Pergamon

Tetrahedron Letters, Vol. 35, No. 13, pp. 2005-2008, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0222-J

Synthesis of Thio- and Seleno-Substituted Methanoanthracenes by Wittig Rearrangement

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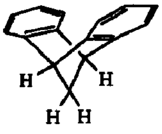
Abstract: When 12-cyano-11-thia- (and 11-selena)-9,10-dihydro-9,10-ethanoanthracenes were deprotonated at 0°C, the resulting carbanions underwent a Wittig rearrangement. After hydrolysis or alkylation, 9,10-dihydro-9,10-methanoanthracene derivatives were isolated. The first synthesis of a seleno-cyanohydrine is also described.

9,10-Dihydro-9,10-methanoanthracene **1**, a dibenzo-analogue of norbornadiene, was synthesized for the first time in 1956 by Vaughan and Yoshimine.[1] These authors used the Diels-Alder reaction of butadiene with norbornadiene followed by dehydrogenation of the resulting adduct on palladium-charcoal to obtain 9,10-dihydro-9,10-methanoanthracene in 2% overall yield.



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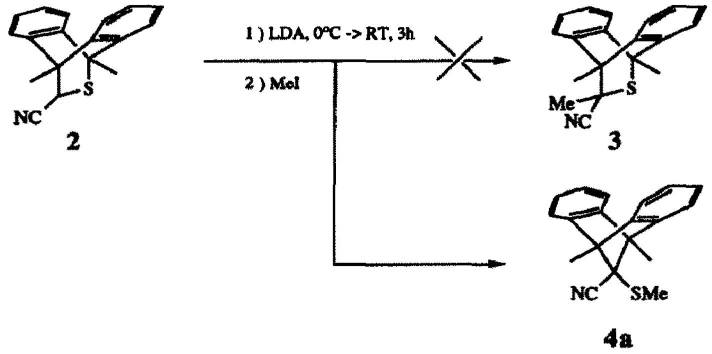
More recently,[2] its theoretical interest led to the development of a more efficient synthesis of this rigid molecule which was obtained in two steps and 26% overall yield from benzonorbornadiene. Some substituted 9,10-dihydro-9,10-methanoanthracene derivatives were also obtained.[3-6]

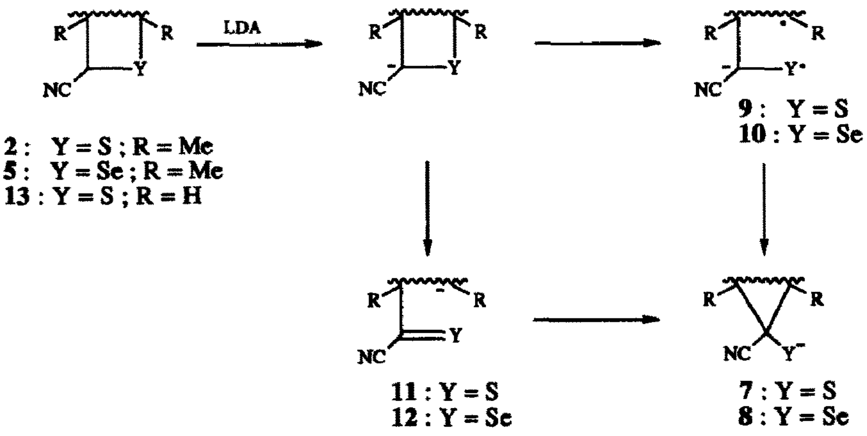
In this communication, we present a new simple two-step strategy for the synthesis of thio- or seleno-substituted 9,10-dihydro-9,10-methanoanthracene derivatives from anthracene and 9,10-dimethylanthracene.

Pursuing our study of reactive thiocarbonyls,[7] we needed to prepare the thia-ethanoanthracenic compound **3**, a convenient retro-Diels-Alder precursor for 2-thioxopropanenitrile. According to the method introduced by Kirby *et al.* in the case of an analogous ester,[8] we tried to obtain **3** from the thioformylcyanide-dimethylanthracene adduct **2**. Thus, compound **2** was deprotonated by LDA in THF at 0°C and subsequently treated by iodomethane. After a usual work-up, a solid was isolated whose mass spectrum gave a molecular peak consistent with the expected structure **3** ($M^{+\cdot} = 291$). However, as the ^1H NMR spectrum showed only two methyl signals at 1.95 (6H) and 2.30 ppm (3H),[9] and the ^{13}C NMR spectrum clearly indicated a high level of symmetry (especially, only 6 peaks observed for the 12 aromatic carbons), [10] we had to renounce to structure **3**.



The NMR data are in agreement with structure **4a**. Other alkylating agents were used, which all gave products of type **4**. The results are summarized in the Table. Analogous products were also obtained from 12-cyano-9,10-dimethyl-11-selena-9,10-dihydro-9,10-ethanoanthracene **5** and from **13**, the non-methylated analogue of **2**. Furthermore,when no alkylating agent was added, direct hydrolysis of the reaction mixture allowed the synthesis of the thio- and seleno-cyanohydrines **4d**, **6c** and **15**. If thio-cyanohydrines are relatively well known compounds,[11] the selenol **6c** is the first isolated seleno-cyanohydrine.

Compounds **4a-d** and **6a-c** may arise from Wittig rearrangement[12] of the carbanion derived from **2** or **5**, into the sulfinyl and selenyl anions **7** and **8**, which will then be alkylated. In this kind of rearrangement a radical-pair mechanism has been proposed.[12] In our case such mechanism will be favored by the formation of the tertiary dibenzylic radicals **9** and **10** (R = Me). However, since no significant difference in the rate of rearrangement has been observed when the non-methylated compound **13** was used as starting material, an ionic mechanism, occuring *via* the intermediates **11** and **12** cannot be ruled out.[8,13]



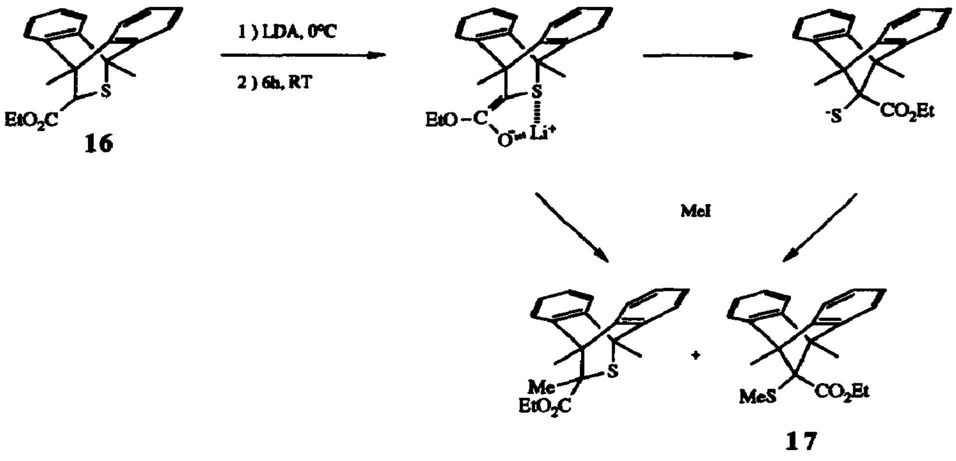
2 : Y = S ; R = Me
5 : Y = Se ; R = Me
13 : Y = S ; R = H

9 : Y = S
10 : Y = Se

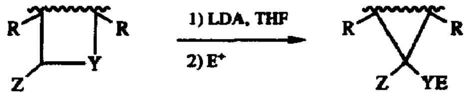
11 : Y = S
12 : Y = Se

7 : Y = S
8 : Y = Se

We have also investigated the reaction of the anion derived from 12-ethoxycarbonyl-9,10-dimethyl-11-thia-9,10-dihydro-9,10-ethanoanthracene **16** with methyl iodide. In this case however, the rearrangement was slower and a nearly 1:1 mixture of C-methylated and S-methylated products was obtained when the anion was allowed to rearrange at room temperature for 6 hours. This may be due to a stabilization of the enolate by an intramolecular chelation of the lithium cation by the sulfur atom. Such chelation is not possible for the anion (C^{-}-C≡N <--> C=C=N^{-}) derived from the nitriles **2**, **5** and **13**.

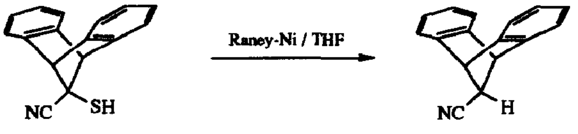


Table



Starting material	Y	Z	R	EX	Product	Yield (%)
2	S	CN	Me	MeI	4a	70
				EtI	4b	62
				$NCCH_2Cl$	4c	55
				H_3O^+	4d	64
5	Se	CN	Me	MeI	6a	66
				EtI	6b	65
				H_3O^+	6c	61
13	S	CN	H	$NCCH_2Cl$	14	52
				H_3O^+	15	61
16	S	CO_2Et	Me	MeI	17	33

As the starting compounds **2**, **5**, **13**, **16** were obtained from thio- and seleno-aldehydes, this method is a new demonstration of the usefulness of these reactive intermediates in synthesis.[14] Furthermore, the rich chemistry of the cyano, alkylthio and alkylseleno groups allows functional modifications which will give access to methanoanthracenes variously substituted at position 11. For example, desulfurization of compound **15** by Raney-Nickel has been performed[15] and led to 11-cyano-9,10-dihydro-9,10-methanoanthracene **18** in quantitative yield.



15 **18**

references and notes

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9. The two methyl singlets of the starting material **1** were observed at 2.32 and 2.35 ppm. 12 Peaks were observed for the aromatic carbons in its ^{13}C NMR spectrum.
10. Typical experimental procedure : the sulfide **2** (1 mmol.) diluted in THF was added dropwise to a solution of LDA in dry THF (20 ml) at 0°C. The reaction mixture was stirred under nitrogen from 0°C to room temperature for three hours. The alkylating agent (1.5 mmol.) was then added and the mixture stirred for another three hours. The reaction was quenched with NH_4Cl-H_2O and extracted with CH_2Cl_2. For the synthesis of **4d**, **6c** and **15**, the alkylation agent was ommited. All the obtained products were isolated by liquid chromatography on silica gel using dichloromethane-petroleum ether mixtures as eluent. Diagnostic data for obtained methanoanthracenes : **4a** : white solid ; mp = 187-188°C ; ^{13}C NMR ($CDCl_3$) : 9.91, 15.81, 62.92, 85.61, 116.63 (CN), 120.68, 121.37, 126.38, 126.78, 147.77, 148.86 ppm. **4b** : ^{1}H NMR : 1.22 (t, Me), 1.94 (s, 2 Me), 2.82 (q, CH_2) ; ^{13}C NMR : 116.83 (CN). **4c** : ^{1}H NMR : 2.03 (s, 2 Me), 3.55 (s, CH_2) ; ^{13}C NMR : 115.28 and 116.22 (2 CN). **4d** : ^{1}H NMR : 1.94 (s, 2 Me), 2.05 (s, SH) ; ^{13}C NMR : 118.48 (CN). **6a** : ^{1}H NMR : 1.94 (s, 2 Me), 2.23 (s, Me) ; ^{13}C NMR : 117.05 (CN). **6b** : ^{1}H NMR : 1.38 (t, Me), 1.96 (s, 2 Me), 2.85 (q, CH_2) ; ^{13}C NMR : 116.93 (CN). **6c** : Yellow solid ; mp= 275-276°C ; ^{1}H NMR : 1.25 (s, SeH), 1.93 (s, 2 Me), 7.0-7.3 (m, 8 aromatic H) ; ^{13}C NMR : 10.62, 62.38, 85.22, 116.51 (CN), 120.68, 121.81, 126.75, 126.76, 148.12, 148.73 ; IR (NaCl) : 2220 cm^{-1} (ν_{CN}) ; MS m/z (%): 325 (1, M$^+$), 244 (100, M$^+$-HSe), 206 (19), 191 (27), 57 (33). **14** : ^{1}H NMR : 3.54 (s, CH_2), 4.8 (s, 2 CH) ; ^{13}C NMR : 116.10 (CN). **15** : ^{1}H NMR : 1.26 (s, SH), 4.61 (s, 2 CH) ; ^{13}C NMR : 118.75 (CN). **16** : ^{1}H NMR : 1.01 (t, Me), 2.05 (s, Me), 2.06 (s, 2 Me), 3.97 q, CH_2) ; ^{13}C NMR : 169.58 (CO). **18** : ^{1}H NMR : 3.44 (t, CH), 4.52 (d, 2 CH) ; ^{13}C NMR : 54.40 (2 CH), 62.74 (CH), 118.71 (CN), 122.14, 123.17, 126.11, 145.93, 146.63 ; IR : 2220 cm^{-1} (ν_{CN}) ; MS m/z : 217 (M$^+$).
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(*Received in France* 6 *January* 1994; *accepted* 26 *January* 1994)