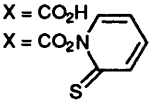
Chemistry of the (*Z*)-Cyclo-oct-4-enyl Radical Including the Preparation of $^{18}O_2$-Labelled (*Z*)-Cyclo-oct-4-enyl Hydroperoxide

A. J. Bloodworth,* David Crich,* † and T. Melvin
Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ

Photolysis of the *O*-acyl thiohydroxamate (**2**), precursor to the (*Z*)-cyclo-oct-4-enyl radical, in the presence of $^{18}O_2$ and a tertiary thiol provides the labelled hydroperoxide (**8**). The parent (*Z*)-cyclo-oct-4-enyl radical is shown to undergo transannular cyclization only under relatively forcing conditions.

Unsaturated hydroperoxides are useful precursors for cyclic peroxonium ions.[1,2] In particular, (*Z*)-cyclo-oct-4-enyl hydroperoxide (**7**) has proven to be a useful substrate for the generation and study of such reactive intermediates.[1,2] We report here an extension to the preparation of (*Z*)-cyclo-oct-4-enyl hydroperoxide (**7**), based on quenching of the (*Z*)-cyclo-oct-4-enyl radical with triplet oxygen in the presence of a tertiary thiol,[2,3] in which use of $^{18}O_2$ affords the corresponding $^{18}O_2$-labelled hydroperoxide (**8**). To the best of our knowledge, this constitutes the first reported isolation of such a species. We also report the full details of a parallel study of the behaviour of the (*Z*)-cyclo-oct-4-enyl radical in the presence of various radical traps.[3]

(**13**)

(**1**) X = CO_2H
(**2**) X = CO_2N 
(**3**) X = Br
(**4**) X = (*Z*)-cyclo-oct-4-enyl
(**5**) X = CN
(**6**) X = COCl
(**7**) X = OOH
(**8**) X = $^{18}O^{18}OH$
(**9**) X = ^{18}OH
(**10**) X = Cl
(**11**) X = H
(**12**) X = 2-pyridylthio

Results and Discussion

The synthesis of secondary alkyl hydroperoxides is not trivial. The displacement of secondary mesylates by alkaline hydrogen peroxide gives, at best, meagre yields.[4] The use of potassium superoxide in nucleophilic displacements leads primarily to formation of dialkyl peroxides in benzene or dimethylformamide or of alcohols in dimethyl sulphoxide; elimination reactions also compete strongly.[5] The attempted use of *m*-chloroperoxybenzoic acid as nucleophile in the Mitsunobu reaction leads to simple rather than peroxy esters.[6] More efficient methods involve either the quenching of incipient carbenium ions with peroxide anion as in the method of Caglioti,[7] or the quenching of free radicals with molecular oxygen as reported, *inter alia*, by Brown[8] and Barton.[9]

(*Z*)-Cyclo-oct-4-enyl hydroperoxide (**7**) has been previously prepared and isolated in this laboratory using both the Caglioti toluene-*p*-sulphonylhydrazone[10] and the Barton *O*-acyl thiohydroxamate[2] methods. In the present study, the *O*-acyl thiohydroxamate method[9,11] was chosen because the source of peroxygen is triplet molecular oxygen which might readily be replaced by $^{18}O_2$ to provide a synthesis of labelled hydroperoxide with potential uses[1,2] in the study of peroxonium ion chemistry.

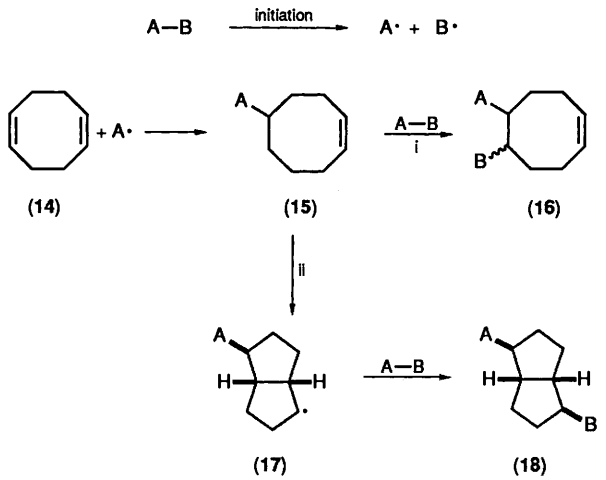
We therefore required a rapid, efficient synthesis of (*Z*)-cyclo-oct-4-enyl carboxylic acid (**1**) from which the *O*-acyl thiohydroxamate (**2**), precursor to the (*Z*)-cyclo-oct-4-enyl radical, could be prepared. Initially we attempted to use the method of Stork and Landesman[12] involving the reaction of *N*-cyclohex-1-enylpyrrolidine with propenal followed by quaternisation with methyl iodide and base promoted Grob-type fragmentation. However, in our hands, this fragmentation was somewhat unsatisfactory, an observation subsequently confirmed independently by other workers.[13] Attempted formation of acid (**1**) or its ethyl ester by reaction of (*Z*)-cyclo-oct-4-enylmagnesium bromide, itself generated from (*Z*)-cyclo-oct-4-enyl bromide (**3**)[14] and magnesium in diethyl ether, with either carbon dioxide or ethyl chloroformate, respectively, gave only low yields of the required product, the main product in each case being a mixture of *meso*- and (±)-(*Z*,*Z*)-cyclo-oct-4-en-5-yl)cyclo-octene (**4**). Eventually the acid (**1**) was prepared[2] in 81% overall yield from the bromide (**3**), *via* the nitrile (**5**) by treatment with sodium cyanide in dimethyl sulphoxide followed by hydrolysis with hydrogen peroxide in aqueous potassium hydroxide. The acid (**1**) was then converted in 92% yield to the corresponding acyl chloride (**6**) by treatment with oxalyl chloride and a catalytic quantity of dimethylformamide in benzene at room temperature.[2] Reaction of (**6**) in the dark at room temperature with *N*-hydroxypyridine-2-thione (**13**), pyridine, and a catalytic quantity of 4-dimethylaminopyridine resulted in isolation, in 60% yield, of the crystalline, yellow *O*-acyl thiohydroxamate (**2**).[2] Thus a stable isolable precursor (**2**) to the (*Z*)-cyclo-oct-4-enyl radical is available in four simple steps and 44% overall yield from the bromide (**3**).

The hydroperoxide (**7**) has been prepared in 55% yield[2,3] from the *O*-acyl thiohydroxamate (**2**) essentially as described for the general case by Barton.[9] It is noteworthy that the whole sequence, from (**3**), was achieved without recourse to a chromatographic purification step. It was necessary to modify the procedure so that it was suitable for adaption to the

† *Current address:* The University of Illinois at Chicago, Department of Chemistry (M/C 111), Box 4348, Chicago, Illinois 60680, USA.

preparation of the $^{18}O_2$-labelled compound. Clearly a small scale closed system was required. Thus, a 50 cm^3 flask was evacuated and filled with an atmosphere of oxygen at room temperature. This was then condensed into an evacuated 125 cm^3 flask containing a large magnetic stirrer bar and the *O*-acyl thiohydroxamate (**2**) (*ca.* 3 mmol) and 3-ethylpentane-3-thiol[15] in diethyl ether (75 cm^3) at −196 °C and 10^{-3} mmHg. The closed vessel was allowed to warm to room temperature and the reaction mixture was then vigorously stirred, and irradiated with a sodium lamp until the solution became colourless. Extractive work-up and chromatography on alumina gave the hydroperoxide (**7**); yields of 19 and 37% were achieved in separate experiments. The stage was then set for the preparation of the labelled hydroperoxide (**8**). The procedure was repeated using $^{18}O_2$ and hydroperoxide (**8**), contaminated with *ca.* 15–20% of the alcohol (**9**) as determined by ^{13}C NMR spectroscopy, was isolated in 7.5% yield. The 70 eV EI mass spectrum of (**8**) showed the presence of a molecular ion at *m/z* 146 (0.05%) together with fragment ions at (*m/z* 127 ($M^{+\cdot}$ − ^{18}OH, 4.36%), 118 ($M^{+\cdot}$ − C_2H_4, 12.31), and 109 ($M^{+\cdot}$ − $^{18}O_2H$, 20.34). The absence of corresponding signals for the unlabelled hydroperoxide (**7**) testifies to the high isotopic purity of the compound prepared. To the best of our knowledge, this is the first reported isolation of an $^{18}O_2$-labelled hydroperoxide; $^{18}O_2$-labelled allylic hydroperoxides have been prepared subsequent to our initial communication,[3] by oxygen exchange from allylic hydroperoxides with $^{18}O_2$, but were reduced *in situ* to the labelled alcohols and analysed as such.[16]

We then turned our attention to a study of the chemistry of the parent (*Z*)-cyclo-oct-4-enyl radical in the presence of radical traps other than oxygen with a view to the eventual clarification of the effect of substituents on the cyclization of substituted cyclo-oct-4-enyl radicals (*vide infra*).



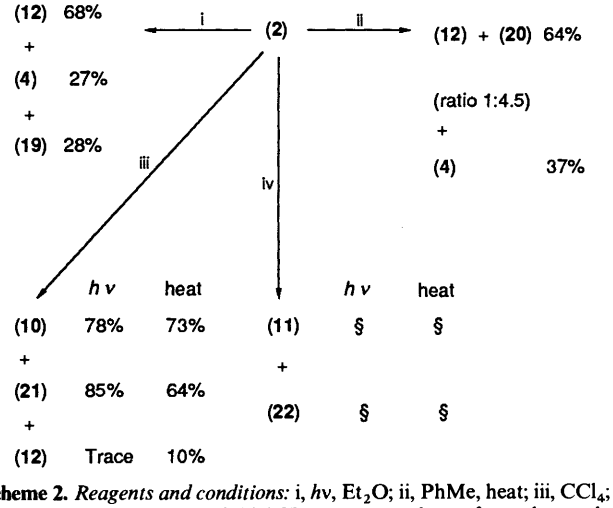
Scheme 1.

The reaction of a compound A–B with (*Z,Z*)-cyclo-octa-1,5-diene (**14**) under radical conditions typically leads either to a simple addition product (**16**) (Scheme 1, path i) or to a product resulting from transannular cyclization of the intermediate radical (**15**) to the radical (**17**) followed by chain transfer to give (**18**) (Scheme 1, path ii). When path ii is followed it is usually assumed, in accordance with the significant difference in strain between *cis*- and *trans*-bicyclo[3.3.0]octanes,[17] that the *cis*-fused system is formed and that quenching of the transannularly cyclized radical (**17**) takes place from the *exo*-face as is known to be the case[18] with similarly constituted radicals.

The product distribution thus depends upon the relative rates of chain transfer and transannular cyclization of the substituted cyclo-oct-4-enyl radical (**15**). One group of reagents (A–B, Scheme 1), comprising thiols,[19] *O*-thioacids,[19] trimethylstannane[20] and hydrogen bromide,[21] is capable of rapidly quenching alkyl radicals by hydrogen atom transfer and leads to substituted cyclo-octenes (**16**; B = H). Similarly, reaction of (**14**) with dinitrogen trioxide[22] and iodobenzene dichloride[23] is reported to provide an excellent yield of (*Z*)-1-nitroso-2-nitrocyclo-oct-5-ene and (*Z*)-1,2-dichlorocyclo-oct-5-ene, respectively. Here, too, rapid chain transfer may be invoked to explain the lack of transannular cyclization. The second group of reagents, made up of acetic anhydride,[24] tetrachloromethane,[25] trichloromethane,[25] *N*-t-butylformamide,[25] and diethylphosphinic acid,[25] quenches radicals less rapidly and so leads to the bicyclo-octane products (**18**). More recently, the reaction of arenesulphonyl halides with (**14**) is reported to follow either path i or path ii (Scheme 1) depending on the nature of the halide and the reaction conditions.[26]

Closer inspection reveals factors additional to the rate of radical quenching. All of those radicals (**15**) that follow path i (Scheme 1) are seen to be subject to rapid reversibility to cyclo-octadiene (**14**) and, in the most part, to be subject to stabilisation by a β-heteroatom and so to be less prone to cyclization.[27,28] More recently, various annelated cyclo-oct-4-enyl radicals have been shown to rearrange to linear tri- and tetra-quinanes in the presence of the efficient hydrogen atom donor tributylstannane.[29] When compared to the addition of trimethylstannane to (**14**), this further indicates that rates of chain transfer with A–B cannot be the only factor involved in determining product distributions. Finally, rationalisation of the diverse results described above is further complicated by the wide range of conditions employed by the various authors. Clearly an investigation into the behaviour of the parent, unsubstituted (*Z*)-cyclo-oct-4-enyl radical in the presence of a range of traps would be valuable.

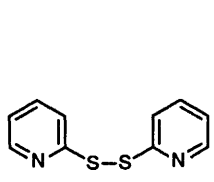
Thus the *O*-acyl thiohydroxamate (**2**) was allowed to react with itself (Scheme 2, paths i and ii), with tetrachloromethane* (Scheme 2 path iii), and with 3-ethylpentane-3-thiol (Scheme 2 path iv) under both photochemical and thermal conditions.

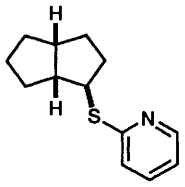


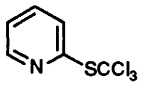
Scheme 2. *Reagents and conditions:* i, *hν*, Et_2O; ii, PhMe, heat; iii, CCl_4; iv, Et_3CSH, C_6D_6. § Bicyclo[3.3.0]octane was absent from the crude product mixture as shown by ^{13}C NMR spectroscopy.

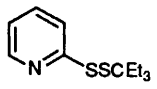
In all reactions but one, namely the thermal decarboxylative rearrangement of compound (**2**) in toluene at reflux, the only cyclo-octene-derived products observed were those resulting

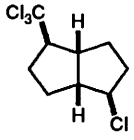
* The formation of sulphide (**12**) as a by-product in tetrachloromethane at reflux can probably be attributed to a residual cage mechanism.[30]


(19)


(20)


(21)


(22)

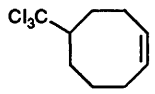

(23)

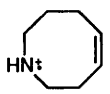
from trapping of the unrearranged cyclo-oct-4-enyl radical. Of particular note is the contrast between the reaction of (**14**) with tetrachloromethane leading to the bicyclo-octane (**23**)[25] and the thermal reaction of (**2**) with tetrachloromethane under broadly similar conditions. Clearly the trichloromethyl substituent in radical (**24**) significantly enhances the rate of transannular cyclization. Both semiempirical molecular orbital and force-field calculations suggest that (*Z*)-cyclo-octene is a highly conformationally mobile species with only a minimal preference for a conformation intermediate between the chair and boat forms.[31] Presumably the picture for the (*Z*)-cyclo-oct-4-enyl radicals bears some resemblance to that for (*Z*)-cyclo-octene itself and the effect of the trichloromethyl and other substituents is to bias the radical towards a conformation from which cyclization occurs readily.

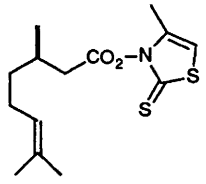
Comparison of the above results, particularly the formation of (**12**) from (**2**) under photolytic conditions, with the observation[32] that the *O*-acyl thiohydroxamate (**25**) leads exclusively to the cyclopentylmethyl sulphide (**26**) on photolysis in diethyl ether at room temperature indicates that the rearrangement of the (*Z*)-cyclo-oct-4-enyl radical into the bicyclo[3.3.0]octan-2-yl radical is significantly slower than the 5-*exo-trig* cyclization of a hept-5-enyl radical[28,33] under similar conditions. Other authors have previously reported the relatively inefficient transannular cyclization of the parent (*Z*)-cyclo-oct-4-enyl radical,[34] but the mechanisms of both generation and quenching of the radical from the cyclo-octenyl halides and pseudohalides employed have been questioned.[35]

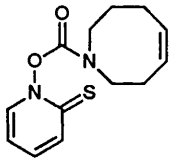
We conclude that the rate of transannular cyclization of the parent (*Z*)-cyclo-oct-4-enyl radical is relatively slow but that it can be significantly accelerated by the addition of *appropriate* ring substituents, an effect which is analogous to that found[28,33] for the 5-hexenyl-cyclopentylmethyl system. However, (*Z*)-cyclo-oct-4-enyl radicals that bear certain heteroatoms β to the radical centre do not readily rearrange, presumably due to β-stabilisation. We also note here the recent report[36] from the Newcomb laboratory in which it is recorded that the *electrophilic* aminium radical cation (**28**), generated under acidic conditions on photolysis of the *O*-acyl thiohydroxamate (**29**) at room temperature, cyclized smoothly giving a high yield of (**30**) after chain transfer.

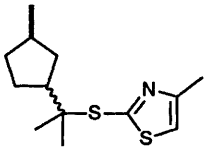
Finally, in our initial communication,[3] we suggested, on the basis of examination of Dreiding models, that the (*E*)-cyclo-oct-4-enyl radical might undergo transannular cyclization somewhat more readily than its (*Z*)-isomer. Perusal of the

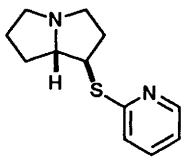

(24)


(28)


(25)


(29)


(26)


(30)


(27)

literature reveals that both calculation[31] and experiment[37] indicate a rigid twist conformation (**27**) for the closely related (*E*)-cyclo-octene which if adopted by the radical would be highly suited to transannular cyclization according to the Beckwith model[33] for 5-*exo-trig*-type cyclizations. This hypothesis has yet to be tested.

Experimental

General.—Unless otherwise indicated NMR spectra were recorded in deuteriochloroform with either a JEOL PMX 60, Varian XL 200, or Varian VXR 400 instrument. Chemical shifts (δ) are in ppm downfield from tetramethylsilane as internal standard. IR spectra were recorded with a Perkin–Elmer 983 spectrophotometer and mass spectra with a VG 7070 F/H mass spectrometer. Solvents were dried and distilled according to standard procedures. Ether refers to diethyl ether.

(*Z*)-[$^{18}O_2$]-*Cyclo-oct-4-enyl Hydroperoxide* (**8**).—*O*-Acyl thiohydroxamate (**2**)[2] (0.72 g, 3.23 mmol) and 3-ethylpentane-3-thiol (0.47 g, 3.5 mmol) were dissolved in anhydrous ether (75 cm^3) in a 125 cm^3 round bottomed flask containing a Teflon coated magnetic stirrer bar. The outside of the flask was then coated with aluminium foil to minimize the risk of light initiated reductive decarboxylation of (**2**).[9,11] This flask was then cooled to −196 °C in a liquid nitrogen bath and evacuated to 10^{-3} mmHg. $^{18}O_2$ (*ca.* 50 cm^3) was then condensed into the reaction vessel. The reaction vessel, closed to the atmosphere, was then allowed to warm to room temperature. The protective aluminium foil was removed and the vessel was placed in a water-bath at room temperature. The reaction mixture was then subjected to vigorous magnetic stirring and irradiated with a 400 W sodium lamp until colourless. The ether was then removed at room temperature under reduced pressure (*ca.* 15 mmHg) and the resultant crude reaction mixture taken up in pentane (10 cm^3). This solution

was extracted into ice-cold aqueous sodium hydroxide (4M, 5 × 10 cm^3) and the combined alkaline phases washed with pentane (10 cm^3). After cooling to −10 °C the alkaline extracts were acidified with hydrochloric acid and re-extracted with dichloromethane (2 × 25 cm^3). The extracts were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give the crude [$^{18}O_2$]hydroperoxide (**8**) (0.19 g). Examination by ^{13}C NMR revealed the presence of the corresponding alcohol. Chromatography on neutral alumina [eluant diethyl ether–light petroleum (b.p. 60–80 °C) (1:1)] gave an enriched sample of the *title compound* (**8**) (35 mg, 7.5%) with δ_C(100 MHz) 129.85, 129.76, 86.79, 31.78, 31.62, 25.69, 25.30, and 22.26; *m/z* 146 ($M^{+\cdot}$, 0.05%), 127 ($M^{+\cdot}$ − ^{18}OH, 4.36%), 118 ($M^{+\cdot}$ − C_2H_4, 12.31%), and 109 ($M^{+\cdot}$ − $^{18}O_2H$, 20.34%).

Photolysis of O-*Acyl Thiohydroxamate* (**2**) *in Deuteriobenzene with* 3-*Ethylpentane*-3-*thiol.*—3-Ethylpentane-3-thiol (30 mg, 0.2 mmol) and compound (**2**) (53 mg, 0.2 mmol) were dissolved in deuteriobenzene (0.5 cm^3), stirred under a nitrogen atmosphere in a water bath at ambient temperature, and irradiated with a 500 W tungsten filament lamp. On complete decolourisation (*ca.* 10 min), ^{13}C NMR spectroscopy (50 MHz, C_6D_6) of the mixture revealed the presence of (*Z*)-cyclo-octene (**11**), δ 130.37, 29.60, 26.53, and 25.86 in agreement with literature data,[38] and the mixed disulphide (**22**), δ 161.52, 149.29, 136.44, 120.80, 120.47, 60.60, 27.86, and 8.44. Significantly, no evidence was found for the presence of bicyclo[3.3.0]octane.

Thermolysis of (**2**) *and* 3-*Ethylpentane*-3-*thiol in Deuteriobenzene.*—3-Ethylpentane-3-thiol (30 mg, 0.2 mmol) and compound (**2**) (53 mg, 0.2 mmol) were heated to reflux, under nitrogen, in a light-shielded flask, in deuteriobenzene (0.5 cm^3) for 1 h. After the reaction mixture had cooled to room temperature, ^{13}C NMR spectroscopy revealed the presence of (*Z*)-cyclo-octene (**11**) and disulphide (**22**), but not of bicyclo[3.3.0]octane, as described above for the photolytic conditions.

Photolytic Decarboxylative Rearrangement of (**2**); *Cyclo-oct*-4-*enyl* 2′-*Pyridyl Sulphide* (**12**).—A solution of compound (**2**) (260 mg, 1 mmol) in dry ether (25 cm^3) was irradiated in a water bath at room temperature and under a nitrogen atmosphere with a 500 W tungsten filament lamp. On completion (decolourisation), the solvent was removed under reduced pressure to give the crude reaction mixture which was subjected to chromatography on silica gel (eluant dichloromethane) to give a mixture of meso- and (±)-(*Z*,*Z*)-5-(*cyclo-oct*-4-*enyl*)*cyclo-octene* (**4**) (30 mg, 27%) with δ_H(60 MHz) 5.4—5.7 (4 H, m, CH=CH) and 1.0–2.7 (22 H, br m); δ_C(50 MHz) 130.43, 130.36, 129.84, 129.44, 44.81, 44.74, 32.98, 31.72, 30.73, 29.90, 28.81, 28.79, 25.94, 25.76, 25.38, and 25.27; *m/z* 218.2038 ($M^{+\cdot}$, $C_{16}H_{26}$ requires 218.2034), 190 ($M^{+\cdot}$ − C_2H_4), and 109 ($M^{+\cdot}$ − C_8H_{13}). Further elution gave *cyclo-oct-4-enyl* 2′-*pyridyl sulphide* (**12**) (150 mg, 68%) as a colourless oil with δ_H(200 MHz) 8.2–8.4 (1 H, dd, *J* 5 and <1 Hz, 6-H), 7.45 (1 H, m, 4-H), 7.15 (1 H, d, *J* 9 Hz, 3-H), 6.94 (1 H, m, 5-H), 5.5–5.8 (2 H, m, CH=CH), 3.6–4.1 (1 H, m, 1-H), and 1.4–2.6 (10 H, br m); δ_C(50 MHz) 159.66, 149.50, 135.75, 130.24, 129.64, 122.37, 119.16, 43.28, 34.92, 34.10, 22.77, 25.59, and 24.88; *m/z* 219.1078 ($M^{+\cdot}$, $C_{13}H_{17}NS$ requires 219.1081), 111 ($C_5H_5NS^+$), and 108 ($C_8H_{12}^+$) (Found: C, 71.2; H, 7.7; N, 6.35. $C_{13}H_{17}NS$ requires: C, 71.19; H, 7.81; N, 6.36%). Finally 2,2′-dipyridyl disulphide (**19**) (30 mg, 28%), identical with an authentic sample,[9] was eluted.

Decarboxylative Rearrangement of (**2**) *in Toluene at Reflux; Bicyclo*[3.3.0]*octan*-2-*yl* 2′-*Pyridyl Sulphide.* (**20**).—Solid *O*-acyl thiohydroxamate (**2**) (260 mg, 1 mmol) was added in one portion to toluene (25 cm^3) at reflux under nitrogen. After 2 h at reflux, removal of the solvent and chromatography of the crude reaction mixture on silica gel (eluant, dichloromethane) gave the dimer (**4**) (40 mg, 37%) followed by an inseparable mixture of (**12**) and (**20**) (140 mg, 64%) in the approximate ratio of 1:4.5. Preparative HPLC [5 μ silica gel; eluant, ether–light petroleum (b.p. 60–80 °C) (6:94)] was used to isolate a pure sample of the *title compound* (**20**) which was a colourless oil with δ_H(200 MHz) 8.36–8.46 (1 H, dd, *J* 5 and <1 Hz), 7.36 (1 H, m), 7.1–7.2 (1 H, d, *J* 8 Hz), 6.9–7.0 (1 H, m), 3.56–3.75 (1 H, q, *J* 7 Hz, 2-H), and 1.0–2.75 (12 H, br m); δ_C(50 MHz): 160.40, 149.44, 135.72, 122.37, 119.03, 50.27, 50.00, 42.60, 34.40, 33.86, 32.87 (2 C), and 25.96; *m/z*: 219.1073 ($M^{+\cdot}$, $C_{13}H_{17}NS$ requires 219.1081), 186 ($M^{+\cdot}$ − SH), 143, and 111.

Photolysis of (**2**) *in Tetrachloromethane;* 5-*Chlorocyclo-octene.* (**10**).—A solution of (**2**) (394 mg, 1.5 mmol) in tetrachloromethane (35 cm^3) was photolysed under a nitrogen atmosphere at room temperature in a water bath with a 500 W tungsten filament lamp. After completion (decolourisation, *ca.* 30 min), the solution was concentrated under reduced pressure and shown by ^1H and ^{13}C NMR spectroscopy to consist of (**10**) and the sulphide (**21**). Separation was achieved by chromatography on silica gel [eluant, ethyl acetate–light petroleum (b.p. 60–80 °C) (1:20)] giving 5-chlorocyclo-octene (**10**) (170 mg, 78%) as a colourless oil with δ_H(200 MHz) 5.6–5.7 (2 H, m, CH=CH), 4.05–4.15 (1 H, m, 5-H), and 1.5–2.5 (10 H, br m); δ_C(50 MHz) 129.56, 129.32, 62.49, 38.77, 36.63, 23.31, and 24.12; *m/z* 144.0712 ($M^{+\cdot}$, $C_8H_{13}Cl$ requires 144.0706), 146 ($M^{+\cdot}$ + 2), 116 ($M^{+\cdot}$ − C_2H_4), and 109 ($M^{+\cdot}$ − Cl), and 2-pyridyl trichloromethyl sulphide (**21**) (290 mg, 85%) as a colourless oil[9] with δ_H(200 MHz) 7.44 (1 H, dt, *J* 8 and 4 Hz), 7.85 (2 H, m), and 8.7 (1 H, m); δ_C(50 MHz) 153.25, 150.64, 137.59, 130.17, 124.69, and 96.70.

Thermolysis of (**2**) *in Tetrachloromethane at Reflux.*—Solid (**2**) (390 mg, 1.5 mmol) was added in one portion to tetrachloromethane (35 cm^3) at reflux under a nitrogen atmosphere. The reaction mixture was then maintained at reflux for 2 h before the solvent was removed under reduced pressure and the residue examined by ^1H and ^{13}C NMR spectroscopy for the presence (negative) of bicyclo[3.3.0]octane-derived products. Chromatography of the reaction mixture on silica gel (eluant, dichloromethane) gave 5-chlorocyclo-octene (**10**) (160 mg, 73%), followed by the sulphide (**12**) (30 mg, 10%) and finally the sulphide (**21**) (190 mg, 64%) each of which had identical spectral characteristics to the samples isolated above.

Acknowledgements

We thank the SERC for the award of an Earmarked Studentship.

References

1 A. J. Bloodworth, J. L. Courtneidge, and H. J. Eggelte, *J. Chem. Soc., Chem. Commun.*, 1983, 1267; A. J. Bloodworth, T. Melvin, and J. C. Mitchell, *J. Org. Chem.*, 1986, **51**, 2612; S. P. Best, A. J. Bloodworth, and M. D. Spencer, *J. Chem. Soc., Chem. Commun.*, 1990, 416.

2 A. J. Bloodworth, T. Melvin, and J. C. Mitchell, *J. Org. Chem.*, 1988, **53**, 1078; and in 'The Role of Oxygen in Chemistry and Biochemistry,' eds. W. Ando and Y. Moro-oka, Elsevier, Amsterdam, 1988, p. 45.

3 For a preliminary communication see A. J. Bloodworth, D. Crich, and T. Melvin, *J. Chem. Soc., Chem. Commun.*, 1987, 786.

4 H. R. Williams and H. S. Mosher, *J. Am. Chem. Soc.*, 1954, **76**, 2987.

5 C-I. Chern, R. DiCosimo, R. De Jesus, and J. San Filippo, *J. Am. Chem. Soc.*, 1978, **100**, 7317; R. A. Johnson, E. G. Nidy, and M. V. Merritt, *ibid.*, 1978, **100**, 7960.

6 D. Crich, H. Dyker, and R. J. Harris, *J. Org. Chem.*, 1989, **54**, 257.
7 L. Caglioti, F. Gasparrini, D. Misiti, and G. Palmieri, *Tetrahedron*, 1978, **34**, 135.
8 H. C. Brown and M. M. Midland, *J. Am. Chem. Soc.*, 1971, **93**, 4078; A. J. Bloodworth and H. J. Eggelte, *J. Chem. Soc., Perkin Trans. 1*, 1981, 3272.
9 D. H. R. Barton, D. Crich, and W. B. Motherwell, *J. Chem. Soc., Chem. Commun.*, 1984, 242; *Tetrahedron*, 1985, **41**, 3901.
10 A. J. Bloodworth, J. L. Courtneidge, R. J. Curtis, and M. D. Spencer, *J. Chem. Soc., Perkin Trans. 1*, in the press (0/01904F).
11 For a review of this area see D. Crich and L. Quintero, *Chem. Rev.*, 1989, **89**, 1413.
12 G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, 1956, **78**, 5129.
13 F. MacCorquodale and J. C. Walton, *J. Chem. Soc., Perkin Trans. 1*, 1989, 347.
14 K. Zeigler and H. Wilms, *Justus Liebigs Ann. Chem.*, 1950, **567**, 43.
15 D. H. R. Barton and D. Crich, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1603; H. Reinheckel and D. Jahnke, *Chem. Ber.*, 1966, **99**, 23.
16 A. L. J. Beckwith, A. G. Davies, I. G. E. Davison, A. Maccoll, and M. N. Mruzek, *J. Chem. Soc., Chem. Commun.*, 1988, 475.
17 L. A. Paquette, *Topics in Curr. Chem.*, 1979, **79**, 43; *ibid.*, 1984, **119**, 1 and references therein.
18 G. Stork and M. Kahn, *J. Am. Chem. Soc.*, 1985, **107**, 500; G. Stork and P. M. Sher, *ibid.*, 1986, **108**, 303; B. Giese, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 969; D. Crich and W. B. Motherwell, 'Best Synthetic Methods: Free Radical Chain Reactions in Organic Synthesis,' Academic Press, London, 1991.
19 J. M. Locke and E. N. Duck, *J. Chem. Soc., Chem. Commun.*, 1965, 151.
20 R. H. Fish, H. G. Kuivila, and I. J. Tyminski, *J. Am. Chem. Soc.*, 1967, **89**, 5861.
21 L. Gale, *J. Org. Chem.*, 1968, **33**, 3643.
22 D. Klamann, W. Koser, P. Weyerstahl, and M. Fligge, *Chem. Ber.*, 1965, **98**, 1831.
23 M. C. Lasne and A. Thullier, *Compt. Rend. Acad. Sci., Ser. C*, 1971, **273**, 1258.
24 G. Pregaglia and G. Gregorio, *Chim. Ind.*, 1963 **45**, 1065, (*CA*, 1963, **59**, 12658h).
25 R. Dowbenko, *J. Am. Chem. Soc.*, 1964, **86**, 946; *Tetrahedron*, 1964, **20**, 1844; L. Friedman, *J. Am. Chem. Soc.*, 1964. **86**, 1885.
26 I. De Riggi, J-M. Surzur, and M. P. Bertrand, *Tetrahedron*, 1988, **44**, 7119.
27 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1971, **93**, 846.
28 A. L. J. Beckwith and K. U. Ingold in 'Rearrangements in Ground and Excited States,' ed. P. de Mayo, Academic Press, New York, 1980, vol. 1, p. 161.
29 J. D. Winkler and V. Sridar, *J. Am. Chem. Soc.*, 1986, **108**, 1708; L. A. Paquette, J. A. Colapret, and D. R. Andrews, *J. Org. Chem.*, 1985, **50**, 201; J. D. Winkler and V. Sridar, *Tetrahedron Lett.*, 1988, **29**, 6219.
30 D. H. R. Barton, D. Crich, and P. Potier, *Tetrahedron Lett.*, 1985, **26**, 5943.
31 N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, 1972, **94**, 5734; O. Ermer and S. Lifson, *ibid.*, 1973, **94**, 4121; G. Favini, C. Rubino, and R. Todeschini, *J. Mol. Struct.*, 1977, **41**, 305; F. A. L. Anet and I. Yavari, *Tetrahedron*, 1978, **34**, 2879.
32 D. H. R. Barton, D. Crich, and G. Kretzschmar, *J. Chem. Soc., Perkin Trans. 1*, 1986, 39; for the use of the reaction of *O*-acyl thiohydroxamates as radical clocks see M. Newcomb and J. Kaplan, *Tetrahedron Lett.*, 1987, **28**, 1615; M. Newcomb and S. U. Park, *J. Am. Chem. Soc.*, 1986, **108**, 4132; M. Newcomb and J. Kaplan, *Tetrahedron Lett.*, 1988, **29**, 3449; J. Lusztyk, B. Maillard, S. Deycard, D. A. Lindsay, and K. U. Ingold, *J. Org. Chem.*, 1987, **52**, 3509.
33 A. L. J. Beckwith and C. H. Schiesser, *Tetrahedron*, 1985, **41**, 3925; D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 317 and references therein.
34 E. C. Ashby, B. Wenderoth, and T. N. Pham, *J. Org. Chem.*, 1984, **49**, 4505; *ibid.*, 1986, **51**, 3598; E. C. Ashby and D. Coleman, *ibid.*, 1987, **52**, 4554; see also G. H. Posner and J. S. Ting, *Tetrahedron Lett.*, 1974, 683.
35 M. Newcomb and D. P. Curran, *Acc. Chem. Res.*, 1988, **21**, 206; E. C. Ashby, *ibid.*, 1988, **21**, 414.
36 M. Newcomb, D. J. Marquardt, and T. M. Deeb, *Tetrahedron*, 1990, **46**, 2329.
37 M. Traetteberg, *Acta Chem. Scand., Ser. B*, 1975, **29**, 29.
38 D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, 1971, **36**, 2757.

Paper 0/02172E
Received 16*th May* 1990
Accepted 12*th June* 1990