Photorearrangement of 2-cyanobicyclo[2.2.1]hept-2-ene. Observation of 1,2- and 1,3-sigmatropic shifts

IKBAL A. AKHTAR, JOHN J. MCCULLOUGH,¹ AND SUSAN VAITEKUNAS Department of Chemistry, McMaster University, Hamilton, Ont., Canada L8S 4M1

AND

ROMOLO FAGGIANI AND COLIN J. L. LOCK

Department of Chemistry and Institute for Materials Research, McMaster University, Hamilton, Ont., Canada L8S 4M1 Received September 29, 1981

IKBAL A. AKHTAR, JOHN J. MCCULLOUGH, SUSAN VAITEKUNAS, ROMOLO FAGGIANI, and COLIN J. L. LOCK. Can. J. Chem. 60, 1657 (1982).

Irradiation of 2-cyanobicyclo[2.2.1]hept-2-ene (2-cyanonorbornene, 4) in hexane, with the full arc of a mercury vapour lamp, gives the rearrangement products 1-cyanobicyclo[4.1.0]hept-2-ene 5 and 7-cyanotricyclo[4.1.0.0^{3.7}]heptane 6 in the ratio 20:1. These products were separated by preparative vpc. The structure of the major product 5 was determined by single crystal X-ray analysis. Reduction of 5 with lithium aluminum hydride gave the corresponding primary amine, which was converted to the *p*-bromobenzenesulfonamide 9, mp 150–151°C, which gave single crystals from ethanol-water. The crystal and molecular structures are described. The minor product 6 was hydrogenated to give 7-cyanobicyclo[2.2.1]heptane. Formation of 5 and 6 may involve concerted $\sigma_{2s} + \pi_{2s}$ and $\sigma_{2a} + \pi_{2a}$ processes respectively, which are photochemically allowed.

IKBAL A. AKHTAR, JOHN J. MCCULLOUGH, SUSAN VAITEKUNAS, ROMOLO FAGGIANI et COLIN J. L. LOCK. Can. J. Chem. 60, 1657 (1982).

L'irradiation du cyano-2 bicyclo[2.2.1] heptène-2 (cyano-2 norbornène, 4) dans l'hexane avec l'arc complet d'une lampe à vapeur de mercure conduit aux produits de transposition suivants: cyano-1 bicyclo[4.1.0] heptène-2 (5) et cyano-7 tricyclo [4.1.0.0^{3,7}] heptane (6) dans un rapport de 20:1. On a isolé ces produits par cpg préparative. On a déterminé la structure du produit majoritaire 5 par analyse aux rayons-X d'un mono-cristal. La réduction du composé *1* par l'alanate de lithium conduit à l'amine primaire correspondante. On transforme cette dernière en *p*-bromobenzènesulfonamide (9), pf 150–151°C, qui donne des monocristaux dans l'éthanol–eau. On décrit la structure du cristal et la structure moléculaire. Le produit secondaire 6, par hydrogénation, conduit a u cyano-7 bicyclo [2.2.1] heptane. La formation des composés 5 et 6 peut impliquer respectivement des processus concertés $\alpha_{2s} + \pi_{2s}$ et $\sigma_{2a} + \pi_{2a}$ qui sont permis photochimiquement.

[Traduit par le journal]

Introduction

We have described (1) the rearrangement of 1-cyanocyclohexene 1, which on direct irradiation in hexane gives the bicyclohexane derivatives 2 and 3. Formation of these products must involve rearrangement of the σ -bonded group, and although these kinds of rearrangements are known in the photochemistry of neutral molecules, they are not numerous (some examples are enone "type A" rearrangements (2*a*), methyl migration (2*b*), and Wagner-Meerwein shifts (2*c*)). To determine the generality of the above rearrangement, and to study the effect of structure on the reaction, we have investigated the photochemistry of 2-cyanobicyclo[2.2.1]hept-2-ene 4. This bicyclic nitrile also rearranges on irradiation, and the structure



¹Author to whom correspondence may be addressed.

work on the products is described. The bicyclic system might be used later for labelling experiments to determine reaction stereochemistry.

Results

The required nitrile 4 was prepared by reaction of 2-chloronorbornene with cuprous cyanide in N-methylpyrrolidinone (1). The 2-chloronorbornene was prepared via 2,2-dichloronorborane, which was obtained by reaction of norcamphor with phosphorus pentachloride. Details are given in the experimental section.

Irradiation of 2-cyanonorbornene 4 in hexane with unfiltered light from a Hanovia 450 W lamp gave two products, identified as 1-cyanobicy-clo[4.1.0]hept-2-ene, 5, and 7-cyanotricyclo- $[4.1.0.0^{3.7}]$ heptane, 6, in the ratio 20:1. The reaction is shown in Scheme 1.

The products were separated by preparative vpc and the gross structural features determined from their spectra. Product 5 had ir: 2240 cm^{-1} (CN stretch); ¹H nmr, δ : 6.02 (1h, doublet, J = 10.0 Hz, vinylic), 5.66 (1H, multiplet, vinylic), 1.1–2.1 (7H,

©1982 National Research Council of Canada/Conseil national de recherches du Canada

^{0008-4042/82/131657-07\$01.00/0}

Can. J. Chem. Downloaded from www.nrcresearchpress.com by GRAND VALLEY STATE UNIVERSITY on 11/14/13 For personal use only.



envelope of aliphatic protons); mass spectrum, m/e: 119 (M⁺, C₈H₉N).

Although $J_{vinyl-vinyl}$ of 10.0 Hz is in the range for a cyclohexene derivative (3), we attempted to distinguish between structure 5 and the isomer 7 by synthesizing the latter (4).² None of the synthetic approaches proved successful, and X-ray crystal structure analysis was used. Reduction of 5 with LiAlH₄ gave the amine 8, which readily formed a *p*-bromobenzenesulphonyl chloride in pyridine (Scheme 1). This gave crystals suitable for X-ray work, which is described below and in the experimental section. The structure 9 is shown ³ in Fig. 1.

The minor product 6 had the following spectral data: infrared, bands at 2215 cm⁻¹ (CN) and 3050 cm⁻¹ (cyclopropyl CH); ¹H nmr, envelope from δ : 1.0–3.0; mass spectrum, m/e: 119 (M⁺). Catalytic hydrogenation gave 7-cyanobicyclo[2.2.1]heptane 10, and structure 7-cyanotricyclo[4.1.0.0^{3.7}] heptane is assigned (Scheme 1).

Description of crystal and molecular structure

The molecule is illustrated in Fig. 1 and selected bond lengths and angles are given in Table 1. There is excellent agreement between the bond lengths in



FIG. 1. The molecule bicyclo[4.1.0]hept-2-en-1-ylmethanamine p-bromobenzenesulphonamide (9), showing the atomnumbering. Hydrogen atoms have been omitted for simplicity.

the cyclohexene moiety and values found previously (5-8). Internal angles at the olefin agree well with previous values, but angles adjacent to the cyclopropane ring $(C(2)-C(1)-C(6), 115.2(6)^{\circ}, C(1)-C(6), 115.2(6)^{\circ})$ C(6)—C(5), 117.1(8)°) and possibly (C(4)—C(5)— C(6) 114.3(9)°) are larger than normal values of 111°. Presumably this increase is caused by steric requirements of the cyclopropane ring. Further distortions are observed by comparing distances of atoms from the C(1)C(2)C(3)C(4) plane or torsional angles within the cyclohexene ring with previous results (6, 8). Thus C(5) is 0.768(9) Å out of the plane compared with 0.340(7) Å for C(6), both in the same direction, whereas a value of ~ 0.38 Å on opposite sides of the plane is more normal (5, 7). Alternately the torsional angles differ significantly

²While this work was in progress, structure 7 (*cis*-fused) was described (4). The vinyl-vinyl coupling is 5.6 Hz.

³The three-membered ring can be seen more clearly in Fig. 2.

AKHTAR ET AL.

TABLE 1. Selected interatomic distances (Å) and angles (deg)

Bond	Length	Bond	Length	Bond	Length
C(1) - C(2) $C(4) - C(5)$ $C(1) - C(7)$ $C(8) - N$ $S - O(2)$ $C(12) - C(13)$ $C(15) - C(16)$	$\begin{array}{c} 1.50(1) \\ 1.53(1) \\ 1.51(1) \\ 1.48(1) \\ 1.438(6) \\ 1.37(1) \\ 1.40(1) \end{array}$	C(2)-C(3) C(5)-C(6) C(6)-C(7) N-S S-C(11) C(13)-C(14) C(16)-C(11)	1.33(2) 1.52(2) 1.48(1) 1.606(1) 1.741(8) 1.36(1) 1.37(1)	C(3) - C(4) C(6) - C(1) C(1) - C(8) S - O(1) C(11) - C(12) C(14) - C(15) C(14) - Br	1.51(2) 1.52(1) 1.47(1) 1.423(6) 1.39(1) 1.36(1) 1.895(9)
Bonds	Angle	Bonds	Angle	Bonds	Angle
C(6) - C(1) - C(2) $C(3) - C(4) - C(5)$ $C(7) - C(1) - C(6)$ $C(2) - C(1) - C(8)$ $C(6) - C(1) - C(8)$ $V - S - O(1)$ $C(1) - S - O(2)$ $S - C(11) - C(12)$ $C(11) - C(12) - C(13)$ $C(14) - C(15) - C(16)$ $C(15) - C(14) - Br$	115.2(6) 111.7(9) 58.5(6) 116.9(7) 119.6(6) 108.5(3) 119.4(3) 119.5(6) 121.2(9) 118.6(9) 118.9(4)	C(1) - C(2) - C(3) $C(4) - C(5) - C(6)$ $C(1) - C(6) - C(7)$ $C(7) - C(1) - C(8)$ $C(1) - C(8) - N$ $N - S - O(2)$ $O(1) - S - C(11)$ $S - C(11) - C(16)$ $C(12) - C(13) - C(14)$ $C(15) - C(16) - C(11)$	124.0(9) $114.3(9)$ $60.6(6)$ $118.4(8)$ $109.6(7)$ $105.4(4)$ $107.4(4)$ $121.5(6)$ $118.4(9)$ $120.2(8)$	$\begin{array}{c} C(2) - C(3) - C(4) \\ C(5) - C(6) - C(1) \\ C(6) - C(7) - C(1) \\ C(7) - C(1) - C(2) \\ C(8) - N - S \\ N - S - C(11) \\ O(2) - S - C(11) \\ O(2) - S - C(11) \\ C(16) - C(11) - C(12) \\ C(13) - C(14) - C(15) \\ C(13) - C(14) - Br \end{array}$	$122(1) \\117.1(8) \\60.9(6) \\115.5(6) \\119.5(3) \\108.4(3) \\107.3(3) \\119.0(8) \\122.6(8) \\118.4(3)$

TABLE 2. Best planes, and dihedral and torsional angles (deg)

Plane			Distance of atoms from the plane (Å)			
1. C(1)C(2)C(3)C(4)			$\begin{array}{c} \hline C(1) & -0.001(7); C(2) & 0.004(9); C(3) & -0.005(9); \\ C(4) & 0.002(9); C(5) & 0.768(9); C(6) & 0.340(7); \\ C(7) & -1.065(9); C(8) & 0.382(7). \end{array}$			
2. C(1)C(6)C(7)					
3. C(11)C(12)C(13)C(14)C(15)C(16)			$\begin{array}{ccc} C(11) & -0.009(7); \ C(12) & 0.010(9); \ C(13) \ 0.004(9); \\ C(14) & -0.010(8); \ C(15) & 0.008(9); \ C(16) \ 0.004(8); \\ S & 0.020(2); \ Br & -0.020(1). \end{array}$			
Dihedral angles	(deg)					
Plant 1 – Plane	2 81.2(9)	Plane 1 – Plane 3	30.0(9) Plan	e 2 – Plane 3 74.5(9)		
Torsional angles (deg)						
C(1)C(2)C(3)C(C(4)C(5)C(6)C(C(3)C(2)C(1)C(C(5)C(6)C(1)C(C(7)C(1)C(8)N C(8)NSO(2) O(1)SC(11)C(16) O(2)SC(11)C(12)		C(2)C(3)C(4)C(C(5)C(6)C(1)C(C(3)C(2)C(1)C(C(2)C(1)C(8)N C(8)NSC(11) NSC(11)C(12) O(1)SC(11)C(12)	$\begin{array}{ccccc} 5) & 31.2(9) \\ 2) & -5.4(8) \\ 7) & 50.3(7) \\ & 59.3(8) \\ & -63.5(6) \\ & -51.4(6) \\ 2) & -168.6(6) \end{array}$	C(3)C(4)C(5)C(6) C(6)C(1)C(2)C(3) C(5)C(6)C(1)C(7) C(6)C(1)C(8)N C(8)NSO(1) NSC(11)C(16) O(2)SC(11)C(16)	-48.7(9) -15.2(8) -111.0(9) -87.6(8) 52.9(6) 131.3(6) 61.9(6)	

from those in $\Delta^{1,11}$ -dicyclohexenyl ketone (6). The resulting form is a modified "boat" and corresponds neither to the C_2 "half-chair" form, observed in other structures (5–9) or the "1–2 diplanaire", calculated by Bucourt to be the next most stable form (10). Clearly the abnormal structure observed here arises from the interaction (one bond separation) of the constraints of the olefin and the cyclopropane ring, both of which will tend to make

Can. J. Chem. Downloaded from www.nrcresearchpress.com by GRAND VALLEY STATE UNIVERSITY on 11/14/13 For personal use only.

torsional angles about their C—C bonds as close to 0° as possible.

Bond lengths and angles within the *p*-bromosulfonamide portion of the molecule agree very well with those observed previously (11). The torsional angles (Table 2) show that the backbone of the molecule is arranged to minimize nonbonded interactions, except that between C(11)—H(16) and O(1) (O(1)SC(11)— $C(16) = 14.2^{\circ}$). Apparently the

CAN. J. CHEM. VOL. 60, 1982



FIG. 2. The packing of p-bromobenzenesulphonamide (9), within the unit cell; a and c^* are parallel to the bottom and sides of the page and the view is down b (hydrogen atoms omitted).

steric requirements of the $--NH_2$ group are more important in determining the orientation of the aromatic ring.

Bond lengths and angles in the cyclopropane unit are normal and the dihedral angle of $108.1(2)^{\circ}$ between C(1)C(6)C(7) and C(5)C(6)C(1)C(2) is similar to values observed previously by others (12) (Range 104.2° to 110.1°) and ourselves (105.7(2)°) (13).

The packing of the molecules is shown in Fig. 2. The overall shape of the molecule resembles a shallow V (see Fig. 1) and the molecules are arranged in layers centred on the 100 faces so that the apices of the V's lie roughly in the face. The V is symmetric about the face and the angle of the V is roughly parallel to the 001 face. Within these layers adjacent molecules related by the 2, axes at x = 0, z= 1/4, 3/4 are hydrogen bonded together through $N \cdots O(2)'$ (2.92(1) Å) to form a spiral chain parallel to b. Adjacent chains in the layer have the apices of the V's pointing in opposite directions along b and contact between the chains involves hydrocarbon fragments and van der Waals interactions. Between layers, in the a direction, contacts at x= 1/2 are hydrocarbon-hydrocarbon, brominebromine, and bromine-hydrocarbon.

Discussion

The tricyclic product **6** is the product of the 1,2-shift of a σ -bond, in the same fashion as reported previously (1). The tricyclo[4.1.0.0^{3,7}]-heptane ring system is well-known, and is formed in solvolysis reactions (14, 24), in photochemistry of unsaturated ketones (15), and in the photo-rearrangement of benzonorbornadiene (16). Note that 1,2-migration of either bond "b" or "c" (Scheme 2) would give product **6**, and labelling studies will be needed to distinguish which bond is involved.

Formation of the major product 5 involves 1,3migration of a σ -bond, and although this process is known in photochemical (17) and thermal reactions



Scheme 2

(18), it was not observed in the photochemistry of 1-cyanocyclohexene (1). Formation of 5 requires 1,3-migration of bond "b" (Scheme 2); in contrast, migration of bonds of the ethano-bridge ("c" or "a") would give the bicyclo[3.2.0]heptane system, e.g. 7 or 11 respectively.

Thus, formation of 6 and 5 involves competing 1,2- and 1,3-sigmatropic shifts. Both processes are



FIG. 3. Possible transition states for the photochemical symmetry allowed 1,2-(A) and 1,3-(B) sigmatropic shifts. A is $\sigma_{2a} + \pi_{2a}$ and B is $\sigma_{2s} + \pi_{2s}$.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by GRAND VALLEY STATE UNIVERSITY on 11/14/13 For personal use only.

symmetry allowed (19, 20) in the excited state ($\sigma_{2a} + \pi_{2a}$ and $\sigma_{2s} + \pi_{2s}$ respectively). The orbitals involved are shown in Fig. 3. We are not sure at present that the reaction is concerted, and plan further work on the mechanism, stereochemistry, and generality of the rearrangement.

Experimental

Materials

The norcamphor, chlorosulphonyl isocyanate, and other organic reagents were obtained from the Aldrich Chemical Company. Hexane for the photolysis was "Spectrograde", or was purified using fuming sulphuric acid (1). Tetrahydrofuran was distilled from LAH immediately before use. Pyridine was distilled and kept over KOH pellets. 2,2-Dichloronorbornane was prepared as described by Bixler and Niemann (21).

Instruments

Irradiations were carried out using a Hanovia 450 W lamp and a quartz water-cooled immersion well. The solution was purged with argon. Ultraviolet spectra were run on a Carey 14 spectrometer, infrared spectra on a Perkin–Elmer 283, and nmr spectra on a Varian EM-390 or a Bruker WH-90 spectrometer. Mass spectra were obtained with a VG Micromass 7601 instrument.

Gas chromatography was performed on a Varian Aerograph 202 instrument with thermal conductivity detectors (preparative) or on a Tracor 560 with flame ionization detectors (analytical). Carrier gas was helium, and columns used are given below. Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn., and Guelph Chemical Laboratories, Guelph, Ontario.

2-Chlorobicyclo[2.2.1]heptene

This compound was prepared from 2,2-dichlorobicyclo-[2.2.1]heptane (21) by dehydrochlorination using potassium *tert*-butoxide (22*b*). It has bp 29–30°/12 Torr, and infrared and ¹H nmr spectra in good agreement with the literature (22).

2-Cyanobicyclo[2.2.1]hept-2-ene

The above vinyl chloride (8.0g, 0.062 mol) and Cu₂(CN)₂ (11.1g, 0.062 mol) were heated under reflux in 50 mL of 1methyl-2-pyrrolidinone for 3h. After cooling the mixture was poured into 300 mL of water containing 12.9 g of NaCN. Benzene (300 mL) was added, and the mixture was filtered through Celite. The layers were separated, and the aqueous phase was extracted with $2 \times 50 \text{ mL}$ benzene. The benzene extracts were washed with 200 mL of 10% aqueous NaCN, $200\,mL$ of water, and dried (Na₂SO₄). The benzene was evaporated and the residue distilled to yield crude 2-cyanobicvclo[2.2.1]hept-2-ene, bp 67-69°C/12 Torr, 2.35 g (35%). The ir showed that 1-methyl-2-pyrrolidinone was present (band at 1700 cm⁻¹). The product was dissolved in 25 mL ether, and washed with 3 \times 50 mL water. After distillation, infrared showed the band at 1700 cm⁻¹ was absent; ir (neat): 2210, 1570 cm⁻¹; ¹H nmr (CC1₄), δ : 6.90 (1H, d, J = 4 Hz, vinylic proton), 3.0-3.2 (2H, m, bridgehead proton), 1.0-1.9 (6H, M, other ring protons). $J_{(vinyl-bridgehead)}$ of 4 Hz is reported (23). Anal. calcd. for C₈H₉N: C 80.63, H 7.60, N 11.75%; found: C 80.14, H 7.60, N 11.95%.

Irradiation of 2-cyanobicyclo[2.2.1]heptene

The unsaturated nitrile 4 (550 mg, 4.5 mmol) in hexane (400 mL) was irradiated under argon for 3 h, using the Hanovia 450 W lamp. Vapor phase chromatographic analysis ($6ft \times \frac{1}{2}$ in. of 3% OV-1, glass column, at 80°C) showed two products, ratio 20:1 with retention times 350 and 455 s respectively. The solution was filtered through Celite, and the hexane distilled

AKHTAR ET AL.

(1atm) through a column of glass helices. The residue was distilled in a Kugelrohr apparatus (100°C/15 Torr) to yield 320 mg of the mixed photoproducts. These were separated by vpc (5 ft $\times \frac{1}{2}$ in. of 7% QF-1 on Chromosorb W at 125°C, with the flow rate of 30 mL/min). The minor product (retention time 19 min) had $m/e = 119 (M^+)$; ir (neat): 3055, 2215 cm⁻¹; ¹H nmr (CDCl₃), δ: 1.2-2.9 (envelope); ¹³C nmr (CDCl₃); 42.6 ppm (d), 37.7 (t), 33.7 (d), 27.2 (d), 25.1 (t), 22.6 (t) ppm. The structure 6 is assigned from the hydrogenation to 7-cyanonorbornane, described below. The major product (retention time 14 min) also had m/e = 119 (M⁺); ir (neat): 1648, 2240 cm⁻¹; ¹H nmr (CDCl₃) δ : 6.02 (1H, d, J = 10.0 Hz) and 5.66 (1H, m, vinylic protons), 1.2-2.2 (7H, m); ¹³C nmr (CDCl₃): 125.3, 123.7, 24.3, 20.2, 19.4, 17.0 ppm. Anal. calcd. for C₈H₉N: C 80.63, H 7.61, N 11.76; found: C 80.61, H 7.61, N 11.90%. The structure 1-cyanobicyclo[4.10]hept-2-ene 5 is assigned from the X-ray work described below.

Hydrogenation of minor product 6 from photolysis

The tricyclic nitrile 6 (81 mg, 5.6×10^{-3} mol) (83% pure by vpc) in ethyl acetate (7.0 mL) was hydrogenated over 10% Pd-on-carbon catalyst at 1 atm. Nine milliliters of H₂ were absorbed (4 × 10⁻³ mol), and vpc analysis (6 ft × $\frac{1}{4}$ in. of 3% OV-1 at 100°C) showed the reaction was essentially complete. The catalyst was filtered, the solvent was evaporated, and the residue distilled (Kugelrohr, 100°/12 Torr) to give 64.3 mg, which was purified by vpc (6 ft. × $\frac{1}{4}$ in. of 7% QF-1 on WP 80/100, at 90°C). This afforded 7-cyanobicyclo[2.2.1]heptane, mp 61–64°C (lit. (24) mp 65–67°).

Preparation of 7-cyanobicyclo[2.2.1]heptane from bicyclo-[2.2.1]heptane-7-carboxylic acid

The method of Lohaus (25) was used. Bicyclo[2.2.1]heptane-7-carboxylic acid⁴, mp 75–78°C (5 mg, 3.6×10^{-5} mol) in pentane (10 mL) was treated with several drops (~100 mg) of chlorosulphonyl isocyanate at 40°C, under argon. After 4 h the mixture was cooled to 20°C, and dimethylformamide was added until gas evolution ceased. After 30 min crushed ice was added, aqueous and pentane layers were separated, and the aqueous layer was extracted with 2 × 10 mL pentane. The pentane layers were combined, dried, and concentrated; vpc analysis (6 ft × $\frac{1}{4}$ in. 3% OV-1 at 100°C) showed a product with the same retention time (192 s) as the above hydrogenation product. The structure 7-cyanotricyclo[4.1.0.0^{3,7}]heptane **6** is assigned to the minor photoproduct.

Preparation of derivative of 5 for X-ray work. Reduction of l-cyanobicyclo[4.1.0]hept-2-ene with lithium aluminum hydride

The major photoproduct 5 (100 mg, 8.4 mmol) in hexane (~1.0 mL) was added to LiAlH₄ in tetrahydrofuran (5.0 mL). The mixture was stirred and heated under reflux for 24 h. Excess LiAlH₄ was decomposed with wet THF, and the mixture was filtered through Celite. Water and ether were added, and the ether layer was separated and dried (Na₂SO₄). The ether was evaporated and the residue distilled (Kugelrohr) to yield bicy-clo[4.1.0]hept-2-en-1-ylmethanamine, 70 mg (68%); ir (neat): 3700–3100 cm⁻¹, no CN band.

Preparation of p-bromobenzensulphonamide of bicyclo[4.1.0]hept-2-en-1-ylmethanamine 8

The products from the above reduction (70 mg) and p-bromobenzenesulphonyl chloride (118 mg) were dissolved in pyridine and kept in the refrigerator for 24 h. The mixture was poured into ice-cold 6 N HCl, and extracted with 3×25 mL of ether. The extracts were dried and evaporated to afford the crude

⁴We thank Dr. J. Warkentin for this sample.

TABLE 3. Crystal data

Compound	C ₁₄ H ₁₆ BrNO ₂ S
Formula weight	342.26
Crystal size (mm)	cylinder, $r = 0.10, l = 0.40$
Systematic absences	$hol, l \neq 2n + 1, oko, k \neq 2n + 1$
Space group	P2./c
Unit cell (Å and deg)	a = 13.551(5), b = 5.993(2), c = 18.832(4)
ζ U,	$\beta = 105.44(2)$
Volume (Å ³)	1474.2(5)
Z	4
$\rho_{calo}[g cm^{-3}]$	1.54
$\rho_{obs}[g \text{ cm}^{-3}]$	1.50(2)
Linear absorption coefficient (cm ⁻¹)	30.89
Max 20, reflections collected	$55^{\circ}, h, k, \pm l$
Standard reflections (esd, %)	61 - 5(1.53), 702(1.53)
Temperature (°C)	22
No. of independent reflections	3410
No. with $I > 3\sigma(I)$	1004
No. with $3\sigma(I) > I > \sigma(I)$, $F_c < F_o$	1089 ^a
No. with $I < \sigma(I)$, rejected	872ª
Final R_1 , $^b R_2$	0.0809, 0.0694
Final shift/error, max(ave) (non-H)	0.0014, 0.0001
max(ave) (all parameters)	4.19, 0.84
g(secondary extinction)	6.64×10^{-8}
No. of variables	156
Final difference map	
Highest peak (e/Å ³); location	0.56; 0.10, 0.35, 0.25
Lowest valley (e/Å ³); location	-0.46; 0.05, 0.40, 0.15
Weighting	$w = (\sigma^2 + (0.03F_0)^2)^{-1}$
Error in an observation of unit weight	1.265

^oMost unobserved reflections occurred above $2\theta = 30^{\circ}$. ^b $R_1 = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$; $R_2 = \{\Sigma w(|F_0| - |F_c|)^2 / \Sigma w F_0^2\}^{1/2}$

derivative, mp 124–140°C. Two cyrstallizations from ethanolwater gave an analytical sample, mp 150–151°C. Anal. calcd. for $C_{15}H_{16}NSO_2Br: C$ 49.13, H 4.71, N, 4.09; found: C 49.22, H 4.79, N 3.92%. A crystal suitable for the following X-ray work was obtained by slow crystallization from ethanol-water.

Collection of the X-ray data

An acicular crystal of the above p-bromosulphonamide, selected after examination under a polarizing microscope for homogeneity, was ground to a cylinder and sealed to a glass fibre for X-ray examination. Precession photographs showed the crystal was monoclinic and unit cell parameters were obtained from a least squares fit of χ , ϕ , and 2θ for 15 reflections in the range $17.7^{\circ} < 2\theta < 25.1^{\circ}$ recorded on a Syntex P2₁ diffractometer using graphite-monochromated MoK α radiation (λ 0.70926 Å). Crystal data and other numbers related to data collection are summarized in Table 3. The density was obtained by flotation in an aqueous zinc bromide solution to which a few drops of liquid detergent had been added in order to wet the crystal. Intensities were also recorded on the Syntex $P2_1$ diffractometer using a coupled θ (crystal) – 2 θ (counter) scan. The methods of selection of scan rates and initial data treatment have been described (26, 27). Corrections were made for Lorentz polarization effects, but not for absorption. This will make a maximum error in F_0 of < 1.0%.

Solution of the structure

The bromine atom was found from a three dimensional Patterson synthesis, and a series of full-matrix least-squares refinements and electron density difference syntheses revealed all the atoms. At this stage the temperature factors of the bromine and sulphur atoms were made sequentially isotropic.

TABLE 4. Atomic positional parameters $(\times 10^4)$ and temperature factors $(\text{\AA}) (\times 10^3)$

Atom	x	у	z	U
Br	-4292.4(8)	-524(2)	7972.7(7)	
S	-544(2)	6225(3)	8407(1)	
C(1)	1874(6)	2792(13)	9419(4)	50(2)
C(2)	2652(7)	4613(15)	9496(5)	63(3)
C(3)	3605(8)	4295(18)	9448(5)	84(3)
C(4)	3970(8)	2046(19)	9269(6)	96(4)
C(5)	3088(8)	630(17)	8809(5)	82(3)
C(6)	2133(6)	635(15)	9087(4)	57(2)
C(7)	2227(7)	743(15)	9888(5)	67(3)
C(8)	800(6)	3479(14)	9281(4)	55(2)
C(11)	-1570(5)	4397(12)	8308(4)	41(2)
C(12)	-1660(7)	2582(16)	7835(5)	68(3)
C(13)	-2463(7)	1123(16)	7736(5)	70(3)
C(14)	-3182(6)	1498(14)	8109(4)	55(2)
C(15)	-3144(7)	3281(15)	8561(5)	61(2)
C(16)	-2317(6)	4755(14)	8663(4)	53(2)
N	495(4)	4792(10)	8589(3)	50(2)
O(1)	-526(4)	7628(9)	9020(3)	54(2)
O(2)	-627(4)	7212(9)	7698(3)	57(2)

Anisotropic temperature factors V_{13} are given by the expression exp[$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12} + ...)$]. For Br, $U_{11} = 0.0639(8)$, $U_{22} = 0.0675(8)$, $U_{33} = 0.158(1)$, $U_{12} = -0.0127(6)$, $U_{13} = 0.0146(7)$, $U_{23} = -0.0012(8)$; for S, $U_{11} = 0.059(1)$, $U_{22} = 0.041(1)$, $U_{33} = 0.041(1)$, $U_{12} = 0.004(1)$, $U_{13} = 0.022(1)$, $U_{23} = 0.003(1)$.