# REACTION OF ARYLSULFONYL COMPOUNDS WITH EXCESS OF ORGANOLITHIUM REAGENT—V<sup>15</sup> ADDITION OF t-BUTYL-ortho-LITHIUMPHENYL SULFONE TO 3-LITHIUM-1,2-DEHYDROBENZENE. A NEW REARRANGEMENT IN THE BIPHENYL SERIES

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Abstract—The reaction of t-butyl phenyl sulfone (Ia) with n-butyllithium at -20 to  $-30^{\circ}$  in THF-ether leads to lithium (2<sup>1</sup>-t-butyl-6<sup>1</sup>-lithium-biphenyl)sulfinate (VI). On hydrolysis 2<sup>1</sup>-t-butylbiphenyl-2sulfinic acid (VII) was obtained whereas carboxylation led to 6<sup>1</sup>-carboxy-2<sup>1</sup>-t-butylbiphenyl-2-sulfinic acid (VIIIa). The structures were confirmed by physical methods as well as by hydrodesulfurization and by cyclization to the dibenzothiophene derivatives under Friedel-Crafts' conditions. A mechanism is suggested for the observed reaction, involving the addition of the ortho-lithium derivative of t-butyl phenyl sulfone (II) to 3-lithium-1,2-dehydrobenzene (IV) followed by rearrangement. The rearrangement includes t-Bu migration from a sulfonyl group to an adjacent aromatic nucleus of biphenyl.

EARLIER papers<sup>1-5</sup> reported the action of three or more moles of alkyl-lithium on one mole of t-butyl phenyl sulfone (I) with elimination of lithium t-butyl sulfinate and formation of 2,6-dilithium-1-alkylbenzene. Metalation of sulfone (Ia) ortho to the t-butylsulfonyl group is the first step of this complex reaction. Ortho-lithium-phenyl-t-butyl sulfone (II) can be readily obtained by using equivalent quantities of reagents.

In an attempt to detect a 2,6-dilithium derivative of t-butyl phenyl sulfone (III, scheme 1) and thus clarify the mechanism of the conversion, we reacted t-butyl phenyl sulfone (Ia) with n-BuLi in ether-THF at a lower temperature  $(-20 \text{ to } -30^\circ)$  than that normally used to obtain 2,6-dilithium-1-alkylbenzenes.<sup>4</sup> After the mixture had been treated with water and the water layer acidified, an acid was unexpectedly isolated which proved to be 2<sup>1</sup>-t-butylbiphenyl-2-sulfinic acid (VII, scheme 1). The IR spectrum of VII shows S=O absorption at 1055 cm<sup>-1</sup> and two bands at 1400 and 1370 cm<sup>-1</sup> with intensity ratios 1:2 characteristic of t-butyl stretching frequences. Five hydrogens connected to the ring produce a band at 700 cm<sup>-1</sup>. No such band was observed in the spectrum. NMR analysis of the methyl ester of VII shows an unresolved multiplet due to aromatic protons, however the integration curve reveals one proton at low field. Hence the position next to an electron attracting SO<sub>2</sub>H-group is occupied by some other substituent (in our case the benzene ring).

By hydrodesulfurization of VII over Raney nickel 2-t-butylbiphenyl (XIII, scheme 2) was obtained. This proves unambiguously that the t-Bu group occupies position 2. We were able to convert VII to sulfinyl chloride (XI) which is readily cyclized by aluminium chloride with elimination of t-Bu to form dibenzothiophene-5-oxide (XII). Hence the sulfinic group occupies the 2 position of the adjacent ring. Since 2-t-butyl- $2^1$ -methylsulfonylbiphenyl (XV, scheme 2) conventionally obtained from VII and



methyl iodide underwent no transformation under conditions of sulfinyl chloride cyclization, it seems unlikely that elimination of the t-Bu is an independent process, although similar eliminations are encountered in practice.<sup>6</sup> Apparently C—S bond formation proceeds via the C atom left by the t-Bu group.

The bulky t-Bu created an angle of about 90° between the planes of the benzene rings of biphenyl thus obstructing ring conjugation. The absence of absorption in UV spectra of 2-t-butylbiphenyl (XIII) and VII at 250 nm typical for unsubstituted biphenyl<sup>7</sup> is in line with the suggestion. Transition from VII to a plane conjugate system of dibenzothiophene gives a gain in energy thus facilitating cyclization.

Cyclization of VII with elimination of t-Bu proceeds under other conditions. For instance by heating VII under reflux in acetic anhydride it was possible to isolate dibenzothiophene (IX) (Scheme 2), which can result from S-oxide (XII) disproportionation.

Carboxylation of the mixture prepared from sulfone (Ia) and n-BuLi under the same conditions as VII produced 61-carboxy-21-t-butylbiphenyl-2-sulfinic acid (VIIIa) (Scheme 1). After hydrodesulfurization of VIIIa, 6-t-butyl biphenyl-2carboxylic acid (XIV, scheme 2) was obtained. The position of the COOH group was established as follows: acid VIII had been converted to dibenzothiophene-1carboxylic acid (X, scheme 2) by heating under reflux in acetic anhydride. The alternative position of the COOH group in the same ring as the SO<sub>2</sub>H-group can be rejected since the NMR spectra of carboxy sulfinic acid (VIIIb, scheme 1) which has an analogous structure and was obtained under similar conditions from t-butylp-tolyl-sulfone. NMR spectra display chemical shifts of protons labelled by the adjacent electron-acceptor group at lower fields compared with other aromatic protons and the number of protons at low fields can be estimated from the integral intensities of signals due to protons. Thus, the isomeric 6<sup>1</sup>-carboxy-2<sup>1</sup>-t-butyl-4<sup>1</sup>,5dimethyl biphenyl-2-sulfinic (VIIIb) and 5-carboxy-21-t-butyl-41,5-dimethylbiphenyl-2-sulfinic acids must have respectively two and one labelled protons. The integral intensity curve revealed signals due to two protons at low fields thus supporting the structure proposed.

Hence sulfone (Ia) reacts with n-BuLi at  $-20 - 30^{\circ}$  in THF-ether to give the lithium (2<sup>1</sup>-t-butyl-6<sup>1</sup>-lithium-biphenyl-2) sulfinate (VI). Its hydrolysis yields the



acid VII and its carboxylation carboxy sulfinic acid (VIII, scheme 1). According to stoichiometry 2 moles of sulfone and 3 moles n-BuLi are needed for such a conversion. In practice, however, better yields obtained if excess n-BuLi is used. The THF is important, as only a small quantity of lithium derivative (VI) is obtained if ether only is used.

Formation of lithium compounds (VI) is the result of an unusual rearrangement involving migration of the t-Bu from the sulfonyl group to the ortho position of the adjacent aromatic ring. This fact is supported by the reaction sequence suggested for the competitive reaction of sulfone (Ia) with MeLi and BuLi and is important evidence in favour of an unstable intermediate. The intermediate is believed to be 3-lithium-1,2-dehydrobenzene (IV) and is capable of adding a relatively weak nucleophile. An analogous situation arises if the reaction is performed at a lower temperature. In addition to 2,6-dilithium compound (III) which evidently easily eliminates lithium t-butyl sulfinate to give 3-lithium-1,2-dehydrobenzene (IV, scheme 1) some monolithium compound (II) is formed. This acts as a nucleophile, attacking the dehydro bond and follows the addition sequence proposed for alkyllithium. We could not identify  $2^1$ , $6^1$ -dilithium-2-t-butylsulfonyl biphenyl (V) which must result from this addition. The position of the t-butyl-sulfonyl group close to the anion centre of the adjacent aromatic ring seems to be responsible for the high rate of rearrangement which results in formation of the lithium derivative (VI).

Another interpretation of this rearrangement may involve simultaneously attack of sulfonyl carbanion on the triple bond through a cyclic 6-membered transition state. This pathway however is not supported in the recent data concerning olefine stepwise addition to arynes.<sup>8,9</sup>

A similar rearrangement is the Truce rearrangement which a mechanism has been elucidated Drozd *et al.*<sup>10,11</sup>



This conversion involves the intramolecular nucleophilic aromatic  $S_N 2$  substitution of a arylsulfonyl group by a benzyl anion. The essential difference in the present rearrangement is that substitution of the arylsulfonyl group by the phenyl anion occurs at a saturated C atom. The process appears to be intramolecular otherwise a greater number of products would be expected. The absence of compounds which differ in the point of attachment of t-Bu group affords additional evidence of the reaction as an intramolecular  $S_N 2$  substitution. We intend to study this problem later.

It is of interest that an increase in the reaction time at room temperature, results in migration of a lithium atom in VI (evidently, intermolecularly) from position "6" to position " $3^1$ ", to substitute a more acidic H atom and to form a more stable lithium compound (XVI, scheme 3). After the mixture had been carboxylated and acidified  $2^1$ -t-butyl biphenyl-3,2-carboxy-sulfinic acid anhydride (XVII) was isolated. The positions of t-butyl and sulfinic groups were established by hydrolysing the



mixture to acid VII. When anhydride XVII underwent Raney nickel hydrodesulfurization  $2^1$ -t-butyl biphenyl-3-carboxylic acid (XVIII) was obtained which differs naturally in its properties from acid XIV (Scheme 2).

#### **EXPERIMENTAL**

UV spectra were measured in EtOH and NMR spectra were determined in CCl<sub>4</sub> using HMDS as internal standard. M.ps were determined using a Kofler hot stage microscope and are uncorrected.

#### 2<sup>1</sup>-t-Butylbiphenyl-2-sulfinic acid (V11)

(a) To 10 g (0.05 mole) of Ia in 100 ml abs THF at  $-70^{\circ}$ , 0.1 mole of 2N n-BuLi in ether was added with stirring. After 2 hr stirring at  $-40^{\circ}$  and 1.3 hr at 0° the mixture was poured into water. The water layer was separated, washed with ether and acidified with dil HCl. The isolated oil crystallized when allowed to stand in a refrigerator. 3.7 g (54%) of VII was obtained, m.p. 115-118°; after recrystallization from dilute EtOH m.p. 123-125°. (Found: C, 70-38; 70-12; H, 6-63; 6-42: S, 11-71; 11-57; C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>S requires: C, 70-04; H, 6-61; S, 11-66°, 0).

Neutralization equiv.: Found: 279; requires: 274.4. IR spectrum (KBr):  $1055 \text{ cm}^{-1}$  (S=O), 1400 and 1370 cm<sup>-1</sup> with an intensity ratio of 1:2 (t-Bu); absorption is absent in the field of 700 cm<sup>-1</sup> (absence of mono-substitution in the benzene ring). The *methyl ester of acid* (VII) was obtained by the action of diazomethane in ether soln, m.p. 119-123° from hexane. (Found: C, 70-77; 70-57; H, 695; 694; S, 11-18; 11-17; C<sub>1.7</sub>H<sub>20</sub>O<sub>2</sub>S requires: C, 70-79; H, 698; S, 11-12). IR spectrum (KBr): 1130 cm<sup>-1</sup> (S=O), 1400 and 1370 cm<sup>-1</sup> with intensity ratio of 1:2 (t-Bu).

(b) The mixture obtained from the same amounts of reagents as in method A was kept at 0° and then was allowed to stand overnight at room temp. After an analogous treatment acid, VII was obtained in 38% yield.

(c) To 6 g (0.03 mole) of la in 150 ml THF at  $-70^{\circ}$ , 0.12 mole of 2N n-BuLi in ether was added with stirring. After stirring for 5 hr at  $-20-30^{\circ}$  the mixture was poured into water. Following the method (a), 54% of VII was obtained.

 $2^{1}$ -t-Butylbiphenyl-2-sulfonic acid was obtained through potassium permanganate oxidation of VII in

alkaline solution, it was isolated as benzylisothiuronium salt, m.p. 223-224° from dilute EtOH. (Found : C, 63.06; 62.89; H, 6.04; 6.11; S, 14.10; 13.99; C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub> requires: C, 63.13; H, 6.18; S, 14.04%).

*Hydrodesulfurization of acid* (VII) *in 2-t-butylbiphenyl* (XIII). 2 g of VII in 130 ml ether was refluxed for 7 hr with 30 g Raney Ni. The ether soln was decanted from the Ni residue, the solvent was removed and the residue was extracted with benzene. After removal of benzene the residue was distilled at 95-100° (0·1 mm, bath temp). 1 g (65  $^{\circ}_{6}$ ) of XIII was obtained, m.p. 37-38-5° from dil MeOH.<sup>9</sup> (Found: C, 91-23; 91-02; H, 8-47; 8-69; C<sub>16</sub>H<sub>18</sub> requires: C, 91-37; H, 8-63  $^{\circ}_{6}$ ); IR spectrum (KBr): 715, 760 and 775 cm<sup>-1</sup> (2-substituted biphenyl).<sup>12</sup> 1400 and 1370 cm<sup>-1</sup> with an intensity ratio of 1.2 (t-bu).

Dihenzothiophene-5-oxide (XII). 1 g of VII and 10 ml SOCl<sub>2</sub> were refluxed for 2 hr, the excess SOCl<sub>2</sub> was removed under vacuum, the resulting oil was dissolved in 20 ml dichloroethane and 0.5 g anhyd AlCl<sub>3</sub> was added at 0°. After stirring for 20 min at 0° the mixture was heated to room temp and allowed to stand overnight. The mixture was poured into water, the organic layer was separated, washed with 5% NaOH aq, with water and dried. After removal of the solvent, 0.4 g (55%) of XII, m.p. 185-187°, was obtained from dil EtOH. The m.p. was not depressed with a known specimen.<sup>13</sup>

2-t-Butyl-2<sup>1</sup>-methylsulfonylhiphenyl (XV). To 1 g of VII in 6 ml abs MeOH NaOMe in MeOH was added until the reaction was alkaline to litmus. It was then mixed with 5 ml of MeI and refluxed for 3 hr. The soln was evaporated, water was added, and the crystals were filtered off and washed with dilute alkali and water, 0-57 g of XV was obtained, m.p. 105-106° from EtOH. (Found: C, 70-60; 70-83; H, 6-86; 7-03; S, 11-25; 11-27; C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>S requires: C, 70-80; H. 6-99; S, 11-12%); IR spectrum (KBr): 1150 and 1310 cm<sup>-1</sup> (SO<sub>2</sub>-group).

Dibenzothiophene (IX) from acid (VII). 1 g of VII was heated at boiling in 10 ml Ac<sub>2</sub>O. The anhydride was removed under vacuum, the residue was dissolved in hexane. On evaporating the soln, the residue was sublimated at  $150^{\circ}/0.1$  mm. The sublimated product was dissolved in 5 ml hot alcohol, filtered from the residue, concentrated to the volume of 2 ml and then cooled. The precipitated crystals were filtered off. 0-05 g IX, m.p. 98-5-99-5° (after several recrystallizations from EtOH) was obtained, which was identical (mixing test and TLC) with a known specimen.

 $6^{1}$ -Carboxy-2<sup>1</sup>-t-butylbiphenyl-2-sulfinic acid (VIIIa). The mixture obtained from 10 g (0.05 mole) of I in 100 ml THF under the conditions of acid synthesis by method (a) was poured on excess solid CO<sub>2</sub> in ether. After analogous treatment a 40% yield of VIIIa was obtained, m.p. 160–163° from acetonitrile. (Found : C, 64-50; 64-36; H, 5-66; 5-68; S, 10-04; 10-02; Neutralization equiv. 159-8; 160-5; C<sub>17</sub>H<sub>18</sub>O<sub>4</sub>S requires : C, 64-13; H, 5-70; S, 10-06%; neutralization equiv. 159-2).

The dimethyl ester of acid (VIIIa) was obtained by treatment with  $CH_2N_2$ ; m.p. 96–98° from hexane. (Found: C, 65-76; 65-77; H, 6-23; 6-37; S, 9-33; 9-36; Mol. weight: 346 (mass-spectrom.)  $C_{19}H_{22}O_4S$  requires: C, 65-87; H, 6-40; S, 9-34  $\frac{9}{10}$ ; Mol. weight 346.

Dibenzothiophene-1-carboxylic acid (X) from acid (VIIIa). 0-3 g of VIIIa was refluxed with 15 ml Ac<sub>2</sub>O. The solvent was removed under vacuum, the residue was treated with benzene, the soln was then filtered free from tar, benzene was removed and the product obtained was sublimated at  $200^{\circ}/0.2$  mm. 0-07 g of X was obtained, m.p.  $176-177^{\circ}$  from a mixture of hexane with benzene. (Found: C, 68-49; 68-69; H, 3-72; 3-51; S, 13-98; 14-19; C<sub>1.3</sub>H<sub>8</sub>O<sub>2</sub>S requires: C, 68-40; H, 3-53; S, 14-03%). The methyl ester of X had m.p.  $68-69^{\circ}$ .

 $6^{1}$ -Carboxy- $2^{1}$ -t-butyl- $4^{1}$ ,S-dimethylbiphenyl-2-sulfinic acid (VIIIb) was obtained in 5.2% yield under the same conditions as VIIIa, m.p. 120–122° from dilute EtOH. (Found: C, 65.64; 65.57; H, 6.73; 6.48; S, 9.20; 9.07; C<sub>1.9</sub>H<sub>22</sub>O<sub>4</sub>S requires: C, 65.87; H, 6.40; S, 9.25%).

 $2^{1}$ -t-Butylbiphenyl-3,2-carboxy-sulfinic acid anhydride (XVII). The mixture obtained under the conditions of method (b) was poured on solid CO<sub>2</sub> in ether, water was then added, the ether layer was separated, the water layer was washed with ether and acidified yielding 21% of XVII, m.p. 168–170° from acetonitrile. (Found: C, 68-35; 68-45; H, 5-62; 5-74; S, 10-65; 10-68; Mol. weight 300 (mass-spectrometr.) C<sub>17</sub>H<sub>16</sub>O<sub>3</sub>S requires: C, 67-97; H, 5-37; S, 10-67%; Mol. weight 300-4).

*Hydrodesulfurization of acid* (VIIIa) to 6-t-butylbiphenyl-2-carboxylic acid (XIV). 1 g of VIIIa was dissolved in 70 ml 75%-alcohol and refluxed for 3 hr with excess Raney Ni. The solution was decanted from Ni, evaporated and the residue was extracted with 10% NaOH. The alkaline extract was filtered and acidified with dil HCl yielding XIV (0.6 g, 75%), m.p. 184–185° from dilute EtOH. (Found: C, 79.81; 79.92; H, 7.13; 7.31;  $C_{12}H_{18}O_2$  requires: C, 80-20; H, 7.12%). The methyl ester of XIV had b.p. 130°/01 mm (bath temp  $n_D^{20}$  1,5590. (Found: C, 80.48; 80.64; H, 7.54; 7.72;  $C_{18}H_{20}O_2$  requires: C, 80-56; H, 7.47%).

Hydrodesulfurization of anhydride (XVII) to  $2^{1}$ -t-butylhiphenyl-3-carboxylic acid (XVIII). 0.8 g of XVII was dissolved in 60 ml of warm 5% NaOH aq and refluxed for 3.5 hr with 15 g of Raney Ni. The alkaline

soln was filtered and acidified. 0.55 g (82°.,) XVIII, m.p. 202° from acetonitrile, was obtained. (Found: C, 79.87; 79.84; H, 7.05; 6.96;  $C_{17}H_{18}O_2$  requires: C, 80.56; H, 7.47%). The methyl ester had m.p. 72-75° from MeOH. (Found: C, 80.00; 79.63; H, 7.50; 7.50;  $C_{18}H_{20}O_2$  requires: C, 80.56; H, 7.47%).

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