S 39. The Cleavage of Sulphonic Esters with Raney Nickel Catalysts.

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On treatment with hydrogen and Raney nickel catalysts, alkyl esters of toluene-*p*-sulphonic acid yield the corresponding alcohols, but aryl esters give the aromatic hydrocarbons. Alkyl and aryl esters of benzylsulphonic acid are rapidly reduced under the same conditions to the hydroxy-compounds, and benzylsulphonanilides to anilines.

LITTLE information has yet been published concerning the catalytic hydrogenolysis of sulphonic esters. Cavallito and Haskell (*J. Amer. Chem. Soc.*, 1944, **66**, 1927) observed that the toluene-*p*-sulphonic esters of 2- and 3-hydroxyquinolines and of 3- and 4-hydroxypyridines were reduced readily to the toluene-*p*-sulphonate salts of tetrahydroquinoline and piperidine respectively in presence of a palladium catalyst. The hydrogenation of derivatives of arylsulphonic acids to arylthiols under drastic conditions with a cobalt sulphide catalyst has been recorded (Lazier and Signaigo, U.S.P. 2,402,641). The requirements of another investigation have led us to make a brief study of the subject, and the results are recorded below.

Freudenberg and Brauns (*Ber.*, 1922, **55**, 3233) discovered that the toluene-*p*-sulphonyl derivatives of sugars could be split by sodium amalgam into toluene-*p*-sulphinic acid and the parent carbohydrate. This technique has since been widely applied (*e.g.* Levene and Compton, *J. Amer. Chem. Soc.*, 1935, **57**, 2306; Reber and Reichstein, *Helv. Chim. Acta*, 1945, **28**, 1164). We have found that in certain cases the carbohydrate may also be regenerated from its toluene-*p*-sulphonyl derivative by hydrogenation with Raney-nickel catalysts at room temperature and atmospheric pressure. Whether this reaction involves a cleavage to sulphinic acid followed by further reduction of this or a preliminary reduction to sulphinic or sulphenic ester followed by cleavage we have not determined. As would be expected on either hypothesis 2 mols. of hydrogen are absorbed, the absorption occupying ½—2 hours in favourable cases. Sulphur is attached to the catalyst, which was previously saturated with hydrogen, and the overall reaction may therefore be represented as follows :

$$(A)\quad \mathrm{R{\cdot}O{\cdot}SO_2{\cdot}C_7H_7 + Ni_x(H)_2 + 2H_2 \longrightarrow R{\cdot}OH + Ni_x(S) + C_7H_8 + 2H_2O}$$

To maintain an active surface throughout the reaction it is necessary to use relatively massive quantities of nickel, about five times the weight of substance being commonly convenient, and large-scale work is thereby restricted. No special advantage seemed to be gained by using the highly active " W-6 " catalyst of Adkins and Billica (*J. Amer. Chem. Soc.*, 1948, **70**, 695), although the reduction time was slightly shortened. The desulphurisation method of Mozingo *et al.* (*ibid.*, 1943, **65**, 1013), in which an alcoholic solution of the substance is boiled with large amounts of nickel but without added hydrogen, may be applied to these hydrogenolyses, but is less effective. The *p*-tosyl derivative of di*iso*propylidene glucose was not reduced in presence of palladium–barium sulphate under the conditions of Mozingo *et al.* (*ibid.*, 1945, **67**, 2092), nor, unlike toluene-*p*-sulphinic acid, was it an effective poison for this catalyst. Apparently cleavage of *p*-tosyl esters does not normally occur on palladium–barium sulphate or on platinic oxide catalysts.

Excellent results were obtained when the process was applied to 6-*p*-tosyl 1 : 2-3 : 4-di*iso*propylidene galactose and 3-*p*-tosyl 1 : 2-5 : 6-di*iso*propylidene glucose. Since β-penta-acetyl glucose and tetra-acetyl β-phenylglucopyranoside were recovered unchanged after boiling their alcoholic solutions with nickel, it was hoped that hydrogenation would offer advantages over sodium-amalgam reduction for alkali-labile substances. However, even with carefully washed nickel under the mildest possible conditions, 6-*p*-tosyl 2 : 3 : 4-triacetyl β-phenylglucoside gave only non-crystalline products, acetylation of which yielded small amounts of 2 : 3 : 4 : 6-tetra-acetyl β-phenylglucoside. Compounds containing free hydroxyl-groups, *e.g.* 6-*p*-tosyl and 5 : 6-di-*p*-tosyl 1 : 2-*iso*propylidene glucofuranose and 2-*p*-tosyl α-methylarabinoside, were readily converted into sulphur-free materials, but only small quantities of the expected products could be separated in a pure state. Vargha, Puskas, and Nagy (*J. Amer. Chem. Soc.*, 1948, **70**, 261) have recorded that sodium-amalgam reduction of such compounds may lead to the formation of anhydro-sugars, and similar complications may have occurred during hydrogenation.

Simple alkyl toluene-*p*-sulphonates are much less stable in hydroxylic media than the tosyl derivatives of sugars. Their cleavage by hydrogenation is therefore of less interest and may be accompanied by hydrolysis. *lævo*Menthyl toluene-*p*-sulphonate absorbed hydrogen more slowly than the carbohydrate compounds and gave pure *lævo*menthol in moderate yield.

Aryl esters of toluene-*p*-sulphonic acid show a behaviour quite different from that of alkyl esters when their alcoholic solutions are shaken with Raney nickel and hydrogen at atmospheric pressure. About $\frac{1}{2}$ mol. of hydrogen is absorbed rapidly and the products are the aromatic hydrocarbon and nickel toluene-*p*-sulphonate. 1 Mol. of toluene-*p*-sulphonic acid would produce one atom of hydrogen and therefore the reaction may be represented as :

$$(B)\quad 2\mathrm{Ar{\cdot}O{\cdot}SO_2{\cdot}C_7H_7} + \mathrm{Ni} + \mathrm{H_2} \longrightarrow 2\mathrm{ArH} + \mathrm{Ni(O{\cdot}SO_2{\cdot}C_7H_7)_2}$$

This evolution of hydrogen by dissolution of the nickel is to be distinguished from the displacement of hydrogen by chemisorption of sulphur. Nevertheless it is not practicable to use less nickel than 5 times the weight of substance. This reaction also may be carried out by simply boiling an alcoholic solution with Raney nickel. Examples are the formation of methyl benzoate, acetanilide, and anisole from the p-*tosyl* esters of methyl salicylate, *o*- and *m*-acetamidophenol, and resorcinol monomethyl ether. Since naphthalene is readily reduced under these conditions, β-naphthyl toluene-*p*-sulphonate absorbs 2·5 mols. of hydrogen yielding tetralin, no change in the rate of absorption being observed. The practical characteristics of the process render it a useful gentle method for the conversion of phenols into hydrocarbons. These reactions of aryl tosylates are analogous to those of heterocyclic compounds observed by Cavallito and Haskell (*loc. cit.*), and also to the reduction of aryl halides. However, a palladium–calcium carbonate catalyst, which reduced bromobenzene rapidly, was quite without effect on *m*-methoxyphenyl toluene-*p*-sulphonate under the same conditions. It may therefore be more profitable to regard the reaction as the direct displacement of the tosyl group by a hydrogen atom, the homolytic analogue of the acid-catalysed desulphonations of aromatic compounds. The hydrogenations described here provide a contrast to the heterolytic reactions of tosyl esters with nucleophilic reagents which cause C–O fission in the alkyl series and S–O fission in the aryl. Lability of the sulphonyl residue to reduction should favour S–O fission and we have therefore studied the hydrogenation of derivatives of benzylsulphonic acid.

These compounds should provide yet another example of the ready hydrogenolysis of a benzyl group linked to an electronegative atom. In accord with this expectation, the alkyl and the aryl esters of benzylsulphonic acid consumed hydrogen much more rapidly than the corresponding tosyl esters, to the extent of 2 mols., and in all cases the product was the hydroxy-compound. The overall reaction is therefore directly comparable to (*A*) above, although it is hardly likely that the intimate mechanism is the same as in the tosyl series. The examples described in the experimental section require no special comment. Benzylsulphonyl chloride, which is easily prepared from *S*-benzylthiouronium chloride and which usually forms crystalline esters in good yield, is therefore a useful reagent for the protection of hydroxyl groups, analogous to the familiar carbobenzyloxychloride.

In view of the importance of arylsulphonamides for the identification and separation of amines, and the difficulty of their hydrolysis to the amines, it was of interest to see whether these also could be decomposed by hydrogenolysis. Toluene-*p*-sulphonamides were found to be resistant to hydrogenation, but the benzylsulphonanilides readily gave the corresponding anilines under mild conditions, 2 mols. of hydrogen being absorbed as in (*A*) above. The risk of alkylation of the product (cf. Winans and Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 306) may be avoided by carrying out the reaction in dioxan, but the speed is much reduced. Since benzylsulphonyl chloride has already been suggested as an alternative to tosyl chloride in the Hinsberg separation of amines (Marvel and Gillespie, *J. Amer. Chem. Soc.*, 1926, **48**, 2943), this process may be of some practical value.

EXPERIMENTAL.

Aryl toluene-*p*-sulphonates were prepared by treating the phenol with a slight excess of tosyl chloride in pyridine at 100° for 20—30 minutes, and were isolated by pouring the mixture into water, when the products crystallised : *Methyl toluene*-p-*sulphonylsalicylate*, prisms from alcohol, m. p. 85—87° (Found : C, 58·6; H, 4·85. $C_{15}H_{14}O_5S$ requires C, 58·9; H, 4·6%); m-*acetamidophenyl toluene*-p-*sulphonate*, needles from alcohol, m. p. 172—173° (Found : C, 58·7; H, 4·85. $C_{15}H_{15}O_4NS$ requires C, 59·1; H, 4·9%); m-*methoxyphenyl toluene*-p-*sulphonate*, from light petroleum (b. p. 60—80°), m. p. 55—57° (Found : C, 61·1; H, 5·25. $C_{14}H_{14}O_4S$ requires C, 60·5; H, 5·0%).

Methyl Benzylsulphonylsalicylate.—Methyl salicylate (1 g.), benzylsulphonyl chloride (Johnson and Sprague, *J. Amer. Chem. Soc.*, 1937, **59**, 1837) (2·5 g., 2 mols.), and dry pyridine (10 c.c.) were heated for 1 hour at 100°. The mixture was poured into water (300 c.c.), and after 1 hour the solid *product* was collected, and washed with sodium hydroxide and water. Recrystallised from alcohol in needles, it had m. p. 83—84° (Found : C, 58·7; H, 4·5. $C_{15}H_{14}O_5S$ requires C, 58·9; H, 4·6%).

3-*Benzylsulphonyl* 1 : 2-5 : 6-*Di*iso*propylidene* D-*Glucose.*—1 : 2-5 : 6-Di*iso*propylidene D-glucose (5 g.), benzylsulphonyl chloride (3·7 g., 1·1 mols.), and dry pyridine (20 c.c.) were mixed and, after 40 hours, were poured into water (300 c.c.). The *product* was separated by chloroform extraction but could not be crystallised (Found : C, 54·7; H, 6·5. $C_{19}H_{26}O_8S$ requires C, 55·1; H, 6·3%).

β-6-Benzylsulphonyl 1 : 2 : 3 : 4-*tetra-acetyl* D-*Glucose*.—β-1 : 2 : 3 : 4-Tetra-acetyl D-glucose (*Org. Synth.*, 1942, **22**, 56) (1 g.) was treated at 0° with benzylsulphonyl chloride (1 g., 1·9 mols.) in dry pyridine (5 c.c.). Next day the mixture was poured into water (150 c.c.), and the *product* collected and recrystallised from alcohol in needles, m. p. 130—131° (Found : C, 50·1; H, 5·05. $C_{21}H_{26}O_{12}S$ requires C, 50·2; H, 5·2%).

6-*Benzylsulphonyl* 1 : 2-3 : 4-*di*iso*propylidene* D-*Galactose*.—A mixture of 1 : 2-3 : 4-di*iso*propylidene D-galactose (Freudenberg, *Ber.*, 1925, **58**, 296) (10 g.), benzylsulphonyl chloride (12 g., 1·6 mols.), and dry pyridine (30 c.c.) was left for 7 hours and then poured into water. The *product* crystallised from ethyl acetate–light petroleum in needles, m. p. 148—149° (Found : C, 55·1; H, 6·6. $C_{19}H_{26}O_8S$ requires C, 55·1; H, 6·3%).

lævo*Menthyl Benzylsulphonate*.—*lævo*Menthol (9·3 g.) in dry pyridine (30 c.c.) was cooled in ice, and benzylsulphonyl chloride (11·5 g., 1 mol.) was added gradually with shaking. After 2 hours the mixture was poured into water (400 c.c.), and the *product* collected and recrystallised from alcohol in needles, m. p. 66—67°, $[\alpha]_D^{16°}$ −57·0° ± 1° (*c*, 2·8 in chloroform) (Found : C, 65·5; H, 8·1. $C_{17}H_{26}O_3S$ requires C, 65·8; H, 8·4%).

Preparation of Raney Nickel Catalysts.—These catalysts were prepared by the modified Mozingo method (*Org. Synth.*, 1941, **21**, 15; *J. Amer. Chem. Soc.*, 1943, **65**, 1013). In some experiments the " W-6 " catalyst of Adkins and Billica (*loc. cit.*) was used. These catalysts were measured by volume, the weights quoted being based on the relationships 3 g. ≡ 5 c.c. for ordinary nickel and 4 g. ≡ 5 c.c. for " W-6 ".

Hydrogenations at Atmospheric Pressure and Room Temperature.—These were carried out in ethanol solution (120—300 c.c.). When absorption of hydrogen was complete, the catalyst was removed by centrifugation and washed thoroughly with alcohol. Isolation of the products was achieved by evaporation of the solvent and crystallisation, or, in the case of the aromatic compounds, ether extraction combined with aqueous washing to remove nickel toluene-*p*-sulphonate. Except with the benzylsulphonic esters poisoning of the catalyst slows the reaction markedly, and therefore the times quoted are not a good indication of the initial reaction velocities.

Substance.	Wt. (g.).	Wt. of catalyst (g.).	Time (hrs.).	Mols. of H_2 absorbed.	Product.
Tosyl derivative of:					
1 : 2-5 : 6-Di*iso*propylidene glucose	0·5	6	2	2	Di*iso*propylidene glucose (96%)
1 : 2-*iso*Propylidene glucose :					
(6-Tosyl)	1	6	24	2	*iso*Propylidene glucose (39%)
(5 : 6-Ditosyl)	1	6	24	4	*iso*Propylidene glucose (25%)
2 : 3 : 4-Triacetyl β-phenyl-glucoside	0·39	13 (" W-6 ")	1·5	2	Not identified
*lævo*Menthol	1	6	8	2	*lævo*Menthol (45%)
β-Naphthol	10	35	12	2·5	Tetralin (43%)
Methyl salicylate	1	6	0·03	0·5	Methyl benzoate (as benzoic acid, 80%) *S*-Benzylthiouronium toluene-*p*-sulphonate (60%)
m-Acetamidophenol	1	6	0·5	0·5	Acetanilide (90%)
Aniline	0·5	3	5	1·3	Reaction incomplete
Benzylsulphonyl derivative of:					
1 : 2-5 : 6-Di*iso*propylidene glucose	0·6	6	0·25	2	Di*iso*propylidene glucose (100%)
1 : 2-3 : 4-Di*iso*propylidene galactose	2	6	0·25	2	Di*iso*propylidene galactose (95%) (identified as the tosyl ester)
1 : 2 : 3 : 4-β-Tetra-acetyl glucose	1	6	0·15	2	An oil, from which some β-penta-acetyl glucose was obtained on acetylation
Methyl salicylate	2	6	0·35	2	Methyl salicylate, as salicylic acid (57%)
*lævo*Menthol	2	6	0·35	2	*lævo*Menthol (86%)
Aniline	10	30	3	2	Aniline, as the toluene-*p*-sulphonamide (53%)
N-Ethylaniline	1	6	0·35	2	*N*-Ethylaniline (44%) as the toluene-*p*-sulphonamide

Hydrogenations under Mozingo Conditions.—(*a*) The sulphonic ester (1 g.) was boiled with Raney nickel (5 g.) in ethanol (50 c.c.) for 3 hours. Under these conditions the following compounds gave the same products as described in the table : the *p*-tosylates of di*iso*propylidene glucose, β-naphthol, methyl salicylate, and *m*-acetamidophenol, and the benzylsulphonates of methyl salicylate and di*iso*propylidene glucose.

(*b*) Under similar conditions but with a reaction time of 7 hours, di*iso*propylidene galactose (71%) was recovered from the corresponding tosyl ester. The hydrogenolysis of 2-*p*-tosyl α-L-methylarabinoside under the same conditions gave a non-crystalline product, from which α-L-methylarabinoside (30%) was isolated. *lævo*Menthyl toluene-*p*-sulphonate, which was incompletely converted after 3 hours' reaction with nickel in *cyclo*hexane, did not yield the required product after 7 hours' heating.

Hydrogenation in Other Solvents.—The hydrogenation of tosyl di*iso*propylidene glucose could be carried out equally well by refluxing with Raney nickel in ether or *cyclo*hexane solution for 3 hours, while the fission of *m*-acetamidophenyl toluene-*p*-sulphonate took place smoothly in dioxan solution under the same conditions.

When the hydrogenation of benzylsulphonanilide at room temperature was carried out in dioxan solution, the initial rate of absorption of hydrogen was only a quarter of that observed with similar quantities in ethanol, and 4 hours were necessary to complete the reaction instead of 20 minutes.

Noble-metal Catalysts.—Attempts to hydrogenate *p*-tosyl di*iso*propylidene glucose (0·5 g.) with 5% palladium–barium sulphate (Mozingo, *Org. Synth.*, 1946, **26**, 77) or Adams's platinic oxide at room temperature and pressure and at 70° under 110 atm. were unsuccessful. No hydrogen was absorbed in the attempted hydrogenation of *m*-methoxyphenyl toluene-*p*-sulphonate (1 g.) with 1% palladium–calcium carbonate (Busch and Weber, *J. pr. Chem.*, 1936, **146**, 1) (1 g.) in the presence of potassium hydroxide (0·5 g.) in alcohol.

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