The Preparation of *tert*-Butylsuccinic Acid

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In a recent publication [1] the conjugate addition of Grignard reagents to maleic esters to give alkylsuccinic esters was described. The directions for the preparation of *tert*-butylsuccinic esters seem, however, to be insufficient to secure the yields reported. Some additional details of the procedure used should therefore be given.

For the preparation of the Grignard reagent from *tert*-butyl chloride directions are given in Ref. [2]. The amount of Grignard reagent required is 4.0 equiv. (In Ref. [1], Table 1, foot-note [g] the amount is erroneously reported to be 0.4 equiv.). Thus for 0.2 mole of ester the Grignard reagent from 0.8 mole of *tert*-butyl chloride should be used. The copper(I) chloride catalyzed addition reaction to give tert-butylsuccinic ester was otherwise carried out essentially as described in previous communications [1-4].

The Grignard reagent (0.8 mole in 500 ml of ether) was cooled in an ice-salt bath (−10 − −18°) for 15 min. The ester, dissolved in 200 ml of ether, was added during 2 h. Concurrently with the ester, 1.4 g of copper(I) chloride (1.75 mole % with respect to the Grignard reagent) was added in seven 0.2 g portions. After further stirring and cooling of the reaction mixture for 15 min, the ice-salt bath was removed, and the stirring was continued at room temperature. After 1 h, another 0.2 g of copper(I) chloride was added, and after another 1 h of stirring the reaction mixture was worked up the conventional way [4].

The *tert*-butylsuccinic acid was isolated as reported in Ref. [1].

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Sulphones of Some Lignin Models

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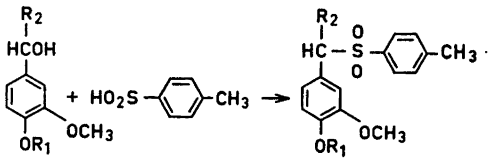
In the reaction between lignin and sulphite, the benzyl alcohol or ether groupings in the lignin are transformed into sulphonic acids. The reaction between lignin and a sulphinic acid would likewise be expected to give sulphones. Hinsberg [1] and Kenyon and coworkers [2,3] have also prepared sulphones from benzyl alcohols and benzhydrols by this method. The introduction of the strongly electron attracting sulphone group into lignin presents a possible approach to the controlled degradation of this product. To study this possibility, the initial step was to study the reaction between some simple model substances (I−IV) and *p*-toluene sulphinic acid.



I $R_1 = R_2 = H$
II $R_1 = CH_3$; $R_2 = H$
III $R_1 = H$; $R_2 = CH_3$
IV $R_1 = R_2 = CH_3$

Vanillyl alcohol (I) and 1-(4-hydroxy-3-methoxyphenyl)-ethanol (III), in which the reactivity of the alcoholic group is enhanced by the *p*-hydroxyl substituent, reacted readily at pH 4.5 and 100°. Veratryl alcohol (II) and 1-(3,4-dimethoxyphenyl)-ethanol (IV) reacted more readily under acid conditions. Aqueous acetic acid, to which a small amount of sulphuric acid had been added, and a reaction temperature of 100° proved to be satisfactory conditions for the preparation of all the four sulphones. These were obtained in good yields as crystalline, easily purified substances. The sulphone from vanillyl alcohol was also formed at room temperature and a longer reaction time.

Experimental. Melting points are corrected. *(4-Hydroxy-3-methoxyphenyl)-methyl p-tolyl-sulphone.* (*a*) Vanillyl alcohol (1.00 g) and

sodium *p*-toluene sulphinate containing 4 moles of water of crystallisation (1.62 g) were dissolved in 1 M acetate buffer of pH 4.5 (40 ml) and kept at 100° for 3 h. The mixture, which crystallised during the heating, was kept overnight at 0° and the crystals (0.94 g), m.p. 169–172°, filtered off and washed with water.

(*b*) The same amounts of vanillyl alcohol and sodium *p*-toluene sulphinate were dissolved in 3 M aqueous acetic acid (40 ml) to which two drops of sulphuric acid were added. The mixture was kept at 100° for 3 h and worked up as above, yielding the crystalline product (1.72 g), m.p. 171–175°.

Recrystallisations from ethanol or benzene yielded the pure substance, m.p. 175–176°. (Found: OCH_3 10.3; S 11.0. $C_{15}H_{16}O_4S$ requires: OCH_3 10.6; S 11.0).

(3,4-Dimethoxyphenyl)-methyl p-tolylsulphone. Veratryl alcohol (1.00 g) and sodium *p*-toluene sulphinate (1.49 g), treated as described in (*b*) above, also yielded a sulphone (1.10 g), m.p. 176–177° after crystallisation from ethanol. (Found: OCH_3 20.2; S 10.4. $C_{16}H_{18}O_4S$ requires: OCH_3 20.3; S 10.5).

1-(4-Hydroxy-3-methoxyphenyl)-ethyl p-tolylsulphone. The alcohol (apocynol, III) was prepared by borohydride reduction of (4-hydroxy-3-methoxy)-acetophenone, essentially as described by Adler and Hernestam [4]. A large excess of borohydride was maintained during the whole reaction by adding fresh amounts of borohydride to the system at intervals.

Apocynol (0.20 g), sodium *p*-toluene sulphinate (0.33 g) and a drop of sulphuric acid were dissolved in a mixture of ethanol (3 ml) and 3 M acetic acid (5 ml) and the mixture kept on the steam bath for 3 h. The oily product which separated during the reaction, crystallised on cooling (0.35 g) and after crystallisation from ethanol afforded the pure sulphone (0.31 g), m.p. 119–121°. (Found: OCH_3 9.8; S 10.5. $C_{16}H_{18}O_4S$ requires: OCH_3 10.1; S 10.5).

1-(3,4-Dimethoxyphenyl)-ethyl p-tolylsulphone. 1-(3,4-Dimethoxyphenyl)-ethanol (0.24 g) and one drop of sulphuric acid were added to a mixture of 3 M acetic acid (5 ml) and ethanol (1 ml) which was then heated on the steam bath for 3 h and worked up as above, yielding the sulphone (0.33 g). The product, after crystallisation from ethanol and benzene, melted at 124–126°. (Found: OCH_3 19.2; S 9.8. $C_{17}H_{20}O_4S$ requires: OCH_3 19.4; S 10.0).

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The Supposed Existence of two Molecular Forms in Crystals of Acetyl Choline Bromide

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X-Ray diffraction data from crystals of acetyl choline bromide have been interpreted in terms of a monoclinic unit cell $a = 11.10$ Å, $b = 13.67$ Å, $c = 7.18$ Å, $\beta = 110.0°$, space group $P2_1$, containing 4 molecules, and a structure has been proposed in which the two acetyl choline ions in the asymmetric unit occur as distinct conformational isomers [1]. The analysis, however, was complicated by the presence in the X-ray photographs of weak, subsidiary reflexions that are not accounted for by the proposed structure.

The main features of these extra reflexions have been described [2] as follows:

(1) *h0l* reflexions with *h* odd are absent but subsidiary reflexions occur slightly displaced from these points.

(2) *h0l* reflexions with *h* even, *l* even have subsidiary reflexions; those with *h* even, *l* odd do not.

(3) *hkl* reflexions have subsidiary reflexions for all values of *h* und *l*.

(4) *hk*0 reflexions are not accompanied by subsidiary reflexions.

It was also mentioned (*i*) that the displacement of the subsidiary reflexions from the ideal reciprocal lattice points decreases towards *hk*0, and (*ii*) that the subsidiary reflexions occur on only one side of the principal reflexions.

The purpose of the present communication is to point out that all these and other features of the subsidiary reflexions can be simply accounted for if it is assumed that the space group is not $P2_1$ but $P2_1/a$ and that the crystals are twinned across the $(10\bar{2})$ plane. Since $2c^* \cos\beta^*/a^*$ is nearly equal to unity (1.057) the *hkl* re-