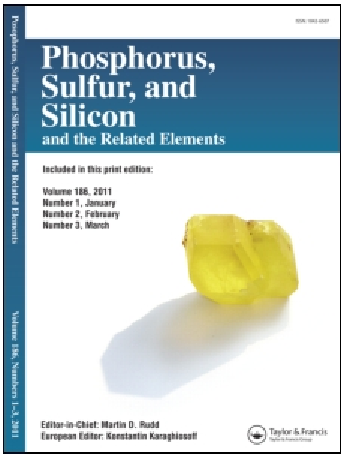

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# Sulfur (Or Selenium)-Mediated Synthesis of Methanoanthracene Derivatives. The First Synthesis of a Seleno-Cyanohydrin

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# SULFUR (OR SELENIUM)-MEDIATED SYNTHESIS OF METHANOANTHRACENE DERIVATIVES. THE FIRST SYNTHESIS OF A SELENO-CYANOHYDRIN

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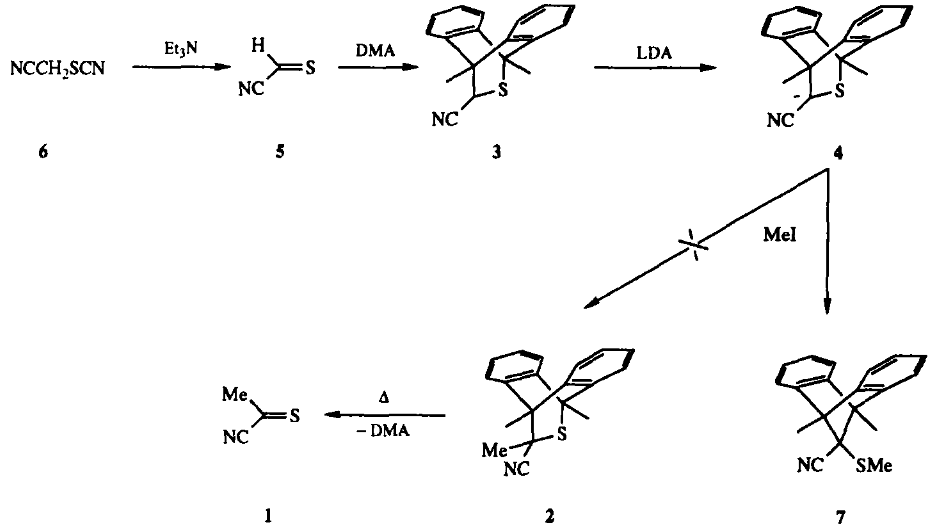
A synthesis of thio- and seleno-substituted 9,10-dihydro-9,10-methanoanthracene derivatives is reported. They are obtained by Wittig rearrangement from 11-thia and 11-selena-9,10-dihydro-9,10-ethanoanthracene derivatives. This rearrangement is applied to the first synthesis of a seleno-cyanohydrin ($R^1R^2C(SeH)CN$).

*Key words:* 9,10-dihydro-9,10-methanoanthracene; Wittig rearrangement; seleno-cyanohydrine; Diels-Alder adducts; thioaldehydes; anthracene derivatives.

## INTRODUCTION

As part of a program aimed at studying reactive thiocarbonyl and selenocarbonyl compounds,[1,2] we needed to prepare a convenient precursor for 2-thioxopropanenitrile 1 (Scheme 1), a non-isolable α-thioxonitrile which was expected to give



SCHEME 1

interesting reactions with thiols and selenols.[3,4] Because the retro-Diels-Alder reaction is a well established method for the *in-situ* generation of thioaldehydes,[5] we looked at a possible synthesis of the thia-ethanoanthracenic compound **2**. This compound would most probably decompose at temperatures *ca.* 100°C into 9,10-dimethylanthracene (DMA) and the desired thione **1**. Furthermore, the designed synthesis of **2** should be sufficiently flexible to allow the introduction of various substituents, including functional ones, onto position 12 of the ethanoanthracene in place of the methyl group.

## RESULTS

12-cyano-9,10-dimethyl-11-thia-9,10-dihydro-9,10-ethanoanthracene **3**, which contains an acidic proton on position 12, was expected to be easily deprotonated, and the intermediate anion **4** to be alkylated without problem, thus giving access to the methylated compound **2** and its analogues. Compound **3**, which is a Diels-Alder adduct of thioformylcyanide **5**, was synthesized in 72% isolated yield by trapping the thioaldehyde **5**, generated by base-induced elimination of HCN from the thiocyanate **6**, with 9,10-dimethylanthracene.[6]

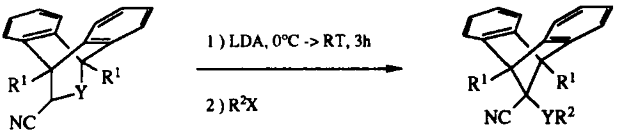
In a first experiment, deprotonation of compound **3** was effected by one equivalent of LDA in THF at 0°C. Iodomethane was added and the reaction mixture was stirred from 0°C to room temperature for three hours. In this case however, the crude product still contained some starting material. As a consequence, in the following experiments the deprotonation was effected with a slight excess of LDA from 0°C to room temperature. Using this procedure, no more **3** was detected in the isolated product and a solid compound, whose mass spectrum was in agreement with structure **2**, was obtained in 70% yield after liquid chromatography. Also, the IR spectrum of this compound showed a weak band at 2220 cm$^{-1}$, as expected for an $\alpha$-heterosubstituted nitrile.[7] In contrast, the recorded NMR spectra could not be attributed to structure **2**. In particular only two types of methyl groups were in evidence ($^1$H NMR: 1.95 (6H), 2.30 (3H); $^{13}$C NMR: 9.91, 15.81 ppm) in place of the three different methyl groups expected for compound **2**. These NMR data point to a symmetric structure and lead us to propose structure **7** for the isolated product.

Thus, overall, 9,10-dimethylanthracene has been transformed in two steps, *via* the thia-ethanoanthracene **3**, into the methanoanthracene derivative **7**, in 50% yield. Methanoanthracenes are strained rigid molecules of theoretical interest.[8] The parent compound, methanoanthracene itself, was synthesized for the first time in 1956 from norbornadiene.[9] The overall yield however was disappointing. More recently it was obtained from benzonorbornadiene in two steps and 26% yield.[8] Only a few substituted methanoanthracene derivatives have been reported. For instance the treatment of a magnesium anthracene derivative with ethyl acetate gave 11-hydroxy-9,10,11-trimethyl-9,10-dihydro-9,10-methanoanthracene in 84% yield[10] and irradiation of 10-*t*-butyl-9-cyanoanthracene led to the 9-cyano-10,11,11-trimethyl methanoanthracene derivative in 52% yield.[11] 9-Hydroxymethyl-9,10-dihydro-9,10-methanoanthracene was synthesized by a multistep procedure from benzyne.[12] Finally, references concerning 9,10-dihydro-9,10-methanoanthracen-11-one will be found in a paper by Irie and Tanida.[13]

As our synthesis of compound **7** competes favorably with previously reported routes to the methanoanthracene framework, we have investigated its scope for the synthesis of variously substituted methanoanthracene derivatives. Our results are summarized in Scheme 2. The three cyanides **3**, **8** and **9** were deprotonated from 0°C to room temperature and alkylated with various halides. The yields of isolated methanoanthracene derivatives ranged from 52 to 70%. In three experiments, the alkylation step was omitted and the reaction mixture quenched with a solution of ammonium chloride in water. In this way the two thio-cyanohydrins **12** and **14** and the seleno-cyanohydrin **17** were obtained. To the best of our knowledge, the selenol **17** is the first described cyanohydrin seleno-analogue. It was isolated in 61% yield. As the other obtained methanoanthracene derivatives, it was characterized by very simple NMR spectra, which demonstrate its high symmetry. In its $^1$H NMR spectrum, the seleno proton was observed as a singlet at 1.25 ppm.

## DISCUSSION

As successful alkylations of carboxylic esters related to nitrile **3** have indeed been performed by Kirby *et al.*,[14] we were first rather surprised by our results. However, this rearrangement is clearly related to the Wittig rearrangement of $\alpha$-oxy-anions into alcoholates.[15] For instance, the formation of compound **7** results from a rearrangement of the carbanion **4** into the thiolate **18**. A proposed mechanism, derived from the mechanism generally involved in the case of $\alpha$-oxy-anions, is shown in Scheme 3. The cleavage of the C—S bond would be favored by the formation of the dibenzylic radical **19**. This one will then cyclize to the thiolate **18**. The greater stability of **18** (as compared with **4**), as well as the irreversibility of the last C—C bond formation would explain the formation of this strained anion. However, the C—S bond cleavage could also take place in an heterolytic way, giving rise to the dibenzylic anion **20**. Either of these two mechanisms can be excluded.

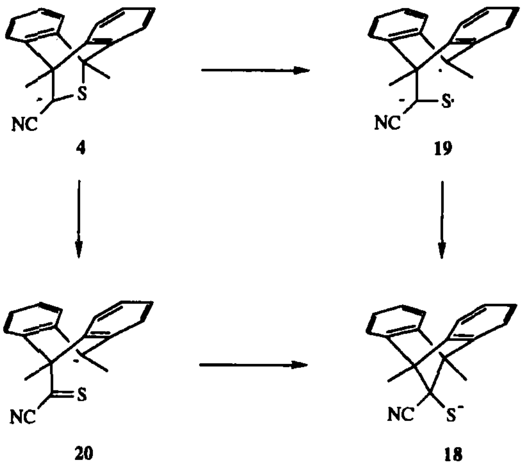


Y = S, $R^1$ = Me : **3**
$R^1$ = H : **8**

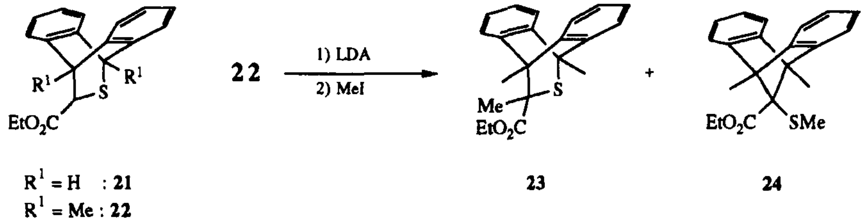
Y = Se, $R^1$ = Me : **9**

| | | | | Yields (%) |
|---|---|---|---|---|
| Y = S, | $R^1$ = Me, | $R^2$ = Me | : **7** | 70 |
| | | $R^2$ = Et | : **10** | 62 |
| | | $R^2$ = $CH_2CN$ | : **11** | 55 |
| | | $R^2$ = H | : **12** | 64 |
| | $R^1$ = H, | $R^2$ = $CH_2CN$ | : **13** | 52 |
| | | $R^2$ = H | : **14** | 61 |
| Y = Se, | $R^1$ = Me, | $R^2$ = Me | : **15** | 66 |
| | | $R^2$ = Et | : **16** | 65 |
| | | $R^2$ = H | : **17** | 61 |

SCHEME 2



SCHEME 3



SCHEME 4

In order to compare our results with that of Kirby *et al.*, who did not observe any rearrangement with ester **21**, we have methylated compound **22** (Scheme 4). In this case, we observed an incomplete rearrangement and isolated a mixture of the C-methylated and S-methylated products **23** and **24** in a *ca.* 1:1 ratio. This clearly demonstrate the greater stability of the enolate derivated from **22** as compared with the carbanion **4** and is tentatively explained by a possible chelation of the lithium cation by the neighbouring sulfur atom. Such chelation will not be possible in the case of **4**.

## EXPERIMENTAL

All experiments were conducted under a slightly positive pressure of $N_2$. THF was dried by distillation over Na just before use. NMR spectra were recorded on Brucker AC 250 and AM 300 spectrometers (solvent: $CDCl_3$, internal reference: TMS). Mass spectra were obtained on a Nermag R10 spectrometer. IR spectra were recorded on Perkin Elmer 684 and 1320 spectrometers. Melting points were measured on a Gallenkamp apparatus. Elemental analysis (C, H, N) were carried out by the "Service Centrale des Analyses du CNRS" at Vernaison. Sulfur analysis were performed by Mrs. M. Lemarié at Caen.

### *Thio- and Seleno-aldehydes Adducts*

Compounds **3**, **8** and **9** were prepared by trapping the corresponding thio- and seleno-aldehydes with anthracene or 9,10-dimethylanthracene. 9,10-Dimethylanthracene, which is a commercially available but expensive compound, was prepared in two steps from anthracene: (i) dichloromethylation with paraformaldehyde and aqueous HCl,[16] (ii) reduction of the resulting di(chloromethyl)-anthracene with lithium aluminium hydride in refluxing THF.[17]

Ester **22** was prepared according to Kirby's method.[6] Cyanides **3** and **8** were synthesized from $NCCH_2SCN$.[18]

*12-Cyano-11-thia-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene* (**3**). Cyanomethylthiocyanate (1.11 g, 11 mmol) was added dropwise to a mixture of 9,10-dimethylanthracene (3.4 g, 16 mmol) and triethylamine (1.3 g, 13 $10^{-3}$ mol) in chloroform (70 ml). The reaction was then stirred under reflux for 20 min. After cooling to room temperature, the organic layer was washed successively with a 1N solution of hydrochloric acid and with water, dried over sodium sulfate and filtrated. The chloroform was evaporated under reduced pressure and the resulting oil submitted to column chromatography (eluent:pentane/dichloromethane (50/50)).

Yield = 72%. mp:170°C. $^1$H NMR:2.32 (s, 3H, Me); 2.35 (s, 3H, Me); 3.90 (s, 1H, CH); 7.1–7.6 (m, 8H, aromatic H). $^{13}$C NMR:17.02, 18.24, 44.02, 45.67, 47.79, 118.34 (CN), 118.93, 119.42, 122.43, 123.57, 126.41, 126.68, 127.31, 127.43, 139.37, 140.93, 144.22, 145.55. MS: m/z (%) = 277 ($M^{+}\cdot$, 4), 206 ($DMA^{+}\cdot$, 100), 191 (45), 71 ($M^{+}\cdot$ − DMA, 22). IR (KBr): $\nu_{CN}$ = 2225 $cm^{-1}$.

The non-methylated compound **8** was obtained in the same way from anthracene.

*12-Cyano-11-thia-9,10-dihydro-9,10-ethanoanthracene* (**8**).

Yield = 20%. $^1$H NMR: 4.16 (d, $J$ = 3 Hz, 1H, CHCN); 4.92 (d, $J$ = 3 Hz, 1H, bridgehead H); 5.28 (s, 1H, bridgehead H); 7.1–7.7 (m, 8H, aromatic H). $^{13}$C NMR: 36.53, 45.82, 47.83, 118.61 (CN), 122.17, 122.32, 124.94, 126.20, 126.70, 126.87, 127.58, 127.67, 136.84, 138.29, 141.69, 142.08. MS: m/z (%) = 249 ($M^{+}\cdot$, 4), 178 ($Anthracene^{+}\cdot$, 100), 71 ($M^{+}\cdot$ − anthracene). IR (NaCl): $\nu_{CN}$ = 2230 $cm^{-1}$.

Following the same procedure 12-cyano-11-selena-9,10-dihydro-9,10-ethanoanthracene **9**[19] was synthesized from dimethylanthracene and $NCCH_2SeCN$[20] in 54% yield.

*Rearrangements*

General procedure

Compounds **3**, **8** or **9** (1 mmol) were added at 0°C to a solution of LDA, prepared from diisopropylamine (1.2 mmol) and butyllithium (1.2 mmol), in 10 ml of THF. The resulting mixture was stirred from 0°C to room temperature for 3 h. The alkylating agent (MeI, EtI or $NCCH_2Cl$, 1.3 eq.) was then added and the reaction mixture stirred for another 3 h before quenching with $NH_4Cl$-$H_2O$. After extraction with dichloromethane, drying of the organic phase over $Na_2SO_4$, filtration and evaporation of the solvent under reduced pressure, an oil was obtained which was submitted to column chromatography (silica gel, eluent:dichloromethane/pentane (50/50)). For compounds **12**, **14** and **17** the alkylation step was omitted.

*11-Cyano-11-methylthio-9,10-dimethyl-9,10-dihydro-9,10-methanoanthracene* (**7**).

Yield = 70%. mp = 187–188°C. $^1$H NMR: 1.95 (s, 6H, 2 Me), 2.30 (s, 3H, Me), 7.0–7.3 (m, 8H, aromatic H). $^{13}$C NMR: 9.91, 15.81, 62.92, 85.61, 116.63 (CN), 120.68, 121.37, 126.38, 126.78, 147.77, 148.86. IR (NaCl): $\nu_{CN}$ = 2220 $cm^{-1}$. MS: m/z (%) = 291 ($M^{+}\cdot$, 13), 244 ($M^{+}\cdot$ − $SCH_3$, 54), 230 (22), 206 ($DMA^{+}\cdot$, 54), 191 (24), 149 (33), 57 (100). Anal.: $C_{19}H_{17}NS$: calc. % S = 10.98; found % S = 11.18.

*11-Cyano-11-ethylthio-9,10-dimethyl-9,10-dihydro-9,10-methanoanthracene* (**10**).

Yield = 62%. mp = 119°C. $^1$H NMR: 1.22 (t, 3H, Me), 1.94 (s, 6H, 2 Me), 2.82 (q, 2H, $CH_2$), 7.0–7.2 (m, 8H, aromatic H). $^{13}$C NMR: 9.86, 14.77, 27.27, 62.83, 85.58, 116.83 (CN), 120.69, 121.36, 126.73, 147.77, 148.83. IR (NaCl): $\nu_{CN}$ = 2220 $cm^{-1}$. MS: m/z (%) = 305 ($M^{+}\cdot$, 17), 244 ($M^{+}\cdot$ − SEt, 82), 206 ($DMA^{+}\cdot$, 100), 191 (47), 106 (29), 84 (52).

*11-Cyano-11-cyanomethylthio-9,10-dimethyl-9,10-dihydro-9,10-methanoanthracene* (**11**).

Yield = 55%. mp = 119°C. $^1$H NMR: 2.03 (s, 6H, 2 Me), 3.55 (s, 2H, $CH_2$), 7.0–7.3 (m, 8H, aromatic H). $^{13}$C NMR: 9.73, 18.28, 62.81, 85.49, 115.28 and 116.22 (2 CN), 120.75, 121.64, 126.78, 127.02, 146.67, 147.84. IR (NaCl): $\nu_{CN}$ = 2220 and 2242 $cm^{-1}$. MS: m/z (%) = 316 ($M^{+}\cdot$, 7), 276 ($M^{+}\cdot$, − $CH_2CN$, 6), 244 ($M^{+}\cdot$ − $SCH_2CN$, 100), 218 (86), 206 ($DMA^{+}\cdot$, 96), 191 (46), 178 (15), 70 (44).

*11-Cyano-11-mercapto-9,10-dimethyl-9,10-dihydro-9,10-methanoanthracene* (**12**).

Yield = 64%. mp = 194°C. $^1$H NMR: 1.94 (s, 6H, 2 Me), 2.05 (s, 1H, SH), 7.0–7.2 (m, 8H, aromatic H). $^{13}$C NMR: 9.36, 62.56, 78.96, 118.48 (CN), 120.95, 121.82, 126.62, 126.97, 147.09, 148.12. IR (NaCl): $\nu_{CN}$ = 2220 $cm^{-1}$ and $\nu_{SH}$ = 2547 $cm^{-1}$. MS: m/z (%) = 277 ($M^{+}\cdot$, 12), 244 ($M^{+}\cdot$ − SH, 100), 230 (55), 217 (34), 206 (DMA$^{+\cdot}$, 98), 191 (88), 178 (29), 71 (28), 43 (41). Anal.: $C_{18}H_{15}NS$: calc. % C = 66.45, % H = 4.65, % N = 4.31, % S = 11.54; found % C = 66.52, % H = 4.63, % N = 4.58, % S = 11.68.

*11-Cyano-11-cyanomethylthio-9,10-methanoanthracene* (**13**).

Yield = 52%. $^{1}H$ NMR: 3.54 (s, 2H, $CH_2$), 4.80 (s, 2H, CH), 7.0–7.4 (m, 8H, aromatic H). $^{13}C$ NMR: 17.17, 59.63, 83.4, 116.10 and 117.42 (2 CN), 123.17, 123.84, 126.92, 127.26, 143.89, 145.00. IR (NaCl): $\nu_{CN}$ = 2220 and 2240 cm$^{-1}$. MS: m/z (%) = 288 (M$^{+\cdot}$, 2), 248 (M$^{+\cdot}$ − $CH_2CN$, 10), 216 (M$^{+\cdot}$ − $SCH_2CN$, 63), 190 (61), 178 (Anthracene$^{+\cdot}$, 100), 70 (27).

*11-Cyano-11-mercapto-9,10-methanoanthracene* (**14**).

Yield = 61%. mp = 232°C. $^{1}H$ NMR: 1.26 (s, 1H, SH), 4.61 (s, 2H, CH), 7.0–7.3 (m, 8H, aromatic H). $^{13}C$ NMR: 60.47, 77.99, 118.75 (CN), 122.98, 123.88, 126.82, 127.09, 144.07, 145.54. IR (NaCl): $\nu_{CN}$ = 2220. MS: m/z (%) = 249 (M$^{+\cdot}$, 6), 247 (M$^{+\cdot}$ − 2H, 16), 216 (M$^{+\cdot}$ − SH, 93), 190 (45), 178 (Anthracene$^{+\cdot}$, 100).

*11-Cyano-11-methylseleno-9,10-dimethyl-9,10-dihydro-9,10-methanoanthracene* (**15**).

Yield = 66%. mp = 156–158°C. $^{1}H$ NMR: 1.94 (s, 6H, 2 Me), 2.23 (s, 3H, Me), 7.0–7.2 (m, 8H, aromatic H). $^{13}C$ NMR: 7.35, 10.41, 62.42, 79.29, 117.05 (CN), 120.73, 121.32, 126.27, 126.68, 148.39, 148.80. IR (NaCl): $\nu_{CN}$ = 2220 cm$^{-1}$. MS: m/z (%) = 339 (M$^{+\cdot}$, 6), 244 (M$^{+\cdot}$ − $SeCH_3$, 100), 230 (25), 206 (DMA$^{+\cdot}$, 27), 191 (28), 178 (17), 81 (15), 43 (46). Anal.: $C_{19}H_{17}NSe$: calc. % C = 67.25, % H = 5.05; found % C = 67.31, % H = 5.23.

*11-Cyano-11-ethylseleno-9,10-dimethyl-9,10-dihydro-9,10-methanoanthracene* (**16**).

Yield = 65%. mp = 103°C. $^{1}H$ NMR: 1.38 (t, 3H, Me), 1.96 (s, 6H, 2 Me), 2.85 (q, 2H, $CH_2$), 7.0–7.2 (m, 8H, aromatic H). $^{13}C$ NMR: 10.46, 15.57, 21.49, 62.32, 78.00, 116.93 (CN), 120.77, 121.32, 126.23, 126.66, 148.29, 148.64. IR (NaCl): $\nu_{CN}$ = 2220 cm$^{-1}$. MS: m/z (%) = 353 (M$^{+\cdot}$, 4), 244 (M$^{+\cdot}$ − SeEt, 100), 206 (DMA$^{+\cdot}$, 20), 191 (24), 43 (52). Anal.: $C_{20}H_{19}NSe$: calc. % C = 67.97, % H = 5.42, % N = 3.97; found % C = 67.90, % H = 5.64, % N = 4.04.

*11-Cyano-11-hydroseleno-9,10-dimethyl-9,10-dihydro-9,10-methanoanthracene* (**17**).

Yield = 61%. mp = 275–276°C. $^{1}H$ NMR: 1.25 (s, 1H, SeH), 1.93 (s, 6H, 2 Me), 7.0–7.2 (m, 8H, 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): $\nu_{CN}$ = 2220 cm$^{-1}$. MS: m/z (%) = 325 (M$^{+\cdot}$, 1), 244 (M$^{+\cdot}$ − SeH, 100), 206 (DMA$^{+\cdot}$, 19), 191 (27), 57 (32). Anal.: $C_{18}H_{15}NSe$: calc. % C = 66.45, % H = 4.65, % N = 4.31; found % C = 66.52, % H = 4.63, % N = 4.58.

In the case of the reaction with **22**, a mixture of the two compounds **23** and **24** was obtained. Only **24** could be isolated in a nearly pure state after chromatography.

*11-Ethoxycarbonyl-11-methylthio-9,10-dimethyl-9,10-dihydro-9,10-methanoanthracene* (**24**).

Yield = 33%. $^{1}H$ NMR: 1.01 (t, 3H, Me), 2.05 (s, 3H, Me), 2.06 (s, 6H, 2 Me), 3.97 (q, 2H, $CH_2$), 6.98–7.18 (m, 8H, aromatic H). $^{13}C$ NMR: 10.25, 14.03, 14.37, 27.27, 61.42, 62.92, 120.07, 120.76, 125.73, 125.77, 149.85, 150.03, 169.58 (CO). MS: m/z (%) = 338 (M$^{+\cdot}$, 36), 291 (63), 245 (33), 217 (43), 206 (DMA$^{+\cdot}$, 100), 191 (60), 178 (40), 49 (46).

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