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In Quest of a Prismene. Organolithium-Induced Desulfonylation on Strained Hydrocarbons

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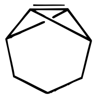
Reaction of a twofold excess of *n*-butyllithium with 1,6-bis(*tert*-butylsulfonyl)tetracyclo[4.2.0.0^{5,7}]octane (**14**) yields a mixture of 3- and 5-*n*-butyl-2-(*tert*-butylsulfonyl)bicyclo[2.2.2]octa-2,5-dienes **15** and **16**, respectively, while the reaction with 2,3-bis(*tert*-butylsulfonyl)quadricyclane (**11**) leads to 5-*n*-butyl-2-(*tert*-butylsulfonyl)bicyclo[2.2.1]hepta-2,6-diene (**24**), and the reaction with 2-(*tert*-butylsulfonyl)hexacyclo[9.5.0.0^{1,3}.0^{2,10}.0^{3,9}.0^{9,11}]hexadecane (**8**) yields a 1:1 mixture of 15-*n*-butyltetracyclo[7.5.2.0.0^{2,8}]hexadeca-2(8),15-diene (**34**) and 1-*n*-butyl-2,3:4,5-dipentanobenzene (**35**). Common to all three reactions is the elimination of *tert*-butylsulfinate and the addition of a butyllithium moiety. A radical mechanism is suggested rather than an elimination via a strained double bond incorporated in a strained cage system.

The last 10 years have witnessed many successful efforts to prove the existence of highly strained olefins which violate Bredt's rule.[1a−c] Among them are tricyclo[4.1.0.0^{2,7}]hept-1(7)-ene (**1**),[2a−e] and dehydroquadricyclanes,[3a−g] such as **2** and 1,2-dehydrocubane (**3**)[4a,b] to name only a few. All of them are severely bent olefins with very short life-times. The existence of these species as short lived intermediates has usually been demonstrated by trapping experiments, e.g. by reaction with a diene or by the addition of lithium alkyl.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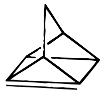
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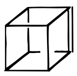
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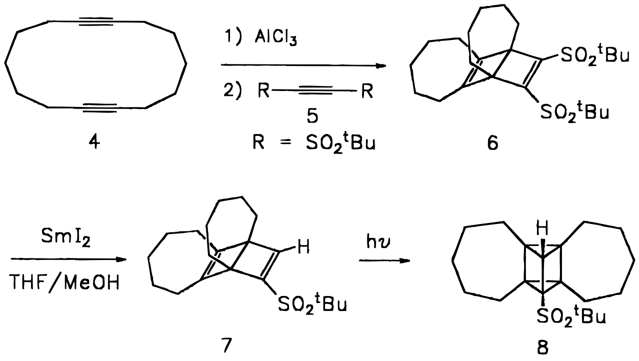
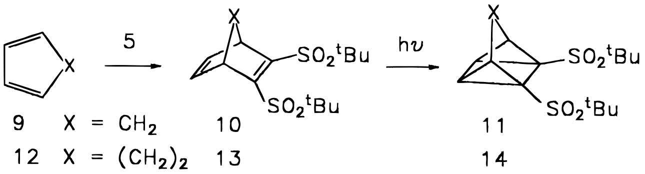
In connection with our investigations of doubly bridged prismanes we noticed that these species are rather stable toward rearrangements to the corresponding benzene derivatives.[5] Therefore we have looked for a doubly bridged prismane for which an elimination would be worth attempting. An appropriate compound which was easily accessible was **8** (see Scheme 1).[6] We have therefore investigated the sulfinate elimination for **8** as well as for **11** and **14**, both of which are readily available via a Diels-Alder reaction[7] and subsequent light induced [2 + 2] cycloaddition (Scheme 2).[8]

Scheme 1



Scheme 2



Elimination Experiments with 11 and 14. Reaction of **14** with *n*-butyllithium (*n*-BuLi) in ether at −20 °C and a subsequent quenching with CH_3OH and CH_3OD, respectively, leads in a fast reaction to two products, **15** and **16**, as indicated in Scheme 3. The structural assignment is based on the analytical properties of the products. The products **15** and **16** point to a common

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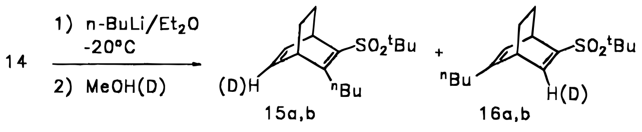
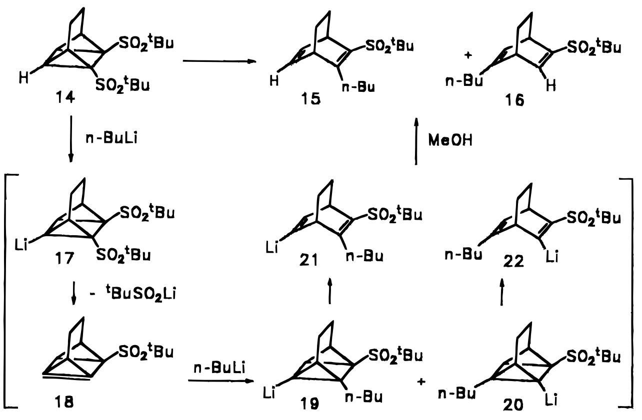
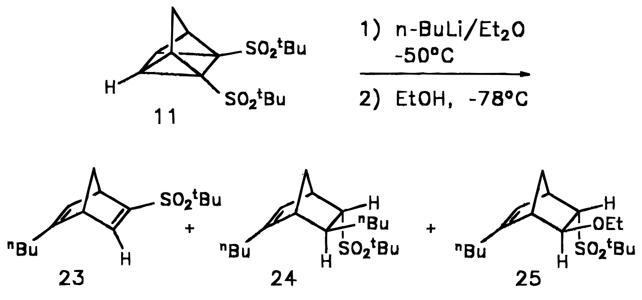
Scheme 3



Scheme 4



Scheme 5

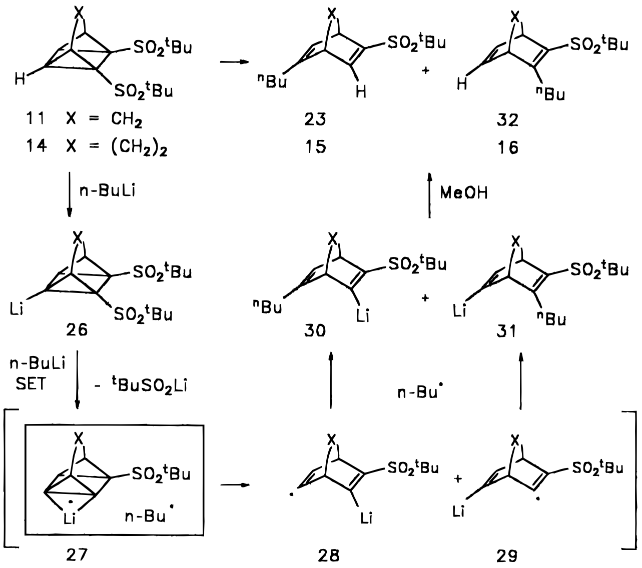


intermediate to which the addition of *n*-BuLi can occur in two different ways. A first possible explanation is provided by the reaction sequence indicated in Scheme 4 with **18** as intermediate.[1−3] A [2 + 2]-cycloreversion and subsequent hydrolysis leads to two different products. This assumption seemed reasonable because similar bridgehead olefins have been shown to be intermediates in other reactions, in which they were trapped by anthracene and furane derivatives. Our further assumption that the tetracyclic compounds **19** and **20** revert to **21** and **22**, respectively, is based on the known thermal lability of **14** and related species.[9a,b]

All our efforts to trap **18** as an intermediate in the presence of 1,3-diphenylisobenzofuran have failed, however. This casts doubt on the postulated mechanism shown in Scheme 4 and in turn led us to study the sulfinate elimination of the quadricyclane derivative **11**. Treatment of an ethereal solution of **11** with *n*-BuLi at −78 °C only led to a reaction after the temperature was raised to −50 °C. The subsequent quenching of the mixture with ethanol at −78 °C gave three products **23**, **24**, and **25** (see Scheme 5). A Michael addition of *n*-BuLi and ethanol, respectively, to **23** and subsequent hydrolysis rationalizes the appearance of **24** and **25**. We were neither able to find a quadricyclane derivative, nor an addition product with the *n*-butyl residue adjacent to the *tert*-butylsulfonyl group.

These findings contrast the results reported for the dehydrohalogenation of chloroquadricyclane.[3g] This led us to assume that another mechanism is in effect for the desulfonylation of **11** and **14**.

Scheme 6



The correct mechanism has to account for the fact that the [2 + 2]cycloreversion in the cases of **11** and **14** must occur with a very low activation energy. This points to a cationic or radical intermediate. From the facts that organolithium compounds are capable of initiating a SET mechanism[10] and cyclopropylmethyl radicals are subject to very fast ring openings to the corresponding homoallyl radicals,[11] we favor a radical intermediate (Scheme 6).

According to this proposal, the lithiated species **26** does not eliminate a sulfinate anion as had been postulated in Scheme 4. A second molecule of *n*-BuLi is necessary to provide an electron in a SET process to yield **27**. A ring opening rearrangement yields the isomeric radicals **28** and **29**. After recombination with the accompanying *n*-butyl radical and hydrolysis, the products are formed. In accord with this mechanism are the facts that at least two molecules of *n*-BuLi are necessary, that a ring opening occurs, and that we could never trap a strained intermediate such as **18** by a Diels−Alder reaction.

Reaction of 8 with *n*-Butyllithium. Treatment of an ethereal solution of **8** with a fivefold excess of *n*-BuLi at 30 °C yields two products, **33** and **34**, in the ratio of 1:1. Quenching experiments with d_1-methanol afford in nearly quantitative yield the corresponding deuterated products (see Scheme 7). This suggests that at first the proton on the prismane skeleton is removed to yield the corresponding lithiated species **35**. To test this we have carried out reaction of d_1-**8** with *n*-BuLi between 0 °C and room temperature and quenched the mixture with methanol. In the reaction mixture we could detect **8**, indicating that a reversible lithiation of the prismane skeleton in **8** occurred.

To learn more about the possible reaction mechanism we varied the solvents and the concentration of *n*-BuLi and we have added LiBr to provide a nucleophile in the solution. We found that the sulfinate elimination occurs in ether and in hexane but not in THF. More than a twofold excess of n-BuLi was necessary, and LiBr neither affects the product distribution nor does it give rise to

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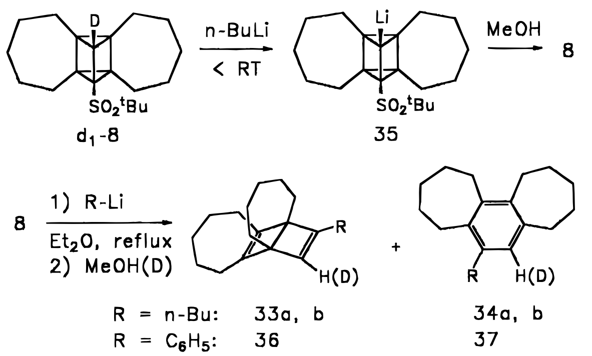
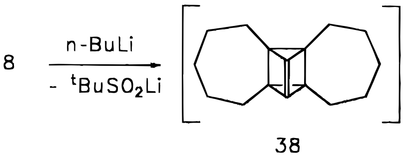
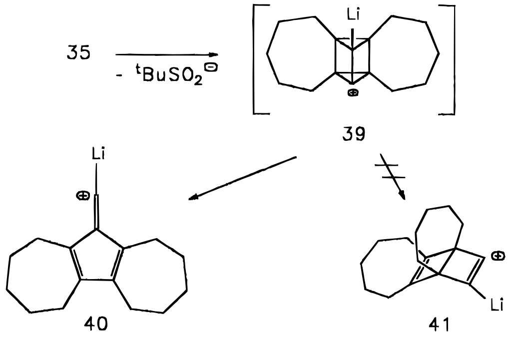
Scheme 7



Scheme 8



Scheme 9



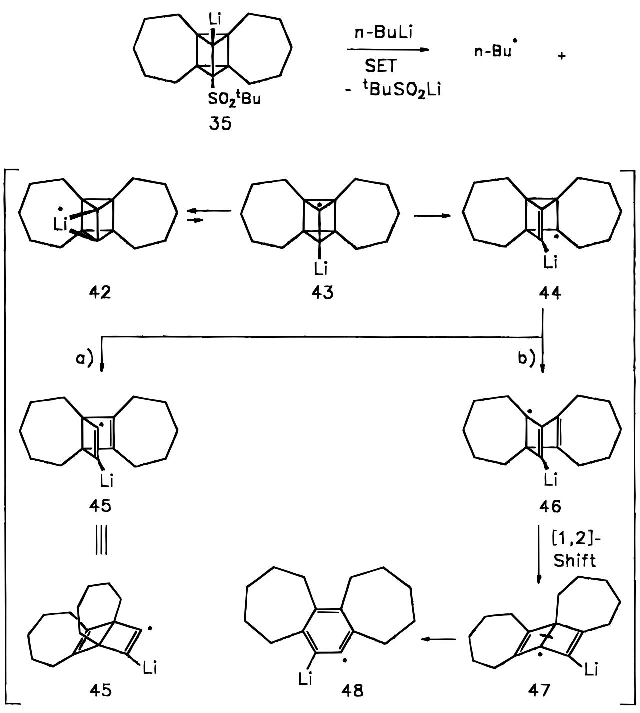
any new products. Carrying out the elimination with phenyllithium yields the anticipated products **36** and **37** in the same 1:1 ratio.

For the possible reaction mechanism we also have to consider an elimination−addition pathway. This would lead (Scheme 8) from **8** via the lithium salt **35** to the prismene derivative **38**. According to calculations on the parent prismene[12] we expect that **38** is a highly strained olefin. We have tried to trap any **38** present as an intermediate with anthracene and diphenylisobenzofurane using LiTMP as base for the elimination reactions. We could not find any of the expected cycloaddition products. This experiment disfavors **38** as an intermediate.

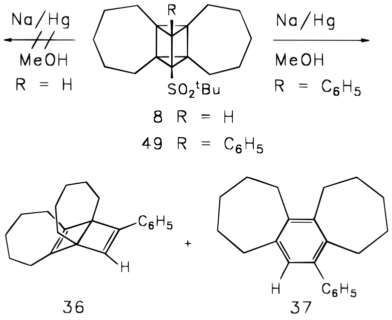
We also disfavor a cationic intermediate such as **39** which might arise from **35** (Scheme 9). In particular, the experiment with LiBr argues against such a possibility, as do the results of quantum chemical calculations which predict a minimum for **40** but not for **41**. In addition since we have never detected any fulvene derivatives, it seems reasonable to disregard a cationic mechanism.

What remains then, is a radical mechanism initiated via a SET process. A possible pathway is given in Scheme 10. We postulate as a first intermediate the prismyl radical **42** which can rearrange to the lithiated Dewar-benzene radicals **45** and **47**. The benzene derivative **48** could then result from **47**. Further support for a radical mechanism comes from the reduction of **49** with Na/Hg as shown in Scheme 11. It is known that

Scheme 10



Scheme 11



desulfonylation with Na/Hg occurs via a radical mechanism.[13] We obtained from this reaction the anticipated Dewar-benzene derivative **37** and the benzene derivative **38** in the ratio of 1:1.

Conclusion

Our investigations on **8**, **11**, and **14** suggest that for the butyllithium-induced elimination of a *tert*-butylsulfonyl group in highly strained systems a radical mechanism is operative.

Experimental Section

General. All reactions were carried out under an Ar atmosphere with magnetic stirring. The diethyl ether used was freshly distilled from Na−benzophenone. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 200 and 50 MHz in $CDCl_3$ if not otherwise noted. Elemental analyses were performed at the Mikroanalytisches Laboratorium der Universität Heidelberg, Germany.

Reaction of 1,6-Bis(*tert*-butylsulfonyl)tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octane (14) with n-Butyllithium. To a suspension of 200 mg (0.58 mmol) of **14** in 10 mL of dry ether was added at −30 °C 1.0 mL of a 1.6 N solution of *n*-butyllithium in hexane. Within a few seconds no starting material could be

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detected (TLC), but two new products were observed. At −20 °C a few drops of methanol were added to quench the products. After removal of the solvent the raw material was purified by column chromatography (silica gel, petroleum ether/ether 2:1), to yield 25 mg (15%) of 3-butyl-2-(*tert*-butylsulfonyl)bicyclo-[2.2.2]octa-2,5-diene (**15**) and 25 mg (15%) of 5-butyl-2-(*tert*-butylsulfonyl)bicyclo[2.2.2]octa-2,5-diene (**16**) as a colorless oil. Quenching of the reaction with CH_3OD led to the deuterated products **15b** and **16b**. **15**: ^{1}H NMR (300 MHz) δ 6.41, 6.32, (m, each 1H), 4.12, 3.71 (m, each 1H), 2.8−2.7, 2.6−2.5 (m, each, 1H), 1.6−1.3 (m, 6H), 1.28 (s, 9H), 0.92 (t, 3H, $^3J_{H,H}$ = 7.1 Hz); ^{13}C NMR (75 MHz) δ 164.3, 134.8, 134.4, 133.0, 60.5, 44.6, 40.8, 32.1, 30.1, 26.1, 24.0, 23.3, 23.0, 13.9; IR (KBr) 2957, 2933, 1460, 1289, 1121, 695, 649 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ) 244 (2.89) nm; HRMS (EI) calcd 282.1653; Found 282.1645. **16**: ^{1}H NMR (300 MHz) δ 7.20 (dd, 1H, $^3J_{H,H}$ = 6.1 Hz, $^4J_{H,H}$ = 2.1 Hz), 5.92 (dd, 1H, $^3J_{H,H}$ = 6.1 Hz, $^4J_{H,H}$ = 1.6 Hz), 3.99, 3.67 (m, each 1H), 2.11 (m, 2H), 1.6−1.2 (m, 8H), 1.27 (s, 9H), 0.87 (t, 3H, $^3J_{H,H}$ = 7.3 Hz); IR (KBr) 2957, 2932, 2872, 1600, 1463, 1294, 1122, 680, 551 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ) 236 (2.28), 244 (3.5), 284 (2.67), 298 (2.43), 306 (2.27) nm; HRMS (EI) calcd 282.1653; found 282.1625.

Reaction of 2,3-Bis(*tert*-butylsulfonyl)quadricyclane (11) with *n*-Butyllithium. To a suspension of 0.80 g (2.4 mmol) of **11** in 10 mL of dry ether was added 4 mL of a 1.6 M solution of *n*-butyllithium in hexane at −78 °C. A brief removal of the cold-bath led to an orange-red color of the solution. After that, the mixture was cooled again to −78 °C and quenched with ethanol. The mixture was poured into a mixture of 50 mL of water and 50 mL of hexane. After separation of the phases, the aqueous layer was extracted twice with ether, and the combined organic layers were dried (Na_2SO_4) and removed in vacuum. The residue was purified by column chromatography (silica gel, petroleum ether/ether 2:1) to yield 20 mg of 5-butyl-2-(*tert*-butylsulfonyl)bicyclo[2.2.1]-hepta-2,5-diene (**23**), 250 mg of *trans*-3,5-dibutyl-6-*endo*-(*tert*-butylsulfonyl)bicyclo[2.2.1]hept-2-ene (**24**), and 64 mg of *trans*-3-butyl-5-ethoxy-6-*endo*-(*tert*-butylsulfonyl)bicyclo[2.2.1]hept-2-ene (**25**), all three substances being colorless oils. **23**: ^{1}H NMR (200 MHz) δ 7.68 (d, 1H, $^3J_{H,H}$ = 3.2 Hz), 6.36 (s, 1H), 3.84 (m, 1H), 3.53 (m, 1H), 2.3−2.2 (m, 4H), 1.5−1.2 (m, 4H), 1.29 (s, 9H), 0.88 (t, 3H, $^3J_{H,H}$ = 7.0 Hz); ^{13}C NMR (50 MHz) δ 159.0, 158.2, 154.2, 133.0, 74.5, 59.3, 55.2 53.0, 30.9 29.4, 23.4, 22.4, 13.8. IR (film) 2958, 2932, 2872, 1567, 1460, 1295, 1113, 698, 687, 675, 607 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ) 240 (2.55), 262 (2.29) nm; HRMS (EI) calcd 268.1497; obsd 268.1464. **24**: Colorless oil which solidifies on refrigeration, mp 35 °C. ^{1}H NMR (300 MHz) δ 5.68 (m, 1H), 3.22 (dd, 1H, $^3J_{H,H}$ = 3.1 Hz, $^3J_{H,H}$ = 4.9 Hz), 3.10 (m, 1H), 2.54 (m, 1H), 2.13 (dt, 2H, $^3J_{H,H}$ = 6.8 Hz, $^4J_{H,H}$ = 1.5 Hz), 2.0−1.0 (m, 10H), 1.40 (s, 9H), 0.89 (t, 6H, $^3J_{H,H}$ = 7.2 Hz); ^{13}C NMR (75 MHz) δ 151.9, 124.7, 66.4, 59.6, 48.7, 46.6, 46.3, 43.3, 34.9, 30.8, 29.5, 29.4, 23.8, 22.7, 14.0, 13.95; IR (KBr) 2960, 2932, 2873, 2859, 1458, 1283, 1113 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ) 242 (2.51), 280 (1.91), 288 (1.85) nm; HRMS (EI) calcd for $C_{19}H_{34}O_2S$: C, 69.88; H, 10.50; found C, 69.89; H, 10.42. **25**: Colorless oil. ^{1}H NMR (200 MHz) δ 5.85 (d, 1H, $^3J_{H,H}$ = 2.0 Hz), 3.76 (dd, 1H, $^3J_{H,H}$ = 2.0 Hz, $^3J_{H,H}$ = 2.1 Hz), 3.66 (dq, 1H, $^2J_{H,H}$ = 9.2 Hz, $^3J_{H,H}$ = 7.0 Hz), 3.48 (t, 1H, $^3J_{H,H}$ = 3.0 Hz), 3.41 (dq, 1H, $^2J_{H,H}$ = 9.2 Hz, $^3J_{H,H}$ = 7.0 Hz), 3.12 (m, 1H), 2.82 (m, 1H), 2.06 (m, 2H), 1.70 (m, 2H), 1.5−1.2 (m, 4H), 1.39 (s, 9H), 1.18 (t, 3H, $^3J_{H,H}$ = 7.2 Hz), 0.88 (t, 3H, $^3J_{H,H}$ = 6.9 Hz); ^{13}C NMR (50 MHz) δ 148.4, 127.4, 82.8, 66.5, 65.3, 59.9, 50.1, 45.9, 44.5, 29.7, 29.3, 23.1, 22.7, 15.4, 13.9; IR ($CDCl_3$) 2960, 2932, 2873, 2260, 2245, 1480, 1284, 1122, 1080 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ) 240 (2.08), 272 (1.36) nm; HRMS (EI) *m*/*z* calcd 314.1915; obsd 314.1935.

Reaction of 8 with *n*-Butyllithium. To a solution of 1 mL of 1.6 M *n*-BuLi in 5 mL of dry ether was added at 0 °C a solution of 100 mg (0.3 mmol) of **8** in 5 mL of dry ether. The reaction was carried out under Ar atmosphere. The yellow solution was warmed to rt for 5 min and quenched with ethanol. For the workup the solution was poured into a mixture of 20 mL of water and 20 mL of petroleum ether. The organic phase was separated and the water extracted twice with 10 mL of petroleum ether. The combined organic phases were dried with Na_2SO_4, and the solvent was removed in vacuum. It remained a colorless oil which was purified by column chromatography (silica gel/hexane). This yielded 35 mg (43%) of **33** and 35 mg (43%) of **34** both as colorless oils. **33**: ^{1}H NMR (200 MHz) δ 6.03 (t, 1H, $^4J_{H,H}$ = 1.5 Hz), 2.2−1.2 (m, 26H), 0.9 (t, 3H, $^3J_{H,H}$ = 7 Hz); ^{13}C NMR (50 MHz) δ 158.6, 149.4, 147.6, 133.6, 62.1, 58.8, 33.8, 29.76, 29.67, 29.57, 29.4, 29.1, 29.0, 28.8, 28.7, 28.2, 26.7, 26.66, 22.6, 14.0; IR (film) 2946, 2908, 2838, 1441 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ) 242 (3.1) nm; HRMS (EI) *m*/*z* calcd 270.2347; obsd 270.2301. **34**: ^{1}H NMR (200 MHz) δ 6.74 (s, 1H), 2.81 (m, 8H), 2.56 (t, 2H, $^3J_{H,H}$ = 7.0 Hz), 1.9−1.2 (m, 16H), 0.93 (t, 3H, $^3J_{H,H}$ = 7.0 Hz); ^{13}C NMR (50 MHz) δ 141.0, 140.7, 139.0, 138.1, 136.7, 128.0, 36.4, 34.1, 34.0, 32.2, 31.5, 29.7, 29.3, 29.0, 28.5, 27.8, 27.6, 27.2, 22.9, 14.0; IR ($CDCl_3$) 2957, 2925, 2853, 2240, 1454, 1442, 1018 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ϵ) 234 (3.66), 270 (2.56), 282 (2.44) nm; HRMS (EI) *m*/*z*: calcd 270.2347; obsd 270.2352.

Reaction of 8 with Phenyllithium. To a solution 1 mL of 1.6 M phenyllithium in 5 mL of dry ether was added at 0 °C a solution of 170 mg (0.5 mmol) of **8** in 5 mL of dry ether. The reaction was carried out as described for the reaction with *n*-butyllithium. After the workup the crude product was separated by column chromatography (silica gel/hexane) yielding 15 mg (10%) of **36** as a colorless oil and 15 mg (10%) of **37** as colorless crystals. **36**: ^{1}H NMR (200 MHz) δ 7.4−7.2 (m, 5H) 6.78 (s, 1H), 2.3−1.3 (m, 20H); ^{13}C NMR (50 MHz) δ 155.0, 149.5, 147.6, 136.0, 135.3, 128.4, 125.4, 127.1, 61.5, 59.3, 33.7, 29.7, 29.65, 29.59, 29.0, 28.92, 28.87, 26.8, 26.7; IR ($CDCl_3$) 2912, 2882, 2840, 1440 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ) 232 (3.91), 270 (3.89) nm; HRMS (EI) *m*/*z* calcd 290.2035; obsd 290.2023. **37**: mp 82 °C; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 7.4−7.2 (m, 5H), 6.79 (s, 1H), 3.0−2.9 and 2.8−2.7 (m, each 4H), 1.9−1.5 (m, 12H); ^{13}C NMR (50 MHz, CD_2Cl_2) δ 143.6, 141.4, 140.2, 138.9, 129.8, 128.4, 128.2, 126.6, 36.7, 32.5, 31.8, 31.0, 30.0, 29.8, 29.0, 28.6, 28.1, 27.8; IR ($CDCl_3$) 2918, 2846, 1438, 1258, 1021, 812 cm^{-1}; UV/vis ($CDCl_3$) λ_{max} (log ϵ) 246 nm (3.78). Anal. Calcd for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found C, 90.96; H, 9.05.

Reaction of 49 with Sodium Amalgam. To a solution of 50 mg (0.14 mmol) of **49** in 10 mL of dry methanol were added 400 mg of sodium hydrogen phosphate and 1 g of sodium amalgam (6%) at rt. After all of the amalgam was converted to mercury, the mixture was poured into 20 mL of water and 20 mL of hexane. The organic phase was separated and dried, and the solvents were removed in vacuum. The ^{1}H NMR spectrum of the crude product showed **36** and **37** in the ratio of 1:1.

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Supporting Information Available: Copies of the ^{1}H and ^{13}C NMR spectra of those compounds for which analytical data are not provided (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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