J. Chem. Soc. (B), 1971

Substitution Reactions in Cyclic Systems. Displacement Reactions of Some Sterically Hindered Tosylates

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Nucleophilic attack upon cyclopentyl, endo-2-norbornyl, endo-5,6-trimethylene-endo-2-norbornyl, endo-5,6-trimethylene-endo-8-norbornyl, and endo-5,6-trimethylene-endo-9-norbornyl cyclic tosylates has been studied. No rearrangement occurred during the reactions. The relative rates of displacement have been found to be very similar to the reactivity observed for solvolyses. Increased steric interaction by alkyl groups on the leaving group causes the displacement rate to decrease.

THE reactions, particularly the solvolyses, of bicyclic and polycyclic bridged-ring systems have recently attracted much attention.¹ It has been suggested that in the solvolysis of the endo-tosylates of non-flexible ring systems the non-bonded steric interactions of the leaving group are larger in the transition state than in the ground state. Thus, increased ground-state steric interactions of the leaving group can slow the rate of solvolysis rather than increase it.² This contrasts with the solvolyses of cyclohexyl systems where increased steric interactions speed the rate.³ Investigations on the attack with strong nucleophiles upon cyclohexyl systems shows that increased interaction on the leaving group has no marked effect on the rate.⁴ We have investigated the effect that increased interactions on the leaving group will have upon displacement rates in ring systems where steric hindrance to ionization has been proposed for solvolysis reactions, since if bond making became more important than bond breaking the rate would become independent of steric interactions on the leaving group. Compounds containing the *endo*-5,6-trimethylene norbornane ring system were used in the investigation since they were readily available and their solvolytic behaviour had already been investigated,^{2a} thus providing a convenient comparison with displacement reactions with strong nucleophiles.

The found displacement rates for the reaction of cyclopentyl, endo-5,6-trimethylene-endo-9-norbornyl (I), and endo-5,6-trimethylene-endo-8-norbornyl (II) tosylates with potassium iodide in anhydrous acetone are given in Table 1.

The reaction was second order in all cases to over 75% of reaction (Figure 1). In other runs where the iodide was 10 times the concentration of cyclopentyl tosylate the reaction showed very clearly pseudo-firstorder kinetics (Figure 2) and not pseudo-zero-order kinetics. A slow E2 elimination followed by rapid

R. V. Russo, *Chem. Comm.*, 1967, 998. ² (a) H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, Proc. Natl. Acad. Sci., U.S., 1966, 56, 1653; (b) H. C. Brown and W. J. Hammar, J. Amer. Chem. 30, 1053, (1) 11. C. Brown and W. J. Hannial, J. Amer. Chem. Soc., 1967, 89, 6378; (c) H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *ibid.*, 1967, 89, 6380; (d) H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. Vander Jagt, *ibid.*, 1967, 89, 6381; (e) H. C. Brown and S. Ikegami, *ibid.*, 1968, 90, 7122; (f) S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *ibid.*, 1968, 90, 7124; (g) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, 1965, 87, 375; (h) J. P. Shaefer and C. A. Elegal, *ibid.*, 1967, 80, 5729 Shaefer and C. A. Flegal, ibid., 1967, 89, 5729.

addition of hydrogen iodide to the olefin formed was excluded as a possibility because the iodide from (I) isolated in 60% yield after chromatography on alumina had less than 0.5% of iodide at the 8-position. The



iodide from (II) obtained in 55% yield by chromatography on alumina had only 5% of its iodide at the 9-position. In addition 5% of unknown material was present. Attack of hydrogen iodide on the olefin should give a mixture. The reaction of this olefin with trichloroacetic acid gave, after hydrolysis, a mixture

TABLE 1

Second-order rate constants for reaction of tosylates with potassium iodide in anhydrous acetone at 25.0°

Tosvlate •	$k_2 \times 10^7$ (1 mole ⁻¹ sec ⁻¹)	Relative rate
Cyclopentyl	3470 0	857
endo-5,6-Trimethylene-endo-	3550 b.c 430 b	106
9-norbornyl (1) endo-5,6-Trimethylene-endo- 8-norbornyl (II)	4.05 d 96.0 b, e	1.00
• norbornji (11)	1443 b, f	

• Runs were 0.100M in tosylate and 0.0200M in potassium iodide except where noted. • Average deviations were less than 5% between runs. • Runs were 0.200m in tosylate and 0.0200m in potassium iodide. d Calculated from data at other temperatures. " Rate measured at 50.0°. J Rate measured at 75.0°.

of alcohols with 55% of exo-8-alcohol and 45% of exo-9-alcohol. Both iodides were treated with zinc and hydrochloric acid in acetic acid. Both gave only a single compound whose v.p.c. retention time and i.r. spectrum were identical with endo-5,6-trimethylenenorbornane proving that no skeletal rearrangements had taken place.

The rate of reaction of the tosylate (II) with iodide is very slow compared with that for cyclopentyl tosylate. The effects are similar to those found for acetolysis.2a

¹ A portion of this work has appeared; I. Rothberg and

³ E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis', Interscience, New York, 1965, pp. 84, 273. 4 E. L. Eliel and R. P. Gerber, Tetrahedron Letters, 1961, 473.

This very slow reaction rate can be rationalized in terms of two factors. First, steric interactions increase as the tosylate group approaches the endo-3-hydrogen and



FIGURE 1 Second-order behaviour for reaction between cyclopentyl tosylate and potassium iodide in acetone. Initial tosylate concentration is 0.100m and iodide is 0.0200m

second torsional interactions⁵ may not be relieved in this system as they could in the cyclopentyl one. For example, the most favourable conformation of the



FIGURE 2 Pseudo-first-order behaviour for iodide in reaction between cyclopentyl tosylate and potassium iodide. Initial tosylate concentration is 0.200m and iodide is 0.0200m. (TF is the titration quantity in ml of 0.0100M silver nitrate used to react with potassium iodide)

9-methylene group is probably flexed down. This is to relieve non-bonded interactions of the endo-8- and endo-10-substituents with endo-2- and 3-hydrogens. If the entering and leaving group become collinear in

⁵ P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 699, 701. ⁶ J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1962, 2nd edn., p. 170; E. P. Grimsrud and J. W. Taylor, *J. Amer. Chem. Soc.*, 1970, **92**, 739. ⁷ R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, 1969, **91**, 6031, and references therein.

91, 6031, and references therein.

the traditional $S_N 2$ transition state ⁶ the exo-8-hydrogen becomes coplanar with the remaining atoms, decreasing the dihedral angle with the exo-5- and exo-9-hydrogens and increasing torsional interactions. We have, at present, no evidence to indicate whether an $S_N 2$ reaction is occurring or whether rapid ion-pair formation occurs followed by a slow displacement as proposed by Sneen.⁷ The slow rate can also be rationalized by steric and torsional effects using the Sneen mechanism. However, before rationalizing the reaction in terms of this mechanism, we are awaiting more information about the requirements for planarity of groups in the tight ionpair, and energetics for separation of the tight ion-pair.

The reaction rate of (I) with iodide is slower than that of cyclopentyl also because of steric and torsional differences, but the differences are not great.

Displacements on the Norbornyl Ring.-Displacements were also examined where the leaving group was on the norbornyl portion of the ring. We investigated the reaction of endo-2-norbornyl, endo-5,6-trimethylene-endo-2-norbornyl (III), and exo-5,6-trimethylene-endo-2norbornyl (IV) tosylates with lithium thiocresoxide in acetone. Thiocresoxide reacts with endo-norbornyl brosylate⁸ to give a sulphide which upon oxidation with hydrogen peroxide yielded exo-norbornyl p-tolyl sulphone (48%). We found that by rigorous degassing and addition of nitrogen to exclude oxygen the yield of sulphide was essentially quantitative $(97.4 \pm 2.4\%)$ as determined by v.p.c. A study was carried out to determine if rearrangements were taking place in displacements with thiocresoxide on the tosylate. [exo-2-²H]endo-2-Norbornyl tosylate was prepared and the product of displacement investigated by n.m.r. There was no indication of methine hydrogen absorption at δ 3.05 p.p.m. so that the displacement is free of carbonium ion-type rearrangements.⁹ We estimate that ca. 5% of hydrogen at the 2-position could have been detected. Displacement product studies were carried out on (III) and (IV). The products were characterized as the sulphones. In each case the displacement appeared to be completely free of rearrangement. This was proven by the following experiments. The sulphone from (III) was converted by reduction with Raney nickel into endo-5,6-trimethylenenorbornane and the sulphone from (IV) was converted into exotrimethylenenorbornane. The two hydrocarbons could be easily separated by v.p.c. and each isomer appeared to be completely free of isomeric impurity. The sulphides could not be separated on a variety of columns but the sulphone from (IV) had an i.r. absorption peak at 590 cm⁻¹ completely absent in the i.r. spectrum of the sulphone from (III). We believe that there could not have been more than 5% of isomeric impurity in the crude sulphone obtained from (III) in essentially

⁸ S. J. Cristol and G. D. Brindell, J. Amer. Chem. Soc., 1954, 76, 5699.

⁹ Displacement with tetraethylammonium acetate gives similar results. L. A. Spurlock and T. E. Parks, J. Amer. Chem. Soc., 1970, 92, 1279.

quantitative yield before recrystallization was carried out.

In Table 2 are the relative rates of displacement of tosylates with thiocresoxide. These relative rates were determined by allowing added equimolar amounts

TABLE 2

Relative rates of displacement of *endo*-tosylates with lithium p-thiocresoxide in acetone at 50°

	Relative rate of thiocresoxide	Relative rates of acetolysis at
Tosylate	displacement	25°
endo-Norbornyl	1.00	00 €
exo-5,6-Trimethylene- endo-2-norbornyl	0.828 ± 0.023 a	0·41 ª
endo-5,6-Trimethylene- endo-2-norbornyl	${}^{0\cdot121}_{0\cdot121} \pm {}^{0\cdot004}_{\pm}{}^{a}_{0\cdot002}{}^{b}_{b}$	0·10 ¢

^a Reaction was 0.100 m in each tosylate and 0.090 m in thiocresoxide. ^b Reaction was 0.100 m in each tosylate and 0.050 m in thiocresoxide. ^c Ref. 2g. ^d Ref. 11. ^e Ref. 2a.

of tosylates to react with a limited amount of thiocresoxide; the following equation was then used to calculate the relative reactivity:

Relative reactivity =

moles of tosylate reacted moles of *endo*-norbornyl tosylate reacted

Clearly, these displacement reactions with strong nucleophiles show relative reaction rates that are very similar to those found for solvolyses. Increased steric interactions decrease the reaction rate. All the displacements appeared to be completely free of the rearrangements found for reactions in which carbonium ions are present. The reaction of norbornyl tosylate with thiocresoxide in acetone does not follow secondorder kinetics. The reaction is greater than second order in thiocresoxide. Possibly this is due to essentially un-ionized lithium thiocresoxide in the nonpolar solvent acetone which attacks as an aggregate, behaviour similar to that of hydrogen chloride when attacking olefins in nonpolar solvents.¹⁰ We are investigating this further.

EXPERIMENTAL

The alcohols and tosylates are known compounds and standard procedures were used to prepare them.^{2,11} Analytical v.p.c. was carried out on 6 ft $\times \frac{1}{8}$ in columns with 10% of Silicone SE-30, Silicone UCC W-982, and Carbowax 20M on 60—80 Chromosorb W with a flow rate of 30 ml of helium per min in each case. Preparative work was on 6 ft $\times \frac{1}{4}$ in columns. The instruments used were an Aerograph 1520 with a thermal conductivity detector and a Hewlett-Packard 5750 with a flame ionization detector. The n.m.r. spectra were run on a Varian A-60 instrument and the i.r. spectra were recorded using a Beckmann IR-10 instrument. All m.p.s are uncorrected and determined on a Thomas-Hoover apparatus. Kinetics of iodide displacements were carried out in acetone purified by the procedure of Conant and Kirner.¹² The displacements by iodide were followed by periodic removal of aliquots of solution which were added to chloroform. The iodide ion was extracted into water and the aqueous phase titrated with 0.0100M-silver nitrate using Eosin Y as an indicator. The second-order rate constants were then evaluated using standard procedures.

Reaction of endo-5,6-Trimethylene-endo-9-norbornyl Tosylate with Potassium Iodide.-Potassium iodide (0.166 g, 1.00 mmol) and endo-5,6-trimethylene-endo-9-norbornyl tosylate (0.3060 g, 1.00 mmol) in acetone (10 ml) were flushed with nitrogen, sealed, and then heated for 12 h at 50°. The contents of the tube were then added to saturated sodium chloride solution (10 ml). The layers were separated and the aqueous portion was extracted with ether $(3 \times 5 \text{ ml})$. The combined organic layers were dried (MgSO₄) and evaporated using a Rinco evaporator under reduced pressure, to give an oily residue. The residue was chromatographed on alumina with pentane to give endo-5,6-trimethylene-exo-9-norbornyl iodide as a yellow oil (0.158 g, 0.600 mmole, 60%). Analysis by v.p.c. (Silicone SE-30, 100°) showed only a single peak (13 min). Titration after solvolysis in an excess of silver nitrate indicated an iodide content of 100.8% of theoretical; v_{max.} (CCl₄) 2940, 1480, 1450, 1330, 1270, 1200, 1170, 1145, 1130, 950, 890, 870, and 630 cm⁻¹ (cf. Ref. 13); 8 4.3 (1H, t, J 7.0 Hz, methine proton) and a complex multiplet from 2.8 to 1.3 p.p.m. (14H). A satisfactory analytical sample was collected with difficulty by preparative v.p.c. (Silicone SE-30, column, detector, injector at 100°) (Found: C, 45.6; H, 5.65; I, 48.3. Calc. for C10H15I: C, 45.8; H, 5.75; I, 48.4%).

Reduction of endo-5,6-Trimethylene-exo-9-norbornyl Iodide.—The exo-9-iodide (37.0 mg, 0.141 mmol) was dissolved in glacial acetic acid (2 ml). Zinc dust (46 mg, 0.71 mmol) was added to the solution which was then saturated with hydrogen chloride, stirred, and heated under reflux. Additional hydrogen chloride was added at 5-h intervals with a total reaction time of 24 h. Ether (5 ml) and water (10 ml) was added to the cooled reaction mixture; the ether layer was separated off and the aqueous phase was extracted with ether $(2 \times 2 \text{ ml})$. The combined organic phase was washed with 10% sodium hydroxide $(2 \times 5 \text{ ml})$ and then with water. The ether solution was diluted with further ether to 10 ml and dried $(MgSO_4)$; the yield for the reduction was determined as 45% using endo-5,6-trimethylenenorbornane as external standard. Only a single peak was obtained for the reduction product. Comparison of v.p.c. retention time (Silicone SE-30, 65°, 7 min) and i.r. spectrum of a sample collected by preparative v.p.c. showed the reduction product to be endo-5,6-trimethylenenorbornane.

Reaction of endo-5,6-Trimethylene-endo-8-norbornyl Tosylate with Potassium Iodide.—The reaction mixture prepared in an identical way as that for the 9-tosylate, was heated at 75° for 100 h, and worked up as previously described to

¹² J. B. Conant and W. R. Kirner, *J. Amer. Chem. Soc.*, 1924, **46**, 232.

F. R. Mayo and J. J. Katz, J. Amer. Chem. Soc., 1947, 69, 1339, 1348; and see also E. S. Gould, 'Mechanism and Structure in Organic Chemistry,' Holt, Rinehart, and Winston, New York, N.Y., 1959, p. 517.
P. D. Bartlett and R. S. Barnes, Abstracts of the 12th

¹¹ P. D. Bartlett and R. S. Barnes, Abstracts of the 12th National Organic Symposium of the American Chemical Society, June 1951, p. 1; K. Takeuchi, T. Oshika, and Y. Koga, Bull. Chem. Soc. Japan, 1965, **38**, 1318.

^{40, 232.} ¹³ L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' J. Wiley, New York, 1958, p. 332; R. M. Silverstein and G. C. Bassler, 'Spectrometric Identification of Organic Compounds,' J. Wiley, New York, 1967, 2nd edn., p. 102.

give endo-5,6-trimethylene-exo-9-norbornyl iodide (55%) after chromatography on alumina. Analysis by v.p.c. (SE-30, 100°) showed 5% of 9-iodide (13 min), 90% of 8-iodide (11 min), and 5% of unknown material (8 min). Titration after solvolysis in an excess of silver nitrate indicated an iodide content of 94% of theoretical; v_{max} . (CCl₄), 2940, 1480, 1455, 1300, 1280, 1170, 1120, 1110, 950, 890, 670, 630 (alkyl iodide), and 575 cm⁻¹ (alkyl iodide); δ 4·2br (1H, q, J 5·0 Hz, methine H) and 2·8—1·0 p.p.m. (complex m, 14H) (Found: C, 45·4; H, 5·65; I, 48·1. Calc. for C₁₀H₁₅I: C, 45·8; H, 5·75; I, 48·4%).

Reduction of the 8-Iodide.—Reduction of endo-5,6-trimethylene-exo-8-norbornyl iodide with zinc and hydrogen chloride in acetic acid was carried out as described previously for the 9-iodide. This gave a product (55%) (by v.p.c. use of an external standard) which was homogeneous when examined by v.p.c. and whose v.p.c. retention time and i.r. spectrum were identical with authentic endo-5,6-trimethylenenorbornane.

Reaction of endo-Norbornyl Tosylate with Lithium p-Thiocresoxide.--endo-2-Norbornyl tosylate (0.179 g, 0.540 mmol) and lithium p-thiocresoxide 8 (0.108 g, 0.675 mmol, 25% excess of 82% pure material) ¹⁴ was added to acetone (5.00 ml) and the solution was evacuated, flushed with nitrogen to exclude oxygen, and sealed. The solution was then heated at 100° for 17 h. The solution was examined by v.p.c. (SE-30, 140°) and showed a yield of $97.4 \pm 2.4\%$ of exo-2-norbornyl p-tolylsulphide by comparison with an authentic sample prepared by addition of p-thiocresol to norbornene.8 The sulphide prepared by tosylate displacement contains ca. 25% di-p-tolyl disulphide. The acetone was evaporated off and the residue taken up in pentane and chromatographed over alumina with pentane. Evaporation of solvent led to sulphide contaminated with disulphide but free of impurities due to condensation of acetone. A sample of sulphide was purified by preparative v.p.c. (SE-30, 140°) and the properties agreed with authentic material. Under these conditions disulphide is not eluted off the v.p.c. column; δ 7.15 (2H, d, J 8.5 Hz, Ar), 7.05 (2H, d, / 8.5 Hz, Ar), 3.05 (1H, m, methine H), 2.25 (3H, s, methyl), 2.20br (2H, s, CH), and 0.9-1.9br p.p.m. (8H, m, CH2).

exo-Norbornyl p-Tolyl Sulphone.—The procedure of Cristol and Brindell⁸ was followed using a sample of sulphide prepared by displacement on tosylate with thiocresoxide. This gave a 99% yield of crude material which was crystallized from ethanol to give pure sulphone (87%), m.p. $78\cdot5-79\cdot5^{\circ}$ (lit.,⁸ m.p. $79\cdot5-80\cdot5^{\circ}$).

endo[2-²H]Norbornyl Tosylate.—Norcamphor was reduced with lithium aluminium deuteride and the crude alcohol was purified by the technique of Winstein and Trifan.¹⁵ The tosylate was prepared by standard techniques. Neither alcohol nor tosylate showed signs of H being present at the 2-position and we believe that displacement of ¹H by ²H occurred in >95% at this position.

Reaction of endo- $[2-^{2}H]$ Norbornyl Tosylate with Lithium p-Thiocresoxide.—This reaction was carried out in an identical fashion to that previously described except that the reaction mixture was heated at $75\cdot0^{\circ}$ for $1\cdot1$ h. Attempted preparative v.p.c. of a sample of sulphide for analysis by n.m.r. was unsuccessful. On SE-30, UCC W-982,

and Carbowax 20M exchange of the 2-²H occurred on the v.p.c. column. We used the sample collected from chromatography on alumina after the pentane had been evaporated off. This contained di-p-tolyl disulphide but the n.m.r. signals of this compound [δ 7.35 (4H, d, J 8 Hz), 7.05 (4H, d, J 8 Hz), and 2.30 p.p.m. (6 H, s)] did not interfere with evaluation of the 2-¹H content of the sulphide.

Reaction of endo-5,6-Trimethylene-endo-2-norbornyl Tosylate with Lithium Thiocresoxide.-endo-5,6-Trimethyleneendo-2-norbornyl tosylate (0.827 g, 2.70 mmol) was added to lithium thiocresoxide (0.589 g, 3.38 mmol, 25% excess of 80% pure material) in acetone (25 ml.). The reaction mixture was degassed in vacuo, flushed with nitrogen, and then sealed. The reaction mixture was then heated at 100° for 4 d. Analysis of a small portion of the reaction mixture by v.p.c. (UCC W-982, 200°) and use of naphthalene as an external standard showed an 81% yield of endo-5,6-trimethylene-exo-2-norbornyl p-tolyl sulphide (20 min) contaminated with di-p-tolyl disulphide (16 min). The solution was filtered and evaporated under reduced pressure to an oil and then chromatographed on alumina with hexane to give 0.673 g of combined di-p-tolyl disulphide and endo-5,6-trimethylene-exo-2-norbornyl p-tolyl sulphide. The response to the detector to di-p-tolyl disulphide was determined on an authentic sample which then allowed estimation of the yields. The mixture contained 63.8% of the sulphide. The detector response to sulphide was determined on this mixture. Separation of a pure sample of sulphide by preparative v.p.c. and by chromatography on alumina and silica gel was unsuccessful so that characterization was carried out on the sulphone derivative.

Preparation of endo-5,6-Trimethylene-exo-2-norbornyl p-Tolyl Sulphone.-endo-5,6-Trimethylene-exo-2-norbornyl p-tolyl sulphide (0.429 g, 1.51 mmol) and di-p-tolyl disulphide (0.244 g, 0.987 mmol) were dissolved in glacial acetic acid (15 ml) and 30% hydrogen peroxide (2.5 ml) was added to the solution which was then heated at 100° for 5 h. The reaction mixture was poured into etherwater (1:1; 200 ml) and cooled by addition of ice; the mixture was then made basic to litmus by addition of ice-cold saturated aqueous sodium hydrogen carbonate. The layers were separated and the aqueous phase was extracted with ether. The combined ether portions were dried (MgSO₄), filtered, and then evaporated under reduced pressure to give an oil (crude yield 0.445 g, 1.51 mmol, 100%), 1320 and 1150 (sulphone) and a trace of absorption in the carbonyl region. Two recrystallizations from pentane containing a couple of drops of ether yielded a white crystalline solid (0.343 g, 1.17 mmol, 78%), m.p. 137-138°, v_{max.} (CCl₄) 2950, 2880, 1450, 1400, 1355, 1320, 1300, 1280, 1150, 1090, 900, 655, and 575 cm⁻¹; identical with i.r. of crude material apart from absence of C=O absorption (Found: C, 69.95; H, 7.45; S, 11.1. Calc. for C₁₇H₂₂O₂S: C, 70·3; H, 7·65; S, 11·05%).

Hydrogenolysis of endo-5,6-Trimethylene-exo-2-norbornyl p-Tolyl Sulphone.—endo-5,6-Trimethylene-exo-2-norbornyl p-tolyl sulphone ($35\cdot1$ mg, $0\cdot121$ mmol) was added to 95% ethanol ($1\cdot0$ ml) and Raney nickel (W-2, suspended in water, W. R. Grace and Co.) (1 g). The reaction mixture was then heated under reflux for 1 h. Analysis by v.p.c. (UCC W-982, 125°) with authentic endo-5,6-trimethylene-norbornane as external standard indicated a yield of 95%

¹⁴ The purity was checked by titration with iodine solution according to the procedure of J. Hine and W. H. Brader, J. Amer. Chem. Soc., 1953, **75**, 3694. The major impurity was di-p-tolyl disulphide.

¹⁵ S.Winstein and D. Trifan, J. Amer. Chem. Soc., 1952, 74, 1147.

of product. The v.p.c. retention time (10 min) and the i.r. spectrum of a sample isolated by preparative v.p.c. after removal of the nickel by filtration was identical with that of *endo-5*,6-trimethylenenorbornane. *exo-5*,6-Trimethylenenorbornane has a v.p.c. retention time of 8 min and none of this could be detected. We believe that there was less than 1% of *exo*-isomer present.

Reaction of exo-5,6-Trimethylene-endo-2-norbornyl Tosylate with Lithium Thiocresoxide.-exo-5,6-Trimethyleneendo-2-norbornyl tosylate (0.827 g, 2.70 mmol) and lithium p-thiocresoxide (0.589 g, 3.38 mmol, 25% excess) were allowed to react under conditions identical with those for the endo-isomer above. After 48 h at 100° analysis of the solution by v.p.c. (UCC W-982, 200°) showed acetone condensation products, di-p-tolyl disulphide (16 min) and exo-5,6-trimethylene-exo-2-norbornyl p-tolyl sulphide (20 min) in 90% yield (naphthalene used as an external standard). The solution was filtered, evaporated under reduced pressure, and then chromatographed through alumina with pentane to give a mixture (0.886 g) of dip-tolyl disulphide and sulphide. Analysis by v.p.c. showed the sulphide to be 73% pure indicating the yield of exo-5,6-trimethylene-exo-2-norbornyl p-tolyl sulphide to be 0.647 g (2.27 mmol, 84%). A quantity of exo-5,6-trimethylene-exo-2-norbornyl p-tolyl sulphide was purified by preparative v.p.c. and found to still contain 10.1% of the disulphide. Correction for the presence of disulphide as described previously for the endo-trimethylene isomer permitted determination of the detector response ratio of sulphide relative to that of naphthalene.

Preparation of exo-5,6-Trimethylene-exo-2-norbornyl p-Tolyl Sulphone.—exo-5,6-Trimethylene-exo-2-norbornyl-

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J. Chem. Soc. (B), 1971

p-tolyl sulphide (0.647 g, 2.27 mmol) and di-*p*-tolyl didisulphide (0.239 g, 0.970 mmol) were dissolved in glacial acetic acid (20 ml) and 30% hydrogen peroxide (3.0 ml) was added to the solution. Work-up of the mixture as described for the *endo*-trimethylene isomer gave crude *exo*-5,6-trimethylene-*exo*-2-norbornyl *p*-tolyl sulphone as an oil (2.29 mmole, 101%); v_{max} 1320 and 1145 cm⁻¹ (sulphone) and C=O impurity. Recrystallization from pentane containing a couple of drops of ether gave a white solid (0.547 g, 1.88 mmol, 83%), m.p. 61—64°. A second recrystallization gave 0.462 g (1.58 mmole, 69%) of white solid, m.p. 64—65°. An i.r. spectrum was identical to that of the crude material with the exception of the carbonyl impurity which was now absent; v_{max} (CCl₄) 2950, 2860, 1445, 1400, 1320, 1310, 1290, 1280, 1145, 1080, 900, 650, 590, 565, and 540 cm⁻¹ (Found: C, 70.1; H, 7.5; S, 11.05. (Calc. for C₁₇H₂₂O₂S: C, 70.3; H, 7.65; S, 11.05%).

Hydrogenolysis of exo-5,6-Trimethylene-exo-2-norbornyl p-Tolyl Sulphone.—exo-5,6-Trimethylene-exo-2-norbornyl p-tolyl sulphone (37.1 mg, 0.128 mmol) was treated with Raney nickel in ethanol as described for the endo-5,6-trimethylene isomer. A single product was obtained in 95% yield (by v.p.c. and use of an external standard) that had identical retention time and i.r. spectrum (after preparative v.p.c.) with that of authentic exo-5,6-trimethylenenorbornane. No endo-5,6-trimethylenenorbornane was found and 1% of this compound could easily have been detected.

We thank the Petroleum Research Fund administered by the American Chemical Society and the Rutgers Research Council for financial support.

[0/1105 Received, June 29th, 1970]