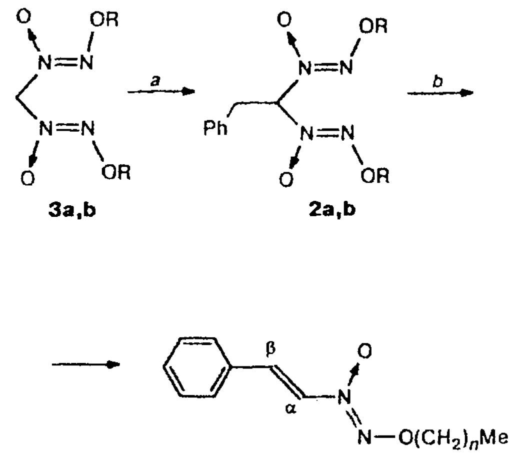

3: R = Me (a), Et (b) 1a,b (*n* = 0 (a), 1(b))

Reagents: *a.* $PhCH_2Cl$, NaOH, Et_4NBr or TEBAC, DMSO; *b.* OH^-.

flash-chromatographed on Silpearl (20 g) using $CHCl_3$ as the eluent. The fraction containing **1a** (2.50 g) was recrystallized from Et_2O to obtain **1a** (1.65 g, 46%) with m.p. 80—81 °C. UV (water), λ/nm (ε): 200 (13700), 232 (8000), 291 (22700). IR (film), ν/cm^{-1}: 3100, 2965, 1480 (N_2O_2), 1310, 1220, 1090, 1050, 995, 885, 865, 850, 780, 710. ^1H NMR (*cf.* Ref. 1), δ (10% in DMSO-d_6): 4.12 (s, 3 H, CH_3); 7.42—7.46 (m, 3 H, *m*-H and *p*-H); 7.68 (d, 1 H, α-H, $J_{\alpha,\beta}$ = 13.7 Hz); 7.75—7.78 (m, 2 H, *o*-H); 8.07 (d, 1 H, β-H); (10% in CCl_4): 4.04 (s, 3 H, CH_3); 7.29—7.41 (m, 6 H, H arom. + α-H); 7.60 (d, 1 H, β-H, $J_{\alpha,\beta}$= 13.3 Hz).

1-(Ethoxy-*NNO*-azoxy)-2-phenylethene (1b) was obtained similarly from **2b**,[2] with benzyltriethylammonium chloride instead of Et_4NBr; R_f for **1b**, 0.12; for **2b**, 0.32; and for **3b**, 0.44. The yield of **1b** was 1.62 g (42%), m.p. 46—47 °C ($CHCl_3$—hexane). ^1H NMR (10% in DMSO-d_6), δ: 1.34 (t, 3 H, CH_3, *J* = 7.1 Hz); 4.40 (q, 2 H, CH_2); 7.40—7.44 (m, 3 H, *m*-H + *p*-H); 7.66 (d, 1 H, α-H, *J* = 13.5 Hz); 7.73—7.76 (m, 2 H, *o*-H); 8.07 (d, 1 H, β-H). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 192 $[M]^+$ (43), 163 $[M-Et]^+$ (17), 135 (17), 133 $[M-Et-NO]^+$ (89), 117 (16), 116 (10), 106 (12), 105 (19), 104 (47), 103 $[PhCH=CH]^+$ (68), 101 (23), 91 $[PhCH_2]^+$ (20), 90 $[PhCH]^+$ (12), 88 (11), 80 (20), 78 (29), 77 $[Ph]^+$ (100), 63 (14), 51 (45), 49 (22), 39 (12).

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Polyfluorinated enamines. New methods for the synthesis of 5-trifluoromethyluracil

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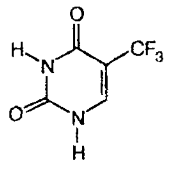
5-Trifluoromethyluracil (**1**) is known to possess high anticancer and antiviral activities.[1] However, the methods for its preparation[2—6] have several disadvantages, such as the multi-stage character,[2] difficultly accessible starting reagents,[3,4] the use of organomercury derivatives,[5] and low yields of the target product.[2,5,6]

We synthesized compound **1** by two new methods, *viz.*, by the reaction of *cis,trans*-3-dimethylamino-2-trifluoromethacryloyl fluoride[7,8] (**2**) with urea and by cyclization with partial hydrolysis of *N*-(3,3,3-trifluoro-2-trifluoromethylprop-1-enyl)urea[9] (**3**). Compounds **2** and **3** were obtained in a few steps from octafluoroisobutene, which is a large-scale by-product of the industrial production of fluoroplastics.



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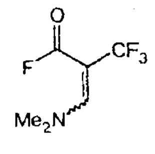

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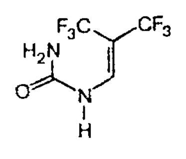

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