FLUOROCARBON DERIVATIVES OF NITROGEN. PART 15 [1]. THERMAL DECOMPOSITION OF PERFLUORO-[2-(DIMETHYLAMINO-OXY)-1-AZACYCLOHEXENE]

RONALD E. BANKS*, M. SAMI FALOU and ANTHONY E. TIPPING*

Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1QD (U.K.)

SUMMARY

Flow pyrolysis of nitrogen-diluted perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexane] (IV) at 350 °C and 1 atm in a stainless-steel tube yielded mainly perfluoro-(6-methyl-2,6-diazahept-2-ene) (VI) and a compound believed to be perfluoro-2,9-diazadeca-2,8-diene, together with small amounts of tetrakis(trifluoromethyl)hydrazine, material tentatively identified as perfluoro-(5-methyl-5-azahexyl) isocyanate, and the artefacts bis(trifluoromethyl)amine and perfluoro-(5-methyl-5-azahexanamide). Formation of the major product (VI) is proposed to involve a nitrene-type rearrangement once homolysis of the N-O bond in IV has occurred and released the oxy radical $\overline{CF_2(CF_2)_3N=\overset{\bullet}{C}-O}$.
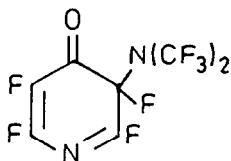
INTRODUCTION

This work is an unfinished extension of studies on the thermal rearrangement of $(CF_3)_2NO$-substituted aromatic compounds reported recently [1]. Noting, in particular, that static pyrolysis of perfluoro-[4-(dimethylamino-oxy)pyridine] (I) at 125 °C in stainless
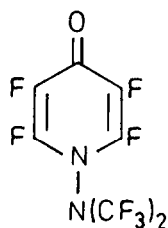

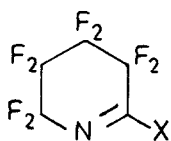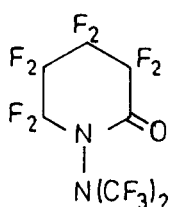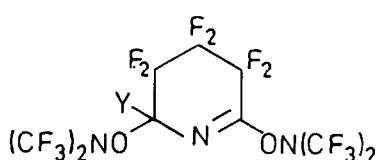* Either of whom will deal with any enquiries.
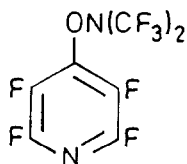
(I)   (II)   (III)

(IV) X=ON(CF$_3$)$_2$ (V)   (VIII) Y=F
(VII) X=F   (IX) Y=ON(CF$_3$)$_2$

steel gives mainly a 2:3 mixture of the isomeric dienones II and III, we
wondered whether similar treatment of
perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene] (IV) would provide
the novel N-substituted lactam V. In fact, it did not [2]: during 6
days at 260 °C in a stainless-steel autoclave, compound IV underwent ca.
80% decomposition to a complex mixture of acyclic products, including
principally perfluoro-2-azapropene (CF$_3$N=CF$_2$),
perfluoro-(6-methyl-2,6-diazahept-2-ene) [(CF$_3$)$_2$NCF$_2$CF$_2$CF=NCF$_3$, VI], and
4-cyanobutanoyl fluoride (NCCF$_2$CF$_2$CF$_2$COF). Unfortunately, that work was
not completed, but we are able to report on the related pyrolysis of
perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene] (IV) under flow
conditions.

RESULTS AND DISCUSSION

Perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene] (IV) is not a
new compound, having been synthesised twenty years ago here via
treatment of perfluoro-1-azacyclohexene (VII) with the
bistrifluoromethylamino-oxylating agents $(CF_3)_2NONa$ or $[(CF_3)_2NO]_2Hg$
[3]. Replacement of the imidoyl fluorine in the azacyclohexene by a
$(CF_3)_2NO$ group can also be effected using a Shreeve Reagent [4], i.e.
$(CF_3)_2NOH-MF$ (M = Cs [5] or K [6]), or the silane $(CF_3)_2NOSiMe_3$ [6].
Baileys's method [6], utilizing
NN-bistrifluoromethylhydroxylamine-potassium fluoride, was employed here
because it is the simplest and most efficient; the yield of IV was >83%
(based on a 92% conversion of VII), and both the known [3,5,6]
di-substituted derivative VIII (ca. 14%) and material believed from [19]F
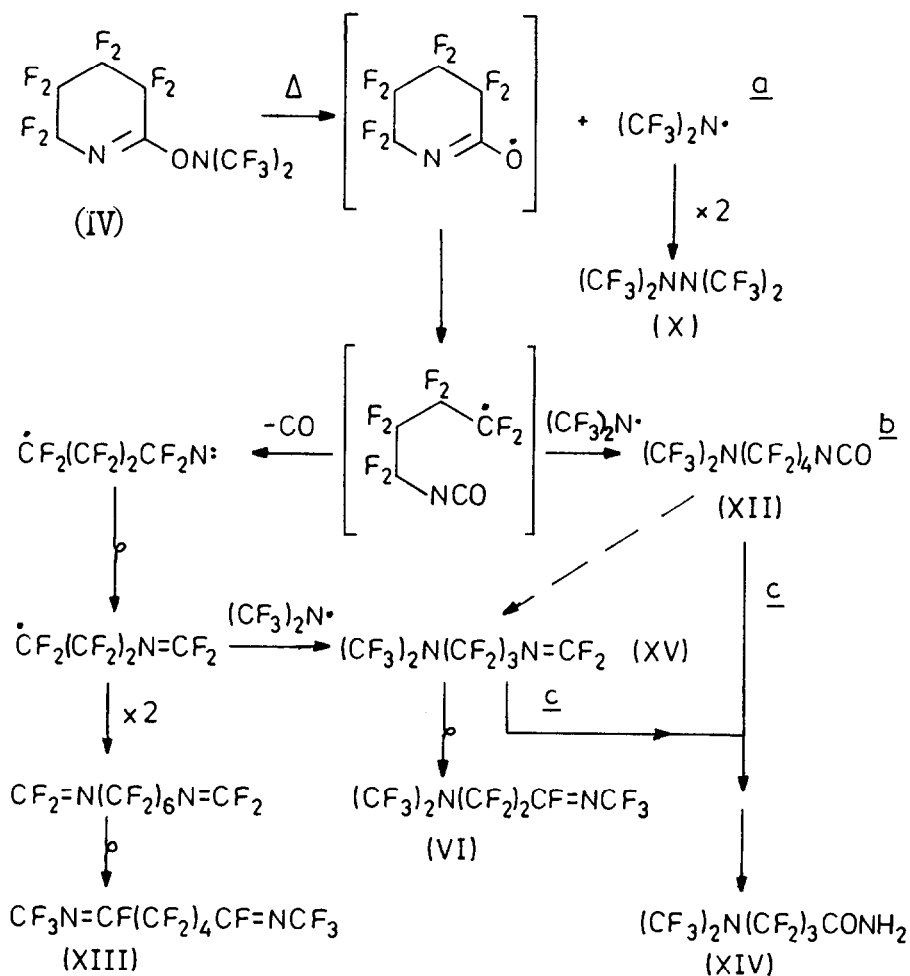NMR analysis to be the tri-substituted entity IX were also formed.

Conditions were established under which vapour-phase flow pyrolysis
of nitrogen-diluted perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene]
(IV) at atmospheric pressure in a stainless-steel reactor heated to
350 °C caused 85% decomposition of the starting material. Only products
capable of being condensed from the gaseous effluent at -78 °C were
collected. No decomposition of the azacyclohexene (IV) occurred when
the reactor was held at 150 °C, and at 330 °C only ca. 20% conversion to
products took place.

The pyrolysate from the experiment conducted at 350 °C was shown to
comprise traces of tetrakis(trifluoromethyl)hydrazine (X) and
bis(trifluoromethyl)amine (XI) and a multi-component liquid that was
separated chromatographically (GLC) into
perfluoro-(6-methyl-2,6-diazahept-2-ene) (VI; 59% yield),* starting
material (IV; 15%), a compound that might have been
perfluoro-(5-methyl-5-azahexyl) isocyanate (XII; 5%),

* Yields are based on the amount of IV converted.

perfluoro-2,9-diazadeca-2,8-diene (XIII; 16%) contaminated with an
unidentified component, and perfluoro-(5-methyl-5-azahexanamide) (XIV;
6%).

Starting from the premise that the weakest bond in
perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene] (IV) connects
nitrogen to oxygen, the above result seems best explained as depicted in
Scheme 1. Detection of the hydrazine $(CF_3)_2NN(CF_3)_2$ and of the equally
well known amine $(CF_3)_2NH$ amongst the products clearly pinpoints the
generation of the aminyl radical $(CF_3)_2N\bullet$; and loss of presumptive
perfluoro-2-azapropene with formation of bis(trifluoromethyl)amine as
shown in the scheme should be acceptable to all who have manipulated
this gaseous aza-olefin in glass apparatus. No precedent in
fluorocarbon chemistry appears to exist, however, for the linchpin of
the mechanistic proposal made here (Scheme 1) that the N-O bond fission
under scrutiny generates a perfluorinated iminyloxy radical (PIO),
β-scission of which sets in motion a sequence of events leading to
perfluoro-(6-methyl-2,6-diazahept-2-ene) (VI). Theoretically, this
oxygen-centred radical has two electronic isomers, PIO_σ and PIO_π (Scheme
2), hence a situation reminiscent of that pertaining to its
much-discussed [7-9] hydrocarbon analogue the succinimidyl radical
arises. Assuming [cf. ref. 8] that β-scission of PIO_σ would result in
the formation of a ground-state isocyanato group, whereas the
corresponding ring-opening of PIO_π would generate an excited-state NCO
function (Scheme 2), it is tempting to speculate that the π-species is
the precursor of the nitrene conjectured to be involved in the
production of perfluoro-(6-methyl-2,6-diazahept-1-ene) (XV) (Scheme 1).
However, the unexpectedly high thermal stability of
perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene] would seem to
indicate that N-O homolysis produces a σ-radical (PIO_σ) which, unlike
PIO_π, does not involve delocalization of the unpaired electron;
β-scission of a high-energy σ-species, followed by decarbonylation of a
"hot" isocyanate thus produced is therefore also a plausible nitrene
source. Meaningful discussion about the relative roles of the two
orbitally isomeric forms of the presumptive PIO radical clearly must
await further studies planned to be undertaken when resources permit.
Note that precedent exists [10] for the 1,3-migration of fluorine
(presumably fluoride-initiated [11]) following a nitrene-mediated
1,2-fluoroalkyl shift [12], as depicted in Scheme 1.

F_2 (ring structure) with $ON(CF_3)_2$

(IV)

$\xrightarrow{\Delta}$

[ring structure with $\dot{O}$] $+$ $(CF_3)_2N\cdot$ <u>a</u>

$\downarrow \times 2$

$(CF_3)_2NN(CF_3)_2$
(X)

$\dot{C}F_2(CF_2)_2CF_2N\colon$ $\xleftarrow{-CO}$ [$F_2 \quad \dot{C}F_2$ ring with NCO] $\xrightarrow{(CF_3)_2N\cdot}$ $(CF_3)_2N(CF_2)_4NCO$ <u>b</u>
(XII)

$\downarrow p$

$\dot{C}F_2(CF_2)_2N=CF_2$ $\xrightarrow{(CF_3)_2N\cdot}$ $(CF_3)_2N(CF_2)_3N=CF_2$ (XV)

$\downarrow \times 2$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow p \qquad\qquad \underline{c}$

$CF_2=N(CF_2)_6N=CF_2$ $\qquad$ $(CF_3)_2N(CF_2)_2CF=NCF_3$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (VI)

$\downarrow p$

$CF_3N=CF(CF_2)_4CF=NCF_3$ $\qquad\qquad\qquad\qquad\qquad$ $(CF_3)_2N(CF_2)_3CONH_2$
(XIII) $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (XIV)

<u>c</u>

Scheme 1

<u>a</u> Defluorination of this radical at the wall of the metal reactor
followed by attack on the $CF_3N=CF_2$ produced by F^-/adventitious H_2O
during handling of the total product accounts for the formation of
$(CF_3)_2NH$.

<u>b</u> It is possible that some decarbonylation of this nascent isocyanate
occurs, giving the nitrene $(CF_3)_2N(CF_2)_4\ddot{N}$ and hence the azomethine
XV.

<u>c</u> Reaction with glass/adventitious H_2O [<u>cf</u>. 13].
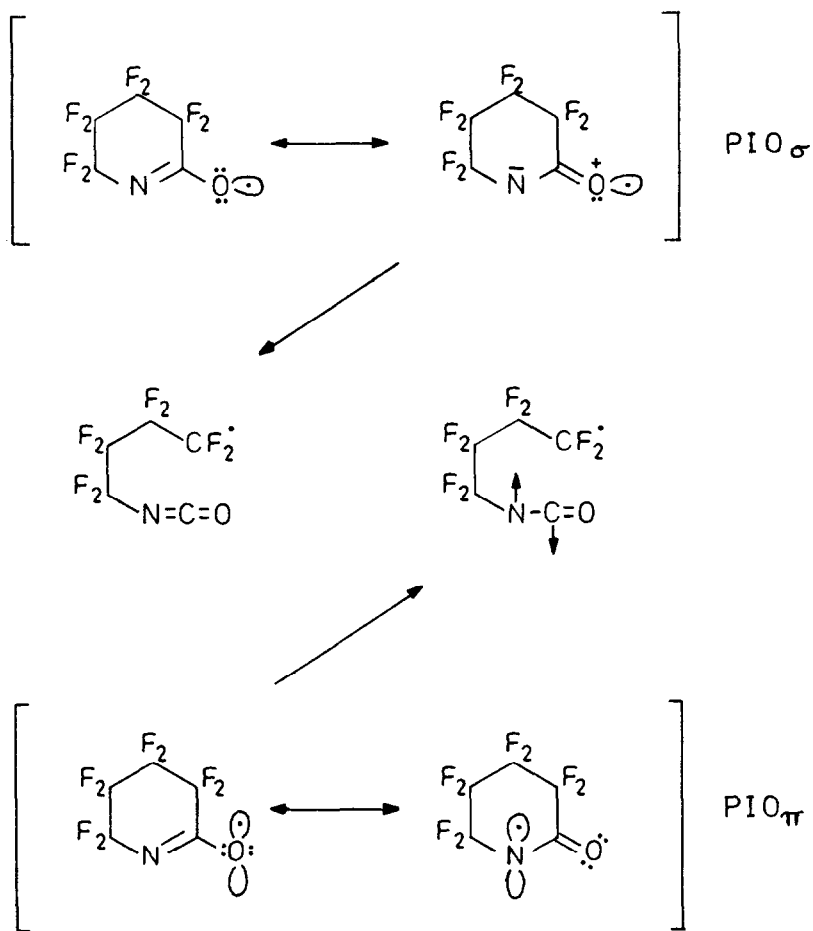
Scheme 2

EXPERIMENTAL

Spectroscopic Analysis

Infrared spectra were recorded on a Perkin-Elmer 197 or 357 spectrophotometer, mass spectra on a Kratos MS45 spectrometer operating

with an ionising voltage of 70 eV, and ^{19}F nuclear magnetic resonance
spectra on a Perkin-Elmer instrument at 84.6 MHz (positive chemical
shift values refer to absorptions to low field of the reference peak).

Synthesis of Perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene] (IV)

Perfluoro-1-azacyclohexene [14] (8.28 g, 33.8 mmol) was condensed,
in vacuo, into a cold (-196 °C) Pyrex Rotaflo tube (270 cm^3) containing
a homogeneous mixture of NN-bistrifluoromethylhydroxylamine [3]
(6.34 g, 37.5 mmol) and anhydrous powdered potassium fluoride (10.9 g,
188 mmol). The Rotaflo valve was closed and the tube was placed in a
steel cabinet to warm to room temperature before being shaken
mechanically for 36 hours. The volatile product (13.6 g) was
transferred to a vacuum system and subjected to trap-to-trap
distillation at 1-2 mmHg to yield NN-bistrifluoromethylhydroxylamine
(traces; -196 and -78 °C traps) and a colourless liquid (13.6 g; -48 and
-23 °C) which was fractionated at 746 mmHg in a 1.5 m x 1.0 cm spinning
band still to provide (i) perfluoro-1-azacyclohexene (0.65 g, 2.65 mmol,
8% recovery), b.p. 40 °C, identified by i.r. spectroscopy; (ii)
perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene] (IV) (10.15 g, 25.76
mmol, 83% based on $C_5F_{10}N$ consumed), b.p. 93-95 °C (lit. [3], 101 °C at
760 mmHg [Siwoloboff]), which gave only one peak when examined by g.l.c.
(1.5 m SE-30 at 80 °C) and possessed spectroscopic properties (i.r., ^{19}F
n.m.r., mass) which compared well with those of analytically pure (C, F,
N) samples [3, 6]; (iii) a three-component liquid residue (2.8 g) shown
by coupled g.l.c./i.r. analysis (1.5 m SE-30 at 80 °C) to comprise
perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene] (IV),
perfluoro-[2,6-bis(dimethylamino-oxy)-1-azacyclohexene] (VIII) [6], and
a compound tentatively identified (see below) as
perfluoro-[2,6,6-tris(dimethylamino-oxy)-1-azacyclohexene] (IX) (nc) in
the ratio (uncalibrated peak areas) 14:84:2.

This bis(trifluoromethyl)amino-oxylation of
perfluoro-1-azacyclohexene was repeated several times to provide
sufficient perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene] (IV) for

the pyrolysis study. Sufficient stillpot residue [fraction (iii)] was thereby collected to enable it to be enriched in the third component by spinning-band distillation and then investigated by ^{19}F n.m.r. analysis. Complex absorption systems assignable to a compound of structure IX appeared at +10.8 {12F; $[(CF_3)_2NO]_2C$}, +8.8 [6F; $(CF_3)_2NOC=N$], −43.3 (2F; $CF_2C=N$), −54.8 (2F), and −62.2 (2F) p.p.m. (ext. CF_3CO_2H).

Thermolysis of Perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene](IV)

The azacyclohexene (IV) (9.98 g, 25.32 mmol) was injected intermittently (50 μl every 2 minutes) into a stream of nitrogen (20 cm^3 min^{-1}) entering a coiled stainless-steel tube (1.5 m x 4 mm i.d.) which was heated to 350 °C and vented to the atmosphere via two small Pyrex traps (25 cm^3) cooled to −78 °C (the apparatus was constructed from an obselete gas chromatograph). The product (8.74 g) recovered from the traps was shown by GLC (1.5 m SE-30, 70 °C) to contain small amounts of tetrakis(trifluoromethyl)hydrazine and bis(trifluoromethyl)amine (confirmed by ^{19}F NMR spectroscopy), unchanged starting material, and four new compounds (the GC peak area ratios for the last five components, in the order described below, was 53:17:5:17:5). Preparative scale GLC (5 m SE-30, 90 °C) was used to isolate the following compounds (in order of increasing retention times): (i) perfluoro-(6-methyl-2,6-diazahept-2-ene) (VI) (nc) [4.63 g, 12.65 mmol, 59% based on (IV) converted] (Found: C, 19.4; F, 73.1; N, 7.4. $C_6F_{14}N_2$ requires C, 19.7; F, 72.7; N, 7.6%),
m/z 347 [top mass peak; $C_6F_{13}N_2^+$ ($\underline{M}^{+\cdot}$−F·), 0.4%], 214 ($C_4F_8N^+$, 20.4%), 202 ($C_3F_8N^+$, 35.4%), 114 ($C_2F_4N^+$, 37.0%), 69 (CF_3^+, 100.0%), $\lambda_{max.}$ (liq. film) 1780 cm^{-1} (strong C=N str.), δ_F (neat liq.; ext. CF_3CO_2H) +53.2 (CF=N; mult.), +23.8 [$(CF_3)_2N$; sept., $^4J_{FF}$ 7.5 Hz], +18.7 ($C\underline{F}_3N=CF$; d, $^4J_{F,CF_3}$ 13.2 Hz), −14.9 ($NC\underline{F}_2CF_2$; mult.), and −40.7 ($NCF_2C\underline{F}_2$; mult.) p.p.m. (rel. int. 1:6:3:2:2); (ii) recovered starting material (IV) (1.49 g, 3.78 mmol, 15%), identified spectroscopically (IR, ^{19}F NMR); (iii) unidentified material (0.44 g) thought to be perfluoro-(5-methyl-5-azahexyl) isocyanate (XII), $\lambda_{max.}$ (liq. film) 2300 cm^{-1} (asym. N=C=O str.); (iv) material deduced from spectroscopic

analysis to be impure perfluoro-2,9-diazadeca-2,8-diene (XIII) (nc)
[1.49 g, 3.48 mmol, 16% based on (IV) converted] {δ_F (neat liq.; ext.
CF_3CO_2H) +53.6 (mult; $C\underline{F}=NCF_3$), +18.7 (14.2 Hz d; $NC\underline{F}_3$), -40.8 (br. mult.
$C\underline{F}_2$), -45.1 (br. mult; $C\underline{F}_2$) p.p.m. (rel. int. 1:3:2:2) with impurity
bands at +24.0 and +17.6 p.p.m.; $\lambda_{max.}$ (liq. film) 1780 cm^{-1} (C=N str.);
$\underline{m/z}$ 409 [top mass peak; $C_8F_{15}N_2^+$ ($\underline{M}^{+\cdot}$-F·), 7.7%], 69 (CF_3^+, 100%)}; and
(v) perfluoro-(5-methyl-5-azahexanamide) (XIV) (nc) [0.44 g, 1.27 mmol,
6% based on (IV) converted], $\lambda_{max.}$ (mull) 3360m (br), 3250 (sh), 3180m
(N-H str.), 1700s (C=O str.), 1610w (NH_2 def.) cm^{-1}, $\underline{m/z}$ 327 [top mass
peak; $C_6H_2F_{11}N_2O^+$ ($\underline{M}^{+\cdot}$-F·), 0.5%], 194 {$C_4H_2F_6NO^+$ [$\underline{M}^{+\cdot}$-$(CF_3)_2N$], 51.8%},
131 ($C_3F_5^+$, 37.0%), 112 (100%), 44 (O=C=$\overset{+}{N}H_2$, 51.1%), δ_F (soln. in Et_2O;
ext. CF_3CO_2H) +24.7 [sept., $(CF_3)_2N$], -12.4 (complex, $(CF_3)_2NC\underline{F}_2$), -42.1
(t, $C\underline{F}_2CONH_2$), and -44.8 (br. s, $C\underline{F}_2CF_2CONH_2$) p.p.m. (rel. int.
3:1:1:1).

REFERENCES

1   Part 14, R.E. Banks, M.S. Falou, R. Fields, N.O. Olawore and A.E.
     Tipping, J. Fluorine Chem., 38 (1988) 217.
2   M.S. Falou, Ph.D Thesis, University of Manchester, 1985.
3   C. Oppenheim, Ph.D Thesis, University of Manchester, 1970; see R.E.
     Banks and C. Oppenheim, J. Fluorine Chem., 12 (1978) 27.
4   D.P. Babb and J.M. Shreeve, Inorg. Chem., 6 (1967) 351; J.A. Lott,
     D.P. Babb, K.E. Pullen, and J.M. Shreeve, ibid., 7 (1968) 2593.
5   R.E Banks and D.R. Choudhury, J. Chem Soc., Perkin Trans. I, (1981)
     1443.
6   A.R. Bailey and R.E. Banks unpublished work; see A.R. Bailey, Ph.D
     Thesis, University of Manchester, 1981.
7   See, for example, J.M. Hay, Reactive Free Radicals, Academic Press
     London and New York, 1974; P.S. Skell and J.C. Day, Acc. Chem. Res.,
     11 (1978) 381; P.S. Skell, U. Lüning, D.S. McBain, and J.M. Tanko,
     J. Am. Chem. Soc., 108 (1986) 121 and references quoted therein.
8   T. Koenig and R.A. Wielesek, Tetrahedron Lett., (1975) 2007.
9   M.J. Field, I.H. Hillier, S.A Pope, and M.F. Guest, J. Chem. Soc.,
     Chem Commun., (1985) 219; M.J.S. Dewar and S. Olivella, ibid.,
     (1985) 301.

10 C.G. Krespan, J. Org. Chem., 51 (1986) 332.

11 P.H. Ogden, J. Org. Chem., 33 (1968) 2518.

12 R.E. Banks, D. Berry, M.J. McGlinchey, and G.J. Moore, J. Chem. Soc. (C), (1970) 1017.

13 D.A. Barr and R.N. Haszeldine J. Chem Soc., (1956) 3428.

14 R.E. Banks, K. Mullen, W.J. Nicholson, C. Oppenheim, and A. Prakash, J. Chem. Soc., Perkin Trans. I, (1972) 1098.