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SYNTHESIS OF THE 9-MESITYL-10-PHENYL-9-BORAANTHRACENE ANION

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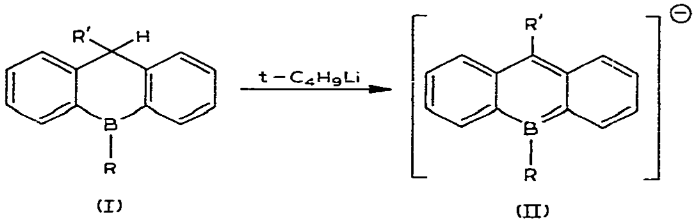
SUMMARY

Derivatives of 10-phenyl-9,10-dihydro-9-boraanthracene were synthesized from tris(2-benzhydrylphenyl)boroxin by pyrolysis with lithium aluminum hydride and tributyl borate. 10-Phenyl-9-boraanthracene could not be obtained from a chemical reaction or on electron impact. The isolation of lithium 9-mesityl-10-phenyl-9-borataanthracene as a crystalline non-solvated salt is described.

INTRODUCTION

In a preliminary communication[1] we reported the synthesis of the 9-mesityl-9-boraanthracene anion (IIa) in solution. In the meantime Jutzi has described the isolation of a solvated lithium salt of the 9-phenyl-9-boraanthracene anion (IIb)[2].



(Ia)–(IIa), R = mesityl, R' = H;
(Ib)–(IIb), R = Ph, R' = H
(Ic)–(IIc), R = mesityl, R' = Ph

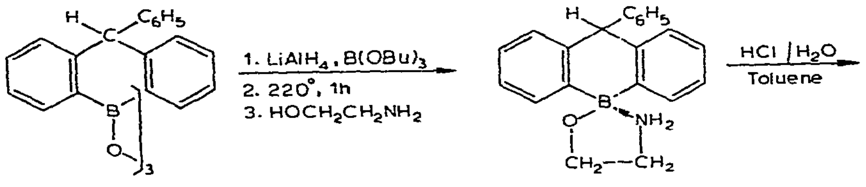
Since for the 9-phospha[3]- and 9-arsaanthracenes[4] substantial stabilization of the anthracene system was achieved by introduction of a phenyl group into the 10-position, we attempted to synthesize the 10-phenyl-9,10-dihydro-9-boraanthracene system. In this paper we describe the synthesis of this ring system and the isolation of the 9-mesityl-10-phenyl-9-boraanthracene anion as a crystalline non-solvated lithium salt.

RESULTS AND DISCUSSION

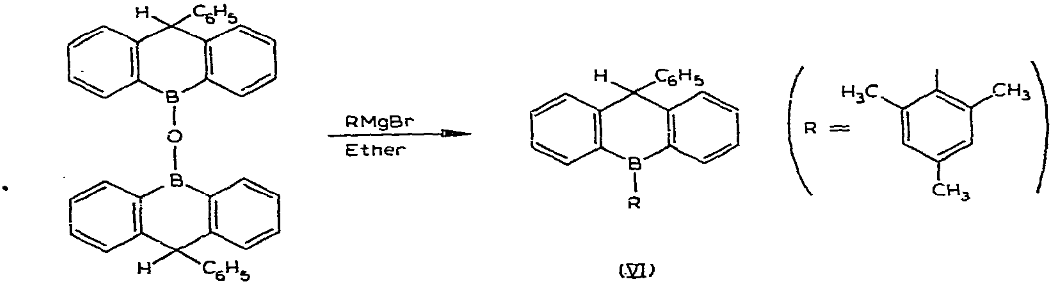
Earlier syntheses of the 9,10-dihydro-9-boraanthracene system (I) involved Grignard derivatives of 2,2'-dihalodiphenylmethanes[5,6]. As the corresponding 2,2'-dihalotriphenylmethanes were not easily accessible[7], it appeared attractive to explore a different route, starting from the more readily available 2-bromotriphenylmethane.

By the usual Grignard procedure, *i.e.* addition of 2-(bromomagnesio)triphenylmethane in tetrahydrofuran solution to an excess of tributyl borate at −70°, the corresponding boronic acid was prepared; it was isolated and purified via its diethanolamine ester. Hydrolysis of the latter gave the boroxin (III).

We formed the ring system of (I) by pyrolysis of a mixture of (III), lithium aluminum hydride, and tributyl borate; presumably the reaction proceeds via the corresponding primary borane (or a butoxy derivative of it), in analogy to the pyrolytic ring closure of boranes reported by Köster *et al.*[8].



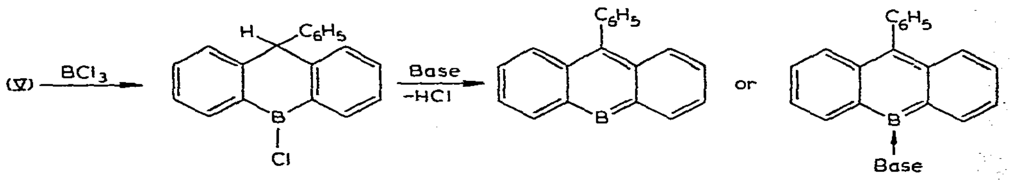
(III) (IV)



(V) (VI)

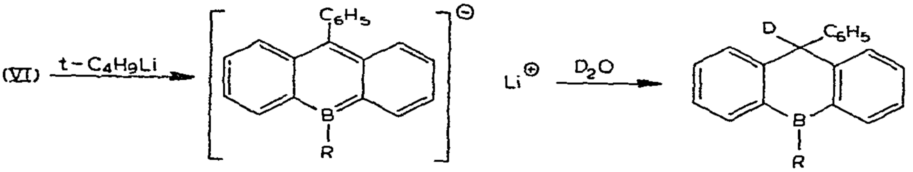
The ring closed product was isolated as the crystalline, air-stable, ethanolamine ester (IV) in 49% yield. Hydrolysis of (IV) with dilute HCl in a water/toluene suspension gave the corresponding borinic acid, which was isolated in nearly quantitative yield as its anhydride (V). Treatment of (V) with mesitylmagnesium bromide in ether yielded 9-mesityl-10-phenyl-9,10-dihydro-9-boraanthracene (VI).

When treated with boron trichloride in chloroform or toluene, (V) gave 9-chloro-10-phenyl-9,10-dihydro-9-boraanthracene (VII) in 70% yield. We have not so far obtained any (UV spectroscopic[6]) evidence that reaction of (VII) with bases[6] leads to 10-phenyl-9-boraanthracene (VIIIa) or its base adduct (VIIIb)[2].



(VII) (VIIIa) (VIIIb)

When (VI) was treated with tert-butyllithium in benzene, a deep red color ascribed to (IIc) gradually developed. Addition of deuterium oxide yielded 83% of the 10-deuterated derivative (VId). (IIc) was rather soluble in benzene, but when (VI) in toluene was treated with tert-butyllithium, in hexane as a diluent, a reasonable yield of (IIc) was obtained as a cherry-red crystalline precipitate. Hydrolysis of the weighed precipitate and titration of the base formed, led to correct analytical results for (IIc), *i.e.* the solvent-free salt. From the organic layer (VI) was recovered in 90% yield.



(IIc) (VId)

The UV spectrum of (IIc) shows a slight shift to longer wavelengths, relative to that of (IIa)[1] (see Fig. 1). The overall shape is much the same, indicating that there is very little electronic interaction of the phenyl group with the chromophoric system. The anthracene region shows a slightly smaller shift (6 nm) than the carbanion region (10 nm). The observation that the ratio of the extinctions of the anthracene region and the carbanion region is lower for (IIc) (E_{371}/E_{445} 2.28) than for (IIa) (E_{365}/E_{435} 2.5) could be tentatively explained by assuming that owing to the additional delocalization of the negative charge in the extra phenyl ring of (IIc) the relative importance of the contribution of the anthracene-type resonance structure is decreased.

An interesting feature of the ^{1}H NMR spectra of (VI) and (VId) is that there are two peaks arising from the mesitylenic *ortho*-methyl groups, indicating that rotation around the B–C mesitylenic bond is slow on the NMR time-scale. This inhibition must, in part at least, arise from the phenyl group in the 10-position, for when the phenyl group is replaced by a carboxyl group[1], the two methyl groups give rise to one peak only.

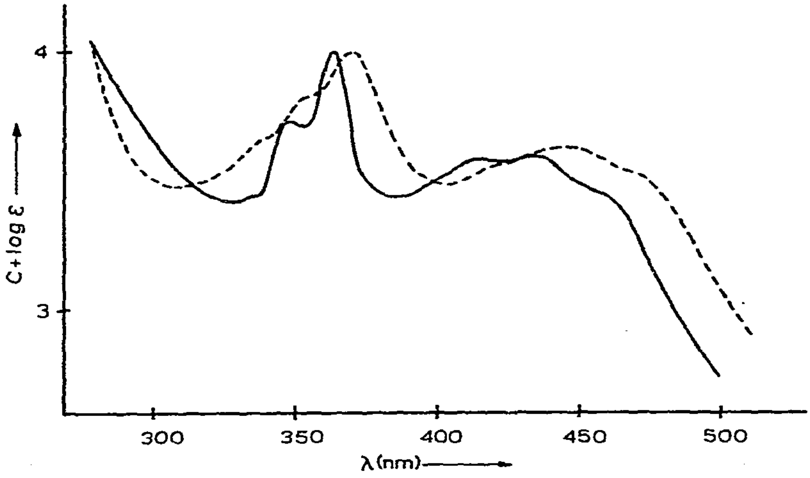


Fig. 1. UV spectra of (IIa) (——) and (IIc) (----) in benzene/pentane. The value of C is unknown.

TABLE 1

MASS SPECTRA OF (VI) AND (VId)

m/e	*Relative intensity (%)*		*m/e*	*Relative intensity (%)*	
	(VI)	*(VId)*		*(VI)*	*(VId)*
249	5.9		254		26.6
250	13.8	8.8	371	7.8	
251	43.4	18.9	372	27.1	11.3
252	100	51.4	373	8.7	33.7
253	28.3	100	374		10.5

The mass spectrum of (VI) (see Table 1) showed no significant peaks except those of the molecular ion [(VI)$^{+\cdot}$, $m/e=372$] and of the molecular ion minus C_9H_{12} {[(VI) − mesitylene]$^{+\cdot}$, $m/e=252$, base peak}. It was tempting to ascribe this peak to 10-phenyl-9-boraanthracene (VIIIa), *i.e.* to assume that the extra hydrogen had been stripped from the 10-position. A comparison of the mass spectra of (VI) and (VId) (see Table 1), however, proved that this was not the case. In (VId) the mesityl group and one *hydrogen* atom are lost from the molecular ion, a conclusion which is confirmed by the observed metastable ions (see Experimental). This observation reopens the question of the structure of the [M − mesitylene]$^{+\cdot}$ ions formed from dihydroboraanthracene derivatives on electron impact[6].

The structures of all compounds were confirmed by elemental analysis, by their ^{1}H NMR, IR and mass spectra, and in many cases by their degradation and interconversion reactions (see Experimental).

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were obtained with a Perkin–Elmer model 237 spectrophotometer, the NMR spectra with a Varian A-60 spectrometer, the UV spectra with a Perkin–Elmer 137 spectrophotometer, and the mass spectra with a Varian MAT CH5 mass spectrometer at 70 eV.

Tris(2-benzhydrylphenyl)boroxin (III)

(*a*) *Diethanolamine ester of (III).* A filtered solution of the Grignard reagent from 135 g (417.7 mmol) of 2-bromotriphenylmethane in 740 ml tetrahydrofuran was added under nitrogen to a solution of 283.5 g of tributyl borate in 500 ml of tetrahydrofuran at −70°. The mixture was stirred at room temperature for 23 h and then refluxed for 1 h. The crude reaction mixture was evaporated *in vacuo*; several 50 ml portions of water and toluene were added and again evaporated *in vacuo* to remove the butanol. The residue was dissolved in toluene and acidified with dil. HCl. After separation, the organic layer was washed with water and evaporated *in vacuo*. The residue was redissolved in 500 ml of toluene and, after filtration the solution was added to 50 g of diethanolamine in 250 ml water. After the mixture had stood for a week, the precipitate was filtered off, washed with cold methanol, and dried *in vacuo* to give 107.2 g (72 %) of the diethanolamine ester of (III), m.p. 222–224.5°. Recrystallization from methanol raised the m.p. to 223–225°. (Found: C, 77.53; H, 6.84; B, 2.97; N, 3.82. $C_{23}H_{24}BNO_2$ calcd.: C, 77.32; H, 6.77; B, 3.03; N, 3.92%.) IR spectrum (KBr), ν_{max} in cm^{-1}: 3180 m (N–H); 1205 s (N→B); 1070 s (C–O). ^{1}H NMR [$(CD_3)_2SO$, TMS internal reference], δ in ppm: 7.77–6.83 (m, 14, aryl protons), 6.73 (s, 1, methine proton), 6.50 (broad s, 1, NH), 4.02–3.60 (m, 4, OCH_2), 3.08–2.57 (m, 4, NCH_2).

(*b*) *Tris(2-benzhydrylphenyl)boroxin* (*III*). 42.7 g Diethanolamine ester of (III) in a mixture of 100 ml of toluene, 50 ml of water and 20 ml of conc. HCl was thoroughly stirred at room temperature for 1 h. After separation, the organic layer was washed with water and evaporated to dryness *in vacuo*, yielding 33.65 g (98%) of crude (III), m.p. 107–120°. Vacuum sublimation gave pure (III), m.p. 94–95°. (Found: C, 84.83; H, 5.65; B, 4.28. $C_{57}H_{45}B_3O_3$ calcd.: C, 84.48; H, 5.60; B, 4.00%.) IR spectrum (KBr), ν_{max} in cm^{-1}: 1340 vs (B–O). ^{1}H NMR (CCl_4, internal TMS), δ in ppm: 7.89–7.68 (m, 3, aryl protons), 7.47–6.81 (m, 39, aryl protons), 6.51 (s, 3, methine protons). Mass spectrum: Found: 810.3610. $C_{57}H_{45}{}^{11}B_3O_3$ calcd.: 810.3648.

(*c*) *Reaction of* (*III*) *with* H_2O_2. After standing for 3 days a mixture of 919.8 mg of (III), 40 g of methanol and 20 ml of 30% H_2O_2 was evaporated *in vacuo*. The residue was dissolved in water and CCl_4. The CCl_4 layer was separated, washed with water and evaporated to dryness *in vacuo*. Vacuum sublimation of the residue gave 801.5 mg (90%) of 2-hydroxytriphenylmethane, m.p. 120–122°, [lit.[9] m.p. 124°], identified by its IR, ^{1}H NMR and mass spectra.

(*d*) *Conversion of* (*III*) *into its dimethyl ester*. A solution of 2 g of (III) in 200 ml methanol was evaporated to dryness *in vacuo*. Vacuum sublimation of the residue gave the ester as a white, crystalline solid, m.p. 82.5–84.5°, yield 1945.6 mg (83%). (Found: C, 80.12; H, 6.67; B, 3.21. $C_{21}H_{21}BO_2$ calcd.: C, 79.77; H, 6.69; B, 3.42%.) IR spectrum (CCl_4), ν_{max} in cm^{-1}: 2950 s, 2860 s (CH_3), 1320 vs (B–O). ^{1}H NMR (CCl_4, internal TMS), δ in ppm: 7.42–6.74 (m, 14, aryl protons), 5.77 (s, 1, methine proton), 3.27 (s, 6, CH_3). Mass spectrum: Found: 316.1635. $C_{21}H_{21}{}^{11}BO_2$ calcd.: 316.1635.

9-(2-*Aminoethoxy*)-10-*phenyl*-9,10-*dihydro*-9-*boraanthracene* (*IV*)

In a nitrogen-swept 100 ml three-necked flask, cooled by liquid nitrogen and provided with a mechanical stirrer, reflux condenser, and a thermometer reaching to the bottom of the flask, 3.1985 g of crude (III), 1.6924 g of lithium aluminum hydride and 3 ml of tributyl borate were thoroughly mixed. The cooling bath was then removed. At about 0° a very exothermic reaction occurred, which was quenched by cooling in liquid nitrogen. When it had reached room temperature, the mixture was pyrolysed with an IR heater at 220–240° (internal temperature) for 1 h (gas evolution). After cooling, 30 ml of toluene was added and the mixture hydrolysed with 6*N* HCl, the temperature being kept below 20°. After filtration, and separation of the layers, the organic layer was washed with water and evaporated *in vacuo*. The residue was dissolved in 30 ml of ether or toluene, filtered, and added to a solution of 3 ml of ethanolamine in 17 ml of H_2O. After standing overnight at room temperature, the precipitate was filtered off, washed with water and ether and dried *in vacuo*. Average yield 49%, m.p. 232–234°. (Recrystallization from toluene is possible.) (Found: C, 80.22; H, 6.92; B, 3.07; N, 4.97. $C_{21}H_{20}BNO$ calcd.: C, 80.53; H, 6.44; B, 3.45; N, 4.47%.) IR spectrum (KBr), ν_{max} in cm^{-1}: 3320 s, 3200 m (N–H); 1180 vs (N→B), 1075 vs (C–O). ^{1}H NMR [$(CD_3)_2SO$, TMS internal reference], δ in ppm: 7.73–6.92

(m, 13, aryl protons), 5.61 (broad, 2, NH_2), 5.29 (s, 1, methine proton), 4.17 [t($J=6$ Hz), 2, OCH_2], 3.00 (m, 2, NCH_2). UV spectrum (ethanol), λ_{max} in nm: 290, 283, 271, 254 (ε is concentration dependent, presumably due to transesterification with ethanol).

Bis(10-phenyl-9,10-dihydro-9-bora-9-anthryl)oxide (V)

3.1058 g of (IV) in a mixture of 50 ml of toluene, 50 ml of water and 10 ml of conc. HCl was thoroughly stirred for 2 h at room temperature. After separation, the organic layer was washed with water and evaporated to dryness *in vacuo*, to give 2.5521 g (98%) of (V), m.p. 181–186°. Vacuum sublimation gave pure (V), m.p. 196–198°. (Found: C, 87.99; H, 5.39; B, 4.22. $C_{38}H_{28}B_2O$ calcd.: C, 87.39; H, 5.40; B, 4.14%.) IR spectrum (KBr), ν_{max} in cm^{-1}: 1400 s (B–O). ^1H NMR ($CDCl_3$, TMS internal reference), δ in ppm: 8.07–7.87 (m, 4, aryl protons), 7.52–7.06 (m, 22, aryl protons), 5.64 (s, 2, methine protons). Mass spectrum: Found: 522.2303. $C_{38}H_{28}{}^{11}B_2O$ calcd.: 522.2326.

Reaction of (V) with H_2O_2. After standing for 12 h, a mixture of 275.7 mg of (V), 40 g of methanol and 10 ml of 30% H_2O_2 was evaporated *in vacuo*. The residue was taken up in water, filtered and the precipitate dried *in vacuo*, yielding 258.8 mg (89%) 2,2′-dihydroxytriphenylmethane, m.p. 128–132°. Recrystallization from CCl_4 and vacuum sublimation gave a pure sample, m.p. 144–145°, (lit.[10a] m.p. 57–60° lit.[10b] 128–129° (?)). (Found: C, 82.46; H, 5.95. $C_{19}H_{16}O_2$ calcd.: C, 82.58; H, 5.84%.) The compound was shown by its m.p. and IR, ^1H NMR and mass spectra to be identical with a sample of 2,2′-dihydroxytriphenylmethane, synthesized by the method of Casiraghi *et al.*[10].

Reaction of (V) with bromine. A mixture of 311.7 mg of (V), 40 g of methanol, 6 g of sodium bicarbonate and 1 ml of bromine was thoroughly stirred for 12 h. After evaporation to dryness, the residue was dissolved in toluene and water. After separation, the organic layer was washed with water and evaporated to dryness, to give 472.5 mg (98%) of 2,2′-dibromotriphenylmethane as a glass. Crystallization from 5 ml methanol afforded 381.5 mg of purified product, m.p. 128–130°. The m.p. and IR and ^1H NMR spectra showed the compound to be identical with an authentic sample prepared in our laboratory from 2,2′-dibromobenzophenone[7].

9-Chloro-10-phenyl-9,10-dihydro-9-boraanthracene (VII)

10 ml of boron trichloride was condensed under nitrogen, into a solution of 2552.1 mg (V) in 60 ml dry chloroform or toluene at −70°. After standing overnight at room temperature the solution was evaporated *in vacuo*. Vacuum sublimation of the residue gave 2008.5 mg (70%) of pure (XII) as pale violet crystals, m.p. 120–122°. [From the residue 20% of unchanged (V) was recovered as the ethanolamine ester (IV).] (Found: C, 79.92; H, 5.25; B, 3.23; Cl, 10.33. $C_{19}H_{14}BCl$ calcd.: C, 79.08; H, 4.89; B, 3.75; Cl, 12.29%.) IR spectrum (CCl_4), ν_{max} in cm^{-1}: 1445 s, 1320 s, 1305 s, 1285 s (B–aryl); 900 m (B–Cl). ^1H NMR (CCl_4, TMS external reference), δ in ppm: 8.90–8.62 (m, 2, aryl protons), 7.97–7.27 (m, 11, aryl protons), 5.74 (s, 1, methine proton). Mass spectrum: Found: 288.0879. $C_{19}H_{14}{}^{11}B^{35}Cl$ calcd.: 288.0877.

9-Mesityl-10-phenyl-9,10-dihydro-9-boraanthracene (VI)

A filtered solution of 31.2 mmol of mesitylmagnesium bromide in 30 ml ether was added at room temperature under nitrogen to a thoroughly stirred suspension of 3.2507 g of (V) in 40 ml of ether. After standing at room temperature for 20 h, the deep-red mixture was hydrolysed with dil. HCl. The ether layer was washed with water until neutral reaction and evaporated to dryness *in vacuo*. Vacuum sublimation of the residue at 165° (0.1 mmHg) gave 3.4414 g (74%) of pure (VI), m.p. 181–183°. (Found: C, 90.65; H, 6.70; B, 2.33. $C_{28}H_{25}B$ calcd.: C, 90.33; H, 6.77; B, 2.90%.) ^{1}H NMR (CCl_4, TMS internal reference), δ in ppm: 7.78–7.55 (m, 2, aryl protons), 7.42–6.94 (m, 11, aryl protons), 6.85 (s, 2, mesitylenic aryl protons), 5.51 (s, 1, methine proton), 2.35 (s, 3, *o*-CH_3), 2.12 (s, 3, *o*-CH_3), 2.00 (s, 3, *p*-CH_3). Mass spectrum: Found: 372.2049. $C_{28}H_{25}{}^{11}B$ calcd.: 372.2039. For the transition 372 $\xrightarrow{*}$ 252 a metastable ion was observed at $m/e = 170.8$, calcd.: 170.77.

9-Mesityl-10-deutero-10-phenyl-9,10-dihydro-9-boraanthracene (*VI*d)*

In a sealed high vacuum system 2.5 ml of 0.90 N tert-butyllithium in pentane (2.25 mmol) was added to a degassed solution of 339.0 mg (0.911 mmol) of (VI) in 50 ml benzene. Gradually the solution turned deep red. After 24 h 1 ml of D_2O was added, and the solution turned bright yellow. On working up as described for (VI), 283.1 mg (83%) of (VId) was obtained (m.p. 181–183° after recrystallization from a petroleum ether (28–40°)/ether mixture). IR and ^{1}H NMR spectra were similar to those of (VI), except for the expected differences due to the presence of deuterium. Mass spectrum: for the transition 373 $\xrightarrow{*}$ 253 a metastable ion was observed at $m/e = 171.7$, calcd.: 171.67.

Lithium 9-mesityl-10-phenyl-9-borataanthracene (*II*c)

11.2 ml 0.1193 of *N* tert-butyllithium (1.336 mmol) in n-hexane was added under nitrogen to a solution of 489.9 mg (1.316 mmol) (VI) in 5 ml of dry, oxygen-free toluene in a 50 ml weighed (N_2!) three-necked flask provided with a glass filter. After standing for 3 h, the solution was filtered off and the deep-red crystalline precipitate washed with two 1 ml portions of n-hexane. After drying *in vacuo* for 16 h the flask and contents were weighed [yield 130.5 mg (26%) of (IIc)], and the precipitate was hydrolysed by adding 5 ml of toluene and 10 ml of water (both oxygen-free). The layers were carefully separated. The water layer was diluted to 100 ml, and 10 ml aliquots titrated with 0.0100 *N* HCl; needed for neutralization: 3.42 ml, calcd.: 3.45 ml (99.1%). Working up of the organic layer as described for (VI), yielded 115.6 mg (90%) (VI), m.p. 175–179°; (181–183° after recrystallization from a petroleum ether (28–40°)/ether mixture).

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* An X-ray diffraction structure determination of (VId) is in progress.

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