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THE REACTION OF ARYLSULFONYL COMPOUNDS WITH THE EXCESS OF ORGANOLITHIUM REAGENT—IV[1]

THE ACTION OF n-BUTYL-LITHIUM ON t-BUTYL-1-NAPHTHYL-SULFONE. THE MECHANISM OF SUBSTITUTION OF t-BUTYLSULFONYL GROUP

F. M. STOYANOVICH, R. G. KARPENKO, YA. L. GOL'DFARB
N. D. Zelinsky Institute of Organic Chemistry, USSR Academy of Sciences, Moscow

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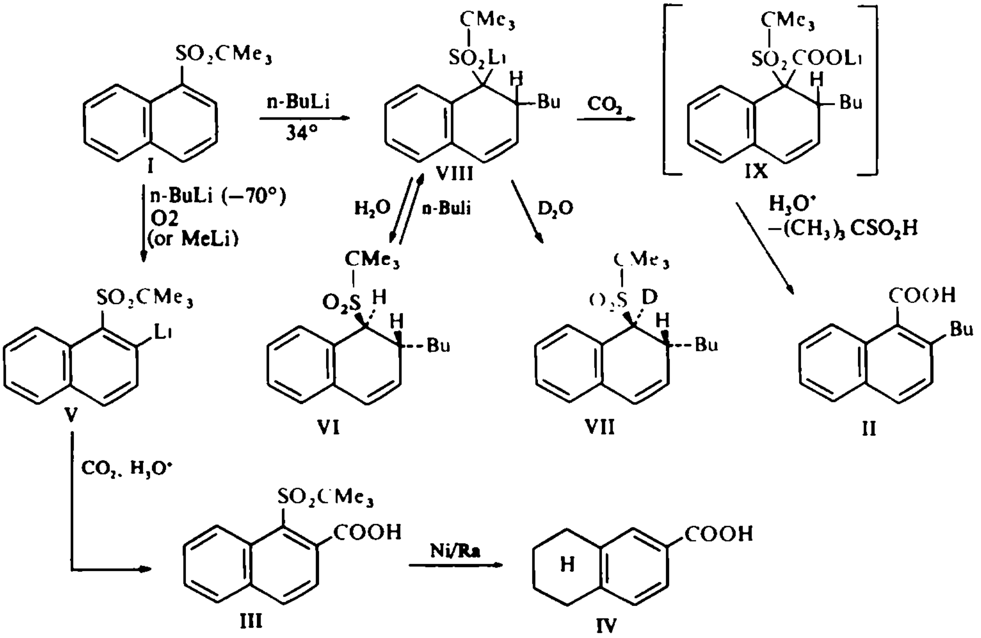
Abstract—n-BuLi was reacted with t-butyl-1-naphthyl sulfone (I) in refluxing ether followed by either carbonization of hydrolysis to give 2-n-butyl naphthoic acid and trans-1,2-dihydro-1-t-butylsulfonyl-2-n-butylnaphthalene respectively. The most likely mechanism involves first 1,2 addition of BuLi to sulfone (I) and, in subsequent step, t-butylsulfinic acid elimination. MeLi metalates sulfone (I) at C—2 of the ring.

EARLIER papers[1-5] reported that three equivalents of RLi (R=Et, n-Pr and n-Bu) convert t-butyl phenyl sulfone to 2,6-dilithium-1-alkylbenzene and lithium t-butylsulfinate. It was observed that only one hydrogen in the ortho position to the t-butylsulfonyl group was replaced by the action of MeLi.

SCHEME 1



At this point it seemed relevant to study the interaction of these organolithium reagents with t-butyl-1-naphthyl sulfone (I).[6] We were surprised to find that the sulfone (I) when treated with three equivalents of BuLi in refluxing ether reacted to give, after carbonization of the reaction mixture, 2-n-butylnaphthoic acid (II) (Scheme 1). The same result was obtained by using a one-to-one ratio of reactants.

2-n-butyl-1-naphthoic acid has been isolated by Huisgen and Zirngibl[7] from its mixture with isomeric, 1-n-butyl-2-naphthoic acid. Both of the isomers have been obtained by the reaction of 1-fluoronaphthalene with n-BuLi followed by carbonization. The repetition of this experiment provided for us a mixture of 2-n-1-naphthoic and 1-n-butyl-2-naphthoic acids. The former was found to be the same as II on gas-chromatographic of its ester and on consideration of a characteristic band at 748 cm^{-1} in the IR-spectrum. No other isomer was found in the crude acid, obtained from sulfone (I) (a minor unidentified compound was however detected).

The mechanism which has been proposed to account for fluoro-displacement in 1-fluoronaphthalene includes metalation at C-2, LiF elimination and 1,2-dehydronaphthalene formation followed by addition of excess of the organolithium reagent. Subsequent carbonization results in formation of the alkylnaphthoic acid mixture, the composition of the latter being independent of the starting halogenonaphthalene.

The absence of the second isomer in our case clearly indicates that the displacement proceeds by a different path for t-butylsulfonyl group as compared to fluorine.

With this consideration in mind we attempted to elucidate the mechanism which is consistent with the observation presented. The following facts emerged.

The sulfone (I) was allowed to react with n-BuLi in refluxing ether, followed by hydrolysis, to give trans-1,2-dihydro-1-t-butylsulfonyl-2-n-butylnaphthalene (VI). The structure and geometry of VI could be unambiguously established with the aid of elementary analysis and IR and NMR spectra. The treatment of the reaction mixture with D_2O enabled us to obtain trans-1,2-dihydro-1-D-1-t-butylsulfonyl-2-n-butylnaphthalene (VII). The IR spectrum of VI showed strong absorption at 1115 and 1290 cm^{-1} (SO_2-stretching). The NMR spectrum of VI (see fig. 1) showed a intensive singlet at $\delta = 1{\cdot}47$ ppm ascribable to protons of t-C_4H_9 group overlapped with multiplet due to n-C_4H_9 group and multiplet at $\delta = 7{\cdot}0$–$7{\cdot}8$ ppm attributable to four aromatic protons. Besides that it displayed signals due to H-1 slightly broadened single peak at $\delta = 4{\cdot}4$ ppm, H-2 (unresolved multiplet at $\delta = 3{\cdot}1$–$3{\cdot}9$ ppm), proton "3" (quartet at $\delta = 6{\cdot}23$ ppm), $J_{H-2,3} = 5{\cdot}2$ c/s, $J_{3,4} = 8{\cdot}5$ c/s), and proton "4" (doublet at $\delta = 6{\cdot}66$ ppm). The signal due to H-1 is shifted downfield. The absence of this signal in spectrum of the deuterated product (VII) supports the assignment.

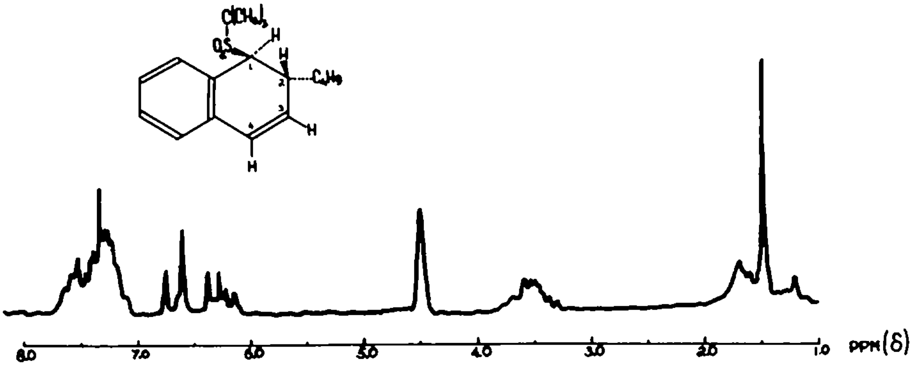


FIG. 1

The fact that there is no splitting of the H-1 signal speaks about the absence of its interaction with H-2. It can take place by the co-perpendicular plane protons disposition. Another fact leading to establish the conformation of VI and VII is the quadruplet of the proton "3" signal ascribed to its additional interaction with H-2. The value of $J_{H-2,3} = 5$ c/s is too great for the distant allylic interaction. Thus H-2 is situated in an equatorial position. It is obvious from the Dreiding models that the dihedral angle between H-1 and H-2 planes (ϕ) = 90°. Hence one can accept that t-butylsulfonyl and n-butyl groups of VI and VII are situated in trans diaxial positions.

Hydrolysis of the adduct VIII afforded the stable conjugate CH-acid VI of the carbanion which corresponds to the organolithium compound VIII. Carbonization of VIII would lead to the formation of lithium salt of the acid IX which readily eliminates the t-butylsulfinic acid to form the acid (II).

The fact that the action of n-BuLi on the sulfone (VI) and the subsequent carbonization of resulting Li compound (VIII) produced with good yields the acid (II) is important evidence in favour of the mechanism postulated.

Although the possibility that nucleophilic displacement can occur at positions different from the point of attachment of the leaving group have been known long ago, it was not until recently that mechanistic developments along this line could give a good account of the observations. Drozd *et al*[9] showed that 4a,9a-dihydro- 1,5,7-trimethylthioxanthene dioxide-10, 10, formed by intramolecular cyclization of mesityl-m-tolylsulfone anion, suffers 1,2-elimination when treated with NaOEt in EtOH. A recent example of the 1,2-addition of the anion of benzyl type followed by elimination on carbonization was provided by Drozd and Zefirova[10] who studied the conversion of m-anisyl mesityl sulfone and found that decarboxylation was accompanied by elimination of the sulfinic acid anion. The intramolecular 1,2-addition-elimination mechanism was also proposed for 1- and 2-naphthyl mesityl sulfones.[11, 12] As far as the present authors are aware no well-established example of intermolecular addition of organometallic compounds to aromatic sulfones has been reported. It is known that the treatment of sulfones with alkyllithium results generally in metalation at ortho-to sulfonyl group rather than in addition of alkyllithium.

We were able to observe the latter reaction under different conditions. The sulfone (I) when treated with BuLi at −70° was found to give, after carbonization, t-butylsulfonyl-2-naphthoic acid (III) rather than acid (II). The acid (III) was hydrodesulfurized over Raney nickel to give 5,6,7,8,-tetrahydro-2-naphthoic acid (IV), described in the literature. During the metalation high recovery of the starting sulfone (I) was obtained. When the reaction mixture after standing at −70°, was refluxed for some time, it furnished the mixture of the acids (II) and (III). Acid (III) was also obtained by the action of MeLi on sulfone I both in the cold and by heating. It should be emphasized, however, that no acid (III) was obtained when n-BuLi and sulfone (I) were allowed to react at room temperature. Apparently 2-lithium-1-naphthyl t-butyl sulfone (V) which after carbonization gives acid (III) could not be regarded as an intermediate in the reaction to form the acid (II). It seems more likely two independent conversions occur in the reaction mixture.

Such a change in the reaction trend induced by organometallic reagents has been previously observed.[13] It was reported recently that MeLi adds across the C=N bond in pyrido/2,3 : b/-thiophene at 30°. The same reaction when conducted at −25° results in the displacement of α-hydrogen in the thiophene ring.

Although we are at present uncertain as to the cause of the change in the position of attachment of the organolithium reagent, the possibility should be kept in mind of the formation of a complex between RLi and sulfonyl group prior to metalation process. It is expected that such a complex is subject to dissociation at a higher temperature.

The conclusion can be drawn from the present study that the mechanism of 1,2-addition-elimination has a more general pattern than was previously accepted. Studies of this mechanism using other reactions are in progress.

EXPERIMENTAL

UV spectra were measured in EtOH and NMR spectra were determined in CCl_4 using HMDS as internal standard. Mps were determined using a Kofler hot stage microscope and are uncorrected.

2-n-Butyl-1-naphthoic acid (II). To 4·96 g (0·02 mole) of sulfone I in 50 ml of absolute ether was added slowly, with stirring, to an equimolecular amount of 2 N n-BuLi in ether. After addition the stirred mixture was maintained at room temperature for one hr and then refluxed for 5 hr. The reaction mix was then poured into dry ice–ether. H_2O was added to the mixture which was warmed to room temperature. The ether layer was removed, washed with H_2O and acidified with dilute hydrochloric acid. An oil was obtained which crystallized when allowed to stand giving 2·4 g (52% yield) of acid (II). Recrystallisation from hexane gave a product m.p. 83–84°. Found: C, 79·02; 78·85; H, 7·04; 6·95. ($C_{15}H_{16}O_2$ requires C, 78·92; H, 7·06%). The Methyl ester bp 118–122° (0·2 mm bath temp), n_D^{23} 1·5630, ν_{max} 748 cm^{-1} (cyclohexane), vibration frequency at 768 cm^{-1} was absent, λ_{max} 225 nm (log ε 4·8). According to the data presented in,[7] 2-n-butyl-1-naphthoic acid has m.p. 84·5–85·2°, methyl ester: n_D^{23} 1·5610, ν_{max} 748 cm^{-1}, λ_{max} 225 nm (log 4·8).

The mixture composed of methyl esters of 1-butyl-2-naphthoic and 2-butyl-1-naphthoic acid which were obtained following[7] and methyl ester of acid II was subjected to GLC analyses. These were carried out with LChM-7A Chromatograph (thermal conductivity detector) using a 0·40 × 0·05 m (i.d.) column filled with 15% PEGA on Chromosorb P and kept at 205°. Relative retention times of 1·0 and 1·7 were determined for esters of 1-butyl-2-naphthoic and acid II respectively. Ester obtained from unpurified acid II contained minor admixture of a compound with relative retention time 3·0.

Using the same procedure sulfone (I) was treated with three-fold excess of BuLi to give acid (II) in 30% yield.

Trans-1,2-dihydro-1-t-butylsulfonyl-2-n-butylnaphthalene (VI). Using the same procedure as described for the acid (II) synthesis, 4·96 g (0·02 mole) of sulfone I in 50 ml of ether and an equimolecular amount of BuLi, was poured into ice-cold water. The ether layer was separated, washed with water and dried. After removal of the solvent the residual crystals were washed with hexane. Recrystallisation from hexane gave 3·6 g (57%) of compound VI, m.p. 87–88°.(Found: C, 70·48; 70·34; H, 8·64; 8·52; S, 10·89; 10·53; $C_{18}H_{26}O_2S$ requires: C, 70·54; H, 8·55; S, 10·46%).

trans-1,2-Dihydro-1-deutero-1-t-butylsulfonyl-1-2-n-butyl-naphthalene (VII). Was prepared as in the preceding case except that the reaction blend was treated with D_2O rather than with H_2O to give the product (64% yield) which after recrystallization from hexane had m.p. 85–87°.

(Found: C, 70·23; 70·33; H, 8·67; 8·43; S, 10·34; 10·48; $C_{18}H_{25}DO_2S$ requires: C, 70·30; H, 8·65; S, 10·43.)

2-n-Butyl-1-naphthoic acid (II) *from* (VI). To 2 g (0·0065 mole) of dihydro compound VI in 20 ml of absolute ether, an equimolecular amount of 2N BuLi in ether was added at room temperature. The mixture was stirred at this temperature for one hr, then refluxed for 3 hr, poured into dry ice–ether and hydrolized. The organic layer was separated, the aqueous layer washed with ether and acidified yielding 0·8 g (53%) of acid (II), m.p. 83–84° after recrystallization from hexane. The m.p. was not depressed when mixed with acid (II).

1-t-Butylsulfonyl-2-naphthoic acid (III). To 4·96 g (0·02 mole) of sulfone (I) in 50 ml ether an equimolecular amount of 2N BuLi was added on stirring and cooling to −70°. The reaction mixture was then stirred for 7 hr. After pouring into dry ice–ether the mixture was treated with H_2O. The aqueous layer was separated, washed with ether and acidified. The resulting oil was extracted with ether and dried over $MgSO_4$. The solvent was evaporated and the solid product washed with benzene yielding 2·1 g (47%) of 1-t-butylsulfonyl-2-naphthoic acid (III). Recrystallization from benzene gave the product m.p. 196–198°. (Found: c, 62·20; 62·10; H, 5·46; 5·68; S, 10·97; 11·18. $C_{15}H_{16}O_4S$ requires C, 61·63; H, 5·51; S, 10·97).

The Methyl ester, m.p. 155°, after recrystallization from benzene. (Found: C, 62·77; 62·80; H, 5·93; 5·74; S, 10·64; 10·59; $C_{16}H_{18}O_4S$ requires C, 62·72; H, 5.92; S. 10·47%).

From the ether layer 1,2 g (54%) of the starting sulfone (I) was obtained. In another procedure the reaction after stirring at −70° for 5 hr was heated at refluxing for 5 hr and then carbonized to give 1·5 g the solid product. TCL on alumina in ether-hexane (3 : 2) showed this product consisted of two compounds having R_f 0·80 (methyl ester of acid II) and 0·37 (methyl ester of acid III).

Hydrodesulfurization of acid (III) Raney nickel (10 g) was refluxed with 0·5 g of acid (III) in 5% NaOH for 3 hr. The aqueous solution was poured off and acidified to give 0·3 g of 5,6,7,8-tetrahydro-2-naphthoic acid IV. M.p. 153–156° after recrystallization from hexane. (Found: C, 75·07; H, 6·64; $C_{11}H_{12}O_2$ requires: C, 74·97; H, 6·87%).

The amide, m.p. 137–140° after recrystallization from alcohol; lit. m.p. 137–8°.[14]

Acid III was obtained also in 25% yield from 2·5 g (0·01 mole) of sulfone (I) in 40 ml of ether and an ethereal solution of MeLi, prepared from 7·1 g of MeI and 0·77 g of Li after refluxing the reaction for 5 hr followed by carbonization. After recrystallization from benzene it had m.p. 196–198°. This melting point was not depressed when mixed with acid III previously obtained.

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