The Interaction of Benzenesulphonyl Chloride, Aluminium Chloride, and Decalin

By **Roy Fields, Geoffrey Holt,** * **Mohamed O. A. Orabi,** and (in part) **Bahman Naseeri-Noori,** The University of Manchester Institute of Science and Technology, Manchester M60 1QD

Benzenesulphonyl chloride and aluminium chloride react preferentially with the *cis*-isomer in a mixture of *cis*- and *trans*-decalins to give 9-chloro-*trans*-decalin and the axial and equatorial isomers of 1- and 2-chloro-*trans*-decalins.
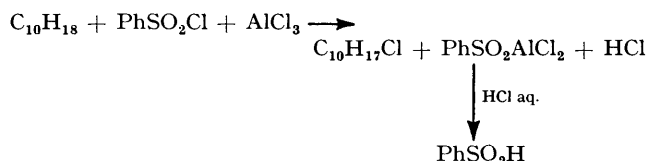
UNDER Friedel–Crafts conditions, acyl halides effect hydride-ion abstraction from alkanes, thereby being reduced to aldehydes, while the resulting carbonium ion, either before or after rearrangement, frequently loses a proton to provide an alkene. The latter with a second molecule of acylating agent provides a β-chloroketone or products which may be regarded as being derived therefrom by dehydrohalogenation or by rearrangement.[1] The literature apparently contains no reference to the interaction of saturated hydrocarbons and benzenesulphonylating agents, but in view of the ease with which arenesulphonyl chlorides are reduced to the corresponding sulphinic acids it seemed worthy of investigation.

Decalin was chosen as substrate since the behaviour of this hydrocarbon towards acetyl chloride and aluminium chloride has been studied in some detail by Baddeley and his co-workers.[2] They suggested that removal of a hydride ion from the 9-position followed by loss of proton gives 9,10-octalin, which then reacts with an acetyl cation to give the oxonium ion (1), which rearranges to the more stable five-membered ring oxonium ion (2); loss of proton from this would give (3), the major product under mild conditions, but in the presence of free AlCl₃, rearrangement of (2) to (4) would allow the formation of the observed hydroxyketone (5) (Scheme 1).

RESULTS

When decalin was treated with benzenesulphonyl chloride and aluminium chloride in 1,2-dichloroethane as solvent, under conditions similar to those used by Baddeley in the acetylation, no reaction took place. However, 1,2-dichloroethane, which appears to be of general utility for acetylation reactions, is not always satisfactory for sulphonylations, particularly those involving formal reduction of the sulphonyl group to sulphinic acid.[3] Since in the reaction between benzenesulphonyl chloride, aluminium chloride, and cyclohexene, the best yields were obtained [3] with a sulphonyl chloride : catalyst ratio of at least 2 : 1, and using carbon disulphide as solvent, these conditions were applied to the present work. The decalin used was an approximately 1 : 1 mixture of *cis* and *trans* isomers, and preliminary experiments showed that using a sulphonyl chloride : catalyst : hydrocarbon ratio of 3 : 1 : 1, an exothermic reaction began at 26—30 °C, hydrogen chloride was evolved, and benzenesulphinic acid was isolated, but the neutral, sulphonyl chloride-free product of the reaction proved to be complex. Significantly however, some 50% of the decalin was recovered, which proved to be exclusively the *trans* isomer; with a catalyst : decalin ratio of 1 : 4, the recovered hydrocarbon consisted of a mixture of *cis*- and *trans*-decalin in the ratio 1 : 2. These results indicate that

the *cis* isomer reacts in preference to the *trans*. It is known [4] that aluminium chloride can convert *cis*-decalin to the *trans* isomer at a rate dependent on the experimental conditions, but a blank experiment showed that under our conditions, the *cis* isomer was not so transformed in the absence of benzenesulphonyl chloride. In accordance with the observed stoicheiometry of the reaction, the neutral product proved to be a mixture of chlorodecalins.

$$C_{10}H_{18} + PhSO_2Cl + AlCl_3 \longrightarrow$$
$$C_{10}H_{17}Cl + PhSO_2AlCl_2 + HCl$$

with an arrow labelled "HCl aq." leading to

$$PhSO_2H$$

G.l.c., using a dichlorodimethylsilane-doped Carbowax column, showed the presence of *trans*-9-chlorodecalin,
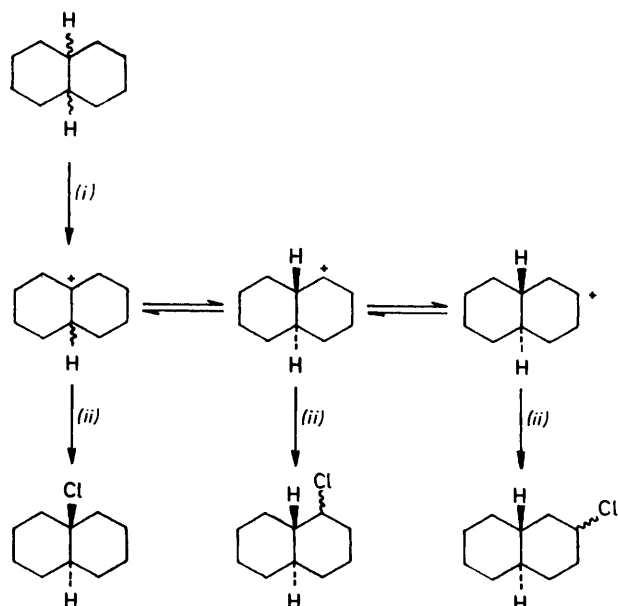

SCHEME 1
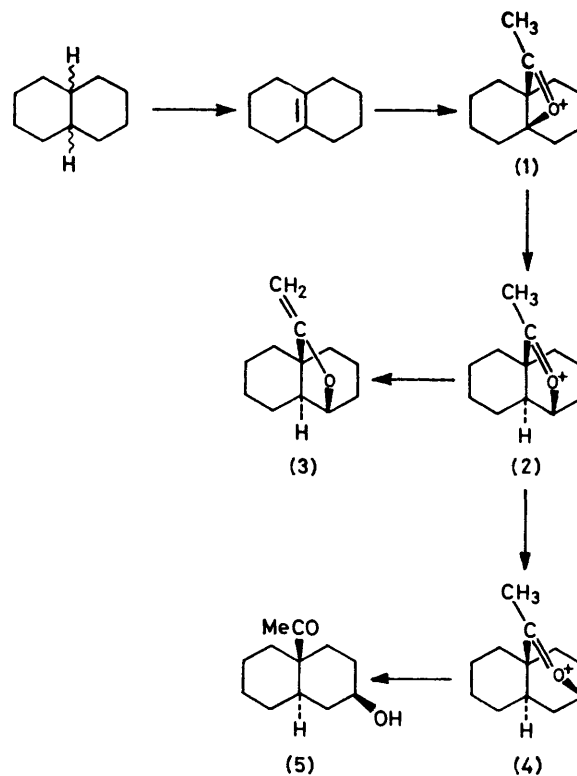
identical in retention time and mass spectrum with a sample prepared by Greene's route,[5] and a larger peak with longer retention time. The i.r. and n.m.r. spectra of this mixture agreed well with the spectra reported by Frainnet *et al.*[6] for the products of the reaction of thionyl chloride

with *trans*-2-decalol, and of chlorination of *trans*-decalin, and identified by them as the axial and equatorial 1- and 2-chloro-*trans*-decalins, together with *trans*-9-chlorodecalin. In particular, the 100-MHz ¹H n.m.r. spectrum showed two compounds with the partial structures (A) and (B), con-

(A)   (B)
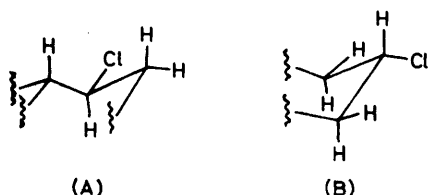
sistent with the equatorial 1- and 2-chlorodecalins with either *cis*- or *trans*-fused rings, together with two other, less well resolved, signals. The behaviour of the mixture obtained in the present work when treated with a limited

SCHEME 2   (*i*) [PhSO₂]⁺;   (*ii*) [AlCl₄]⁻

amount of potassium hydroxide in ethanol, calculated to remove the 9-chlorodecalin, and then with an excess of the base in order to remove the axial chloro-compounds, was also in accord with the reports of Frainnet *et al.* for the compounds with a *trans*-ring junction [6a] rather than with a *cis*-ring junction.[7] The spectra of the remaining chloro-compounds also agreed well with those given by Frainnet *et al.* for the equatorial 1- and 2-chloro-*trans*-decalins.[6]

Confirmation of the stereochemistry of the ring junction was provided by the agreement of the g.l.c. retention time of the 1- and 2-chlorodecalins with that of *cis*-9-chloro-decalin, prepared by equilibration of the *trans*-isomer with zinc chloride and concentrated hydrochloric acid,[5] since Frainnet *et al.* have shown that the 1- and 2-chloro-*trans*-decalins have a retention time similar to that of *cis*-9-chloro-decalin,[6] but that the 1- and 2-chloro-*cis*-decalins, prepared independently,[7] have a considerably longer retention time.[8] The relative yields of the chloro-*trans*-decalins formed in the present work, derived from the g.l.c. peak areas and n.m.r. integrations, are given in the Table, and the reaction is summarised in Scheme 2.

Proportions of chlorodecalins

Isomer	Proportions		
	a	*b*	*c*
trans-(9)	27	4	38
trans-(1a)	7	21	
trans-(1e)	13	30	
trans-(2a)	18	20	62
trans-(2e)	35	25	

[a] Present work. Benzenesulphonyl chloride : AlCl₃ : decalin 3 : 1 : 4, solvent CS₂.   [b] *trans*-Decalin + chlorine (I₂–EtOH at 0 °C) (ref. 6b).   [c] Present work. AlCl₃ + Me₃CCl + decalin, after Bartlett *et al.*, ref. 9.

DISCUSSION

A mixture of monochlorodecalins stated to be predominantly the 9-isomer was obtained by Bartlett *et al.*[9] by the action of t-butyl chloride and aluminium chloride on decalin of unspecified stereochemistry. This identification was based on the chemical reactivity of the product, and without the aid of spectroscopic techniques now available. It was moreover, found necessary to employ a somewhat complex mixing and quenching flow system, otherwise yields were very low.* In contrast, the benzenesulphonyl chloride reaction may be carried out using simple apparatus.

The observation of a greater temperature rise when the acetylating agent is added to *cis*-decalin compared with the *trans*-isomer [10] is consistent with the isomer preference observed in the present work. Presumably the 9-hydrogen of *cis*-decalin is more accessible than that of the *trans*-isomer to the bulky ion pair [PhSO₂]⁺-[AlCl₄]⁻, and the energy difference between the *trans*-isomer and the flat 9-carbonium ion must be greater than that between *cis*-decalin and the same ion. If, as Baddeley has suggested,[2] there is an equilibrium between the 9-, 1-, and 2-carbonium ions [*cf.* Scheme 1, (1), (2), and (4) respectively], then the observed products could be formed by simple chloride-ion addition to those carbonium ions, and in view of Greene's work,[5] the *trans*-isomer would be expected to form *ca.* 90% of the 9-chloro-compound. Although *cis*-decalin is the reactive isomer, the isolated products are all chloro-*trans*-decalins. Formation of the flat 9-carbonium ion readily allows this change in stereochemistry as in the isomerisation of *cis*- to *trans*-decalin. The equatorial : axial ratios for the 1- and 2-chlorodecalins, as shown by the areas of the α-hydrogen absorption in the n.m.r. spectrum, fit well with those expected for thermodynamic product control using an equatorial preference for chlorine [11] of 1.2—2.0 kJ mol⁻¹. The low yield of 9-chlorodecalin compared with the 1- and 2-isomers presumably reflects the stability of the chloro-compounds themselves, rather than that of the carbonium ions from which they arise.

A major difference between this work and that of

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* This was confirmed in the present work; the reaction carried out simply in a separating funnel gave a low yield of a mixture of chlorodecalins in which the 9-isomer was present in larger proportion than when benzenesulphonyl chloride was used, although in contrast to the previous report, the mixture of secondary chlorodecalins still predominated (see Table).

Baddeley [2] is that we have usually used only one molecular proportion of sulphonylating agent, with an excess of benzenesulphonyl chloride to avoid the presence of uncomplexed aluminium chloride, whereas Baddeley used an excess of acylating agent, and this brought about addition of acyl cation to 9,10-octalin arising from the initially formed 9-carbonium ion. In this process the carbonyl oxygen of the acyl group was said to stabilise the developing 1-carbonium ion (2) and hence lead to the vinyl ether (3). Such stabilisation clearly could not occur in the present work, and is evidently unnecessary, since the 1- and 2-chlorodecalins are the major products. The benzenesulphonyl cation apparently does not add to the alkene, but rather is reduced to benzenesulphinic acid, as in the reaction with cyclohexene and cyclopentene.[3] When two, rather than one molecular proportion of sulphonylating agent was used in the present work, reaction set in at a lower temperature, and more than one molecular proportion of the sulphonylating agent was reduced to sulphinic acid. The neutral organic product was, however, tarry and complex, and although mass spectrometry indicated the presence of $C_{10}H_{16}Cl_2$, the product was clearly not a simple addition compound of chlorine and 9,10-octalin.

EXPERIMENTAL

General.—Decalin was shaken with 70% H_2SO_4 several times, washed, dried (MgSO$_4$), and distilled. G.l.c. showed it to be a *ca.* 1 : 1 mixture of *cis* and *trans* isomers. Reagent-grade benzenesulphonyl chloride was dissolved in chloroform and shaken with water until the washings were only faintly acidic. The solution was dried, and the benzenesulphonyl chloride distilled under reduced pressure. Reagent-grade lump aluminium chloride was weighed and finely powdered immediately prior to use. G.l.c. was carried out on a Pye series 104 model 641 instrument, using nitrogen carrier gas and a dual flame-ionisation detector. N.m.r. spectra were obtained on Perkin-Elmer R12 and R20 (60 MHz) and Varian HA100 (100 MHz) spectrometers, i.r. spectra on Perkin-Elmer 237 and 261 instruments, and mass spectra on an A.E.I. MS 902 instrument.

The Reaction of Benzenesulphonyl Chloride and Aluminium Chloride with Decalin.—Decalin (56 g, 0.40 mol) was added (15 min) to benzenesulphonyl chloride (53 g, 0.30 mol) and aluminium chloride (14 g, 0.10 mol) in carbon disulphide (80 ml) at 0 °C. The mixture was stirred and a slow stream of dry nitrogen was passed through the apparatus, the effluent gases being passed through an absorber so arranged that the hydrogen chloride carried over could at definite time intervals be titrated against 1M-NaOH solution. Initially, there was no reaction but on raising the temperature of the mixture to 26—30 °C, an exothermic reaction began and external cooling was necessary to maintain this temperature. Stirring was continued while hydrogen chloride (1.06 mol) was carried over during 4 h, after which the evolution was very slow. The cooled mixture was added slowly and with stirring to ice (200 g), water (150 ml), and light petroleum (b.p. 60—80 °C) (500 ml). After removal of a small amount (*ca.* 0.5 g) of insoluble material, the organic layer was separated and

washed (water, aqueous Na$_2$CO$_3$, water) to give a neutral solution (A). The combined aqueous layer and washings, after acidification (dilute H_2SO_4) were treated with ferric chloride (13 g) in water (100 ml) as outlined by Thomas.[12] After 3 h, the red-brown precipitate was filtered off, washed (dilute H_2SO_4, water), and dried to provide ferric benzenesulphinate (9.0 g). On the basis of a blank experiment using sodium benzenesulphinate dihydrate (2.00 g) and ferric chloride (3.0 g), which provided ferric benzenesulphinate (1.30 g), the yield of benzenesulphinic acid is thus 69%.

The neutral organic layer [solution (A) above] was stirred with aqueous ammonia (120 ml, s.g. 0.880) for 2 h, to give benzenesulphonamide (27 g, 0.17 mol), m.p. and mixed m.p. 152—155 °C. In a blank experiment under similar conditions using authentic benzenesulphonyl chloride (8.8 g) benzenesulphonamide (6.85 g, 87%) was isolated suggesting that solution (A) contained 0.20 mol benzenesulphonyl chloride. The organic layer was then washed (water, dilute aqueous HCl, water), and dried (MgSO$_4$), and the bulk of the solvent was distilled through a short column.

The residue (56 g) was distilled through a 24-in Nester–Faust spinning-band column to yield three fractions: (*i*) b.p. 69—73 °C at 17 mmHg (36 g), shown by i.r. spectroscopy and g.l.c. to be a mixture of *cis*- and *trans*-decalin (1 : 2) in addition to a small amount of a mixture of monochlorodecalins; (*ii*) b.p. 90—102 °C at 17 mmHg (9 g) shown by i.r., [1]H n.m.r., and mass spectra to be a mixture of monochlorodecalins (see below); and (*iii*) residue (3 g), in which mass spectrometry indicated the presence of $C_{10}H_{16}Cl_2$.

Examination of fraction (ii). G.l.c. (1 m, 10% Carbowax and 5% dichlorodimethylsilane on Celite, 107 °C) showed two components in the ratio 1 : 4. The former had a retention time identical with that of *trans*-9-chlorodecalin and the retention time of *cis*-9-chlorodecalin (see below) was within the envelope of the rather broad major component (28—34 min, maximum at 31.6 min). A sample of fraction (*ii*) (2.8 g), which from g.l.c. contained 9-chlorodecalin (0.56 g, 3 mmol) was heated under reflux with ethanol (7.5 ml) containing potassium hydroxide (0.29 g, 3 mmol) for 1 h. After dilution with water, the mixture was extracted with ether, and concentration of the dried (MgSO$_4$) extract gave an oil (B) (2.4 g). G.l.c. of this product showed that the peak corresponding to 9-chlorodecalin had disappeared and had been replaced by one having a retention time identical with that of 9,10-octalin. N.m.r. indicated the absence of vinylic hydrogen. The product (B) of the above reaction (1.5 g) was heated under reflux for 24 h with potassium hydroxide (0.73 g) in absolute ethanol (20 ml). Work-up as above gave an oil (1.2 g), g.l.c. of which showed that about one-third of the component with the longest retention time (35 min) had been converted into material which had a much shorter retention time. The n.m.r. spectrum of the product showed the absence of the bands at δ 4.15 and 4.45 attributed to the equatorial hydrogen of the axial 1- and 2-chloro-*trans*-decalin and the presence at δ 5.5 of at least two types of vinylic hydrogen.

Several variants of the above reaction were carried out. When the molar ratio of benzenesulphonyl chloride : aluminium chloride : decalin was changed from 3 : 1 : 4 to 3 : 2 : 4, reaction set in spontaneously at 18—20 °C, more than 1 molecular proportion (*ca.* 1.5) of benzenesulphonyl chloride was consumed, and almost double the quantity of HCl was evolved. The neutral organic product

of the reaction was much more complex and appeared (mass-spectrometry) to contain both mono- and di-chlorodecalins. With a benzenesulphonyl chloride : $AlCl_3$: decalin (1 : 1 *trans* : *cis* mixture) molar ratio of 3 : 1 : 1, half the decalin was recovered and this was exclusively the *trans*-isomer. *Ca.* 1 mol proportion of benzenesulphonyl chloride was consumed.

9,10-*Octalin and* 9-*Chlorodecalin.*—*cis*-1-Decalol was dehydrated with boric acid to give a mixture of 9,10- and 1,9-octalin, and treatment of this mixture with P_2O_5 as described by Dauben *et al.*[13] gave almost exclusively the 9,10-isomer as evidenced by n.m.r., which showed a large doublet at δ 1.65 and 1.85 for the CH_2 hydrogens and only a trace of vinylic hydrogen at δ 5.4—5.6. Treatment of 9,10-octalin with concentrated hydrochloric acid that had been saturated with hydrogen chloride as described by Greene and Lowry [5] provided 9-chlorodecalin, essentially the *trans*-isomer. It was enriched in the *cis*-isomer, as described by Greene,[5] by means of zinc chloride in concentrated hydrochloric acid at 50 °C for 6 days. G.l.c. on the original material gave a retention time of 23.6 min at 107 °C, with a small peak due to 9,10-octalin at 6.58 min. The equilibrated product showed two main peaks with retention times 22.2 min (*trans* isomer) and 30 min (*cis* isomer).

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