CONDENSED HETEROAROMATIC SYSTEMS CONTAINING A THIOPHENE RING*

COMMUNICATION 15. PREPARATION AND SOME TRANSFORMATIONS OF BENZO-[b]-NAPHTHO-[2,3-d]-THIOPHENE†

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In recent years many investigators have given constantly increasing attention to the chemistry of condensed heteroaromatic systems. This is primarily caused by the increasing use of sulfur and high-sulfur petroleums in the petroleum refining industry and the associated problems that arise in connection with establishing the structure of the sulfur compounds present in petroleums, which makes it necessary to have a large number of standard compounds of rigidly proved structure. In this connection we will mention that thiophene systems, containing three or more carbocyclic condensed rings, are among the principal components of the high-molecular portion of sulfur-containing petroleums [2].

A large number of polycyclic systems containing the thiophene ring is known, but the data on the chemical properties of these compounds is quite scanty. Benzo-[b]-naphtho-[2,3-d]-thiophene (benzo-[b]-thiophanthrene by a different momenclature) has been studied fairly exhaustively, but also in this case there is no information on the preparation of derivatives and the chemical properties of this system (see, for example, [3]). The reason for the scantiness of these data is the laborious nature of preparing such condensed heterocycles and the complexity of studying their behavior.

As a continuation of our investigations on the chemistry of condensed thiophene-containing systems we studied the acylation of dibenzothiophene with succinic anhydride and the acid chloride of the monoester of succinic acid in the presence of $AlCl_3$ [1], which enabled us to pass over to the synthesis of benzo-[b]-naphtho-[2,3-d]-thiophene and an investigation of its transformations.

The cyclization of the acid chloride of 4-(2-dibenzothienyl)butyric acid (I) in the presence of $AlCl_3$ by the Werner method [4] gave us 7-keto-7,8,9,10-tetrahydrobenzo-[b]-naphtho-[2,3-d]-thiophene (II) in 73% yield. The reduction of (II) with hydrazine hydrate gave 7,8,9,10-tetrahydrobenzo-[b]-naphtho-[2,3-d]-thiophene (III) in 63% yield, while the dehydrogenation of the latter with selenium at 350° gave benzo-[b]-naphtho-[2,3-d]-thiophene (IV). The conclusion that the use of selenium powder for dehydrogenation in the naphthobenzothiophene series is less convenient and gives a much lower yield of reduction products, when compared with Pd/C in xylene [5], is erroneous. We obtained (IV) in up to 51% yield when (III) was dehydrogenated with selenium powder (10 h, 350°), whereas in [5] the yield of (IV) reached 41% when the analogous operation was run using Pd/C. The dehydrogenation with selenium was also used by us successfully in a number of other cases.

In order to obtain various derivatives of benzo-[b]-naphtho-[2,3-d]-thiophene (IV) and study the substitution reactions in this series we made a study of the effect of metalating agents on (II) and (IV). In this paper are reported some of the data on the reaction of lithium metal with (IV), and of Grignard reagents with (II). The results of the reaction of (IV) with n-BuLi will be reported later.

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* See [1] for Communication 14.

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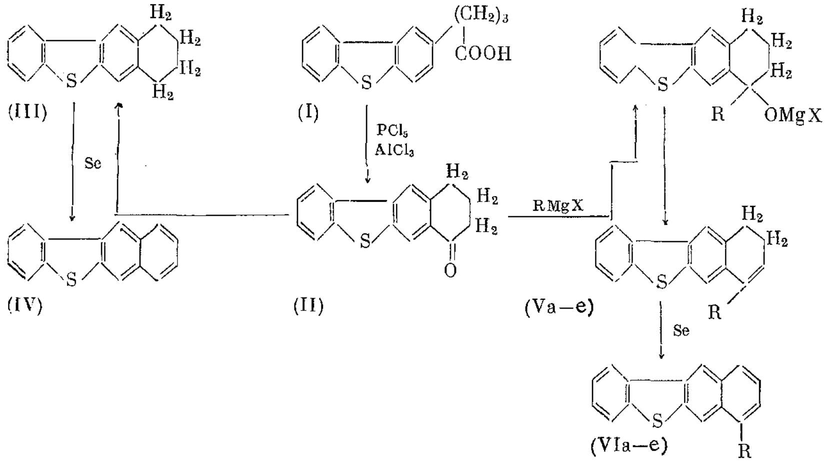
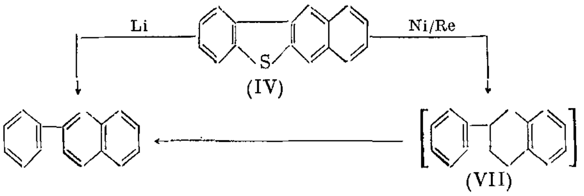
7-Substituted derivatives of 9,10-dihydrobenzo-[b]-naphtho-[2,3-d]-thiophene (Va-e) are formed in 40-70% yield when RMgX is reacted with (II). Dehydrogenation of these derivatives with selenium powder gave a number of new substituted benzo-[b]-naphtho-[2,3-d]-thiophenes (VIa-e), containing a substituent in the 7-position, in 40-60% yield. It is necessary to mention that if the temperature during dehydrogenation with selenium exceeds 340°, then dealkylation of the alkyl-substituted benzo-[b]-naphtho-[2,3-d]-thiophenes occurs in this case.



R = CH_3 (a); n-C_3H_7 (b); n-C_4H_9 (c); C_6H_5 (d); $CH_2C_6H_5$ (e)

The action of lithium and sodium on condensed aromatic compounds has been studied in considerable detail [6, 7] and, in particular, it has been shown that lithium and sodium add with ease to anthracene and naphthacene at room temperature in either ether or ether – benzene medium. Starting with the fact that benzo-[b]-naphtho-[2,3-d]-thiophene is the sulfur isolog of naphthacene, it is possible to assume that the substitution reaction with lithium metal will take place in the given case. However, as our experiments disclosed, the metalation reaction fails to take place when benzo-[b]-naphtho-[2,3-d]-thiophene is treated with lithium metal at room temperature in ether – benzene medium, and instead the elimination of the sulfur atom from the naphthobenzothiophene system is observed, with the formation of β-phenylnaphthalene in up to 60% yield. The fact that the naphthobenzothiophene system is desulfurized when treated with lithium metal was confirmed by comparing the obtained product with an authentic sample of β-phenylnaphthalene (mixed melting point, UV spectra). In addition, the treament of (IV) with skeletal nickel gave a partially hydrogenated β-phenylnaphthalene, the dehydrogenation of which with selenium powder gave β-phenylnaphthalene, identical with that obtained by the action of lithium metal on (IV):



We will mention that the fact that condensed heteroaromatic systems are desulfurized by lithium metal was first observed by Gilman on the example of dibenzothiophene: biphenyl was obtained in 30.5% yield when dibenzothiophene was refluxed with lithium metal in dioxane [8], while in tetrahydrofuran at 25° the products were 3,4-benzothiocoumarin (after carbonization of the reaction product), which was obtained in 48% yield, and traces of biphenyl [9]. As our experiments disclosed, dibenzothiophene, the same as benzothiophene and thiophene, fails to undergo either desulfurization or metalation under the conditions where the elimination of sulfur in the benzo-[b]-naphtho-[2,3-d]-thiophene system is observed: namely, by shaking for 40-50 h with lithium metal at room temperature in ether – benzene mixture.

EXPERIMENTAL

4-(2-Dibenzothienyl)butyric Acid (I). The acid was obtained in 90% yield by the procedure described in [1]; mp 128-129°. According to [4]: mp 129.5-130.5°.

7-Keto-7,8,9,10-tetrahydrobenzo-[b]-naphtho-[2,3-d]-thiophene (II). To a solution of 4.1 g of acid (I) in 200 ml of anhydrous chlorobenzene at 0-5°, with stirring, was added 5.1 g of PCl_5. After 1 h (20°) the mixture was heated for 30 min on the water bath at 96-98°, cooled to 0°, and then 3.7 g of $AlCl_3$ was added to it in 30 min. The obtained mixture was heated for 30 min at 40-60°, then allowed to stand for 12 h (20°), and poured over a mixture of ice and 20 ml of HCl. After the usual workup we obtained 2.8 g (73.2% yield) of (II); mp 176-178°. According to [4]: mp 178-179°; [5]: 176-178°. Acidification of the alkaline extract with hydrochloric acid gave 0.2 g of the starting acid (I); mp 125-128°.

7,8,9,10-Tetrahydrobenzo-[b]-naphtho-[2,3-d]-thiophene (III). A mixture of 2.8 g of ketone (II), 1.3 ml of 98% hydrazine hydrate, 27 ml of diethylene glycol and 2.2 g of KOH was heated at 190-200° for 12 h, cooled to 5°, and treated with dilute HCl solution. We obtained 1.8 g (63%) of (III); mp 109-110°. According to [4]: mp 110.5-111°.

Benzo-[b]-naphtho-[2,3-d]-thiophene (IV). A mixture of 1.5 g of (III) and 0.93 g of selenium powder was heated for 10 h at 350° (the evolution of H_2Se was observed when the temperature reached 270°). The black reaction mass was dissolved in a 4:1 benzene – petroleum mixture, and the solution was passed through an Al_2O_3 column. After distilling off the solvent, the residue was recrystallized from ethyl alcohol. We obtained 0.75 g (50.8%) of (IV); mp 158-159°. According to [4]: mp 158.5-159°. Found: C 81.88; 81.89; H 4.31, 4.09; S 13.50, 13.56%. $C_{16}H_{10}S$. Calculated: C 82.05; H 4.27; S 13.24%.

7-Methylbenzo-[b]-naphtho-[2,3-d]-thiophene (VIa). To a mixture of 2.7 g of magnesium shavings and 100 ml of absolute ether, with stirring, was added a solution of 16 g of methyl iodide in 16 ml of absolute ether in drops. After the magnesium had dissolved, to the reaction mixture was added in drops a warm solution of 10 g of ketone (II) in 30 min. The mixture was refluxed for 10 h on the water bath, after which it was treated with dilute (1:4) H_2SO_4 solution and extracted with ether. The extract was washed with 10% NaOH solution, then with water, and dried over Na_2SO_4. After distilling off the ether the crystalline deposit was dissolved in a benzene – petroleum ether mixture and the solution was passed through an Al_2O_3 column. The solvent was distilled off, and the residue was recrystallized from ethyl alcohol. We obtained 5.9 g (60%) of 7-methyl-9,10-dihydrobenzo-[b]-naphtho-[2,3-d]-thiophene (Va); mp 121-121.5°. Found: C 81.51; H 5.44; S 12.87%. $C_{17}H_{14}S$. Calculated: C 81.60; H 5.60; S 12.80%.

A mixture of 1.5 g of (Va) and 0.7 g of selenium was heated for 6 h at 270-310°, after which it was cooled, dissolved in petroleum ether, and the solution was chromatographed on Al_2O_3. After distilling off the solvent the residue was recrystallized from a mixture of ethyl alcohol and benzene. We obtained 0.4 g (54%) of (VIa); mp 175-176°. Found: C 82.30; H 4.88; S 12.75%. $C_{17}H_{12}S$. Calculated: C 82.25; H 4.83; S 12.90%.

The other 7-substituted derivatives of 9,10-dihydrobenzo-[b]-naphtho-[2,3-d]-thiophene and benzo-[b]-naphtho-[2,3-d]-thiophene were obtained in a similar manner; the data for these are given in Table 1.

Action of Lithium Metal on Benzo-[b]-naphtho-[2,3-d]-thiophene. To a solution of 2.7 g of (IV) in a 1:1 mixture of absolute ether and benzene (thiophene-free), in an atmosphere of anhydrous nitrogen, was added 1.8 g of finely cut lithium. The mixture was shaken for 45 h at room temperature (a light red color appeared after 6 h, which then changed to a brown color). Then the mixture was filtered in a dry nitrogen atmosphere through a metal screen. Here 0.04 g of unreacted lithium was recovered. The filtrate was washed several times with water and dried over Na_2SO_4. After distilling off the solvent the residue was recrystallized from alcohol. We obtained 1.3 g (55%) of β-phenylnaphthalene; mp 101-102°. From [10]: mp 101.5-102°. Found: C 94.08, 93.87; H 5.89, 5.87%. $C_{16}H_{12}$. Calculated: C 94.11; H 5.88%.

A similar treatment of (III) gave the starting (III) with mp 109-110°. The mixed melting point with the starting (III) was not depressed.

Action of Lithium Metal on Dibenzothiophene. A mixture of 2 g of dibenzothiophene, 0.15 g of lithium, 25 ml of absolute ether, and 20 ml of absolute benzene (thiophene-free) was shaken in an anhydrous nitrogen atmosphere for 42 h at room temperature, after which it was poured on a mixture of finely crushed solid CO_2 and absolute ether. After treatment with water and extraction with ether the organic layer was separated, dried, and the solvent was distilled from it. The residue represented the starting dibenzothiophene, which melted at 96-99° without recrystallization. We failed to isolate any reaction products when the aqueous layer was acidified.

Only the starting products were isolated when benzothiophene and thiophene were treated with lithium under analogous conditions.

TABLE 1. 7-Substituted Derivatives of 9,10-Dihydrobenzo-[b]-naphtho-[2,3-d]-thiophene and Benzo-[b]-naphtho-[2,3-d]-thiophene

Compound		Yield, %	Mp, °C	Empirical formula	Found, %			Calculated, %		
No.	name				C	H	S	C	H	S
Vb	7-Propyl-9,10-dihydrobenzo-[b]-naphtho-[2,3-d]-thiophene	66	—*	$C_{19}H_{18}S$	81,83	6,82	11,35	81,79	6,51	11,70
VIb	7-Propylbenzo-[b]-naphtho-[2,3-d]-thiophene	41	97—98	$C_{19}H_{16}S$	82,73	5,74	11,53	82,34	5,82	11,79
Vc	7-Butyl-9,10-dihydrobenzo-[b]-naphtho-[2,3-d]-thiophene	42	—*	$C_{20}H_{20}S$	82,01	6,90	10,78	81,98	6,88	11,14
VIc	7-Butylbenzo-[b]-naphtho-[2,3-d]-thiophene†	38	129—131	$C_{20}H_{18}S$	82,56	6,43	11,00	82,55	6,20	11,22
Vd	7-Phenyl-9,10-dihydrobenzo-[b]-naphtho-[2,3-d]-thiophene	62	98—100	$C_{22}H_{16}S$	84,46	5,30	10,24	84,42	5,15	10,43
VId	7-Phenylbenzo-[b]-naphtho-[2,3-d]-thiophene	58	122—123	$C_{22}H_{14}S$	85,12	4,59	10,19	84,97	4,54	10,50
Ve	7-Benzyl-9,10-dihydrobenzo-[b]-naphtho-[2,3-d]-thiophene	52	125—126	$C_{23}H_{18}S$	84,42	5,58	10,00	84,47	5,55	9,98
VIe	7-Benzylbenzo-[b]-naphtho-[2,3-d]-thiophene	50	178—179	$C_{23}H_{16}S$	85,10	5,17	9,73	84,99	4,96	10,04

* The compounds were isolated as oily liquids and were purified by chromatographing on Al_2O_3.

† Based on the GLC analysis data the compound is contaminated with Vc.

Action of Skeletal Nickel on Benzo-[b]-naphtho-[2,3-d]-thiophene. To a solution of 1.8 g of (IV) in 15 ml of absolute benzene (thiophene-free) was added 5 g of a suspension of skeletal nickel in alcohol. The stirred mixture was refluxed for 4 h, after which the hot solution was filtered and the nickel on the filter was washed well with alcohol. The solvent was distilled off, while the residue (1.2 g, 70% yield) represented the partially hydrogenated β-phenylnaphthalene (VII). Found: C 92.66, 92.71; H 7.64, 7.47%. $C_{16}H_{16}$. Calculated: C 92.30; H 7.69%.

An 0.5 g mixture of the obtained product (VII) and 0.3 g of selenium was heated at 270° for 4 h, and at 300° for 2 h. Then 0.11 g of selenium was added and the mixture was heated at 270-310° for 2 h. After this the mixture was extracted with benzene and chromatographed on Al_2O_3. After distilling off the solvent the residue was recrystallized from alcohol. We obtained 0.4 g (82% yield) of β-phenylnaphthalene; mp 101-102°. The mixed melting points with an authentic sample of β-phenylnaphthalene, and with the β-phenylnaphthalene obtained by the action of lithium metal on (IV), were not depressed. The UV spectra proved to be identical.

CONCLUSIONS

1. A study was made of the action of lithium metal and skeletal nickel on benzo-[b]-naphtho-[2,3-d]-thiophene, and of Grignard reagents on 7-keto-7,8,9,10-tetrahydrobenzo-[b]-naphtho-[2,3-d]-thiophene.

2. The action of lithium metal on benzo-[b]-naphtho-[2,3-d]-thiophene leads to the elimination of the sulfur atom and the formation of β-phenylnaphthalene.

3. A number of new 7-substituted derivatives of benzo-[b]-naphtho-[2,3-d]-thiophene, and specifically 7-methyl-, 7-propyl-, 7-butyl-, 7-phenyl, and 7-benzylbenzo-[b]-naphtho-[2,3-d]-thiophene, were obtained by the reaction of Grignard reagent with 7-keto-7,8,9,10-tetrahydrobenzo-[b]-naphtho-[2,3-d]-thiophene and subsequent dehydrogenation of the 7-substituted derivatives of 9,10-dihydrobenzo-[b]-naphtho-[2,3-d]-thiophene with selenium powder.

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