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Vinyl-to-Benzyl Isomerization and Electrocyclizations in Lithio Derivatives of *o*-Tolylstilbenes

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(*Z*)-2-(2-Methylphenyl)-1,2-diphenylvinyllithium (**1**) isomerizes in THF solution to give 1-[2-(lithiomethyl)phenyl]-1,2-diphenylethene (**2**). Although **2** cannot be observed directly in this case, its intermediacy becomes evident from the independent preparation by metallation of 1-[2-(ethoxymethyl)phenyl]- (**5**) and 1-(2-methylphenyl)-1,2-diphenylethene (**7**), with formation of the same sequential products from all three sources. **2** cyclizes by reversible attack on the *syn*-phenyl group to give a cyclohexadienide anion **3** containing a seven-membered ring. **3** exhibits ^1H NMR coalescence phenomena and rearranges under thermodynamic control to the 1,2-diphenyl-1-indanide anion **10**.

Vinyl-Benzyl-Isomerisierung und Elektrocyclisierungen bei Lithiumderivaten des *o*-Tolylstilbens

(*Z*)-2-(2-Methylphenyl)-1,2-diphenylvinyllithium (**1**) lagert sich in THF-Lösung zu 1-[2-(Lithiomethyl)phenyl]-1,2-diphenylethen (**2**) um. Die Benzyllithiumverbindung **2** kann hierbei zwar nicht direkt beobachtet werden, ist aber wegen ihrer unabhängigen Bildung bei der Metallierung von 1-[2-(Ethoxymethyl)phenyl]- (**5**) und 1-(2-Methylphenyl)-1,2-diphenylethen (**7**) mit den gleichen Folgeprodukten zwangsläufige Zwischenstufe. **2** cyclisiert unter reversiblem Angriff auf den *syn*-ständigen Phenylkern zum Cyclohexadienid-Anion **3** mit siebengliedrigem Ring. **3** zeigt Koaleszenzphänomene im Protonenresonanzspektrum und isomerisiert bei thermodynamischem Reaktionsabschluß zum 1,2-Diphenyl-1-indanid-Anion **10**.

The predominant *Z*-configuration at equilibrium of 2-(2-methylphenyl)-1,2-diphenylvinyllithium (**1**) has been established by stereospecific chemical interconversions$^{1)}$ with related *o*-tolylstilbene derivatives. The present work is devoted to the elucidation of a surprising sequence of structural isomerizations, leading from **1** to further organolithium derivatives of increasing stability. The evidence so obtained will subsequently$^{2)}$ be applied to a related example with even better separability of the individual isomerization steps.

A. Seven-membered Ring Closure

The *Z*-isomer is the only observable form of the vinyllithium compound **1** in tetrahydrofuran (THF) solutions between – 70 and (temporarily) + 40 °C$^{1)}$. However, the ^1H NMR methyl signal of **1** diminished and finally disappeared in [D_8]THF solution at + 24 or + 64 °C with a half-life of ca. 15 h or 1 h, respectively, to produce a new compound **3** with rather broad NMR absorptions.

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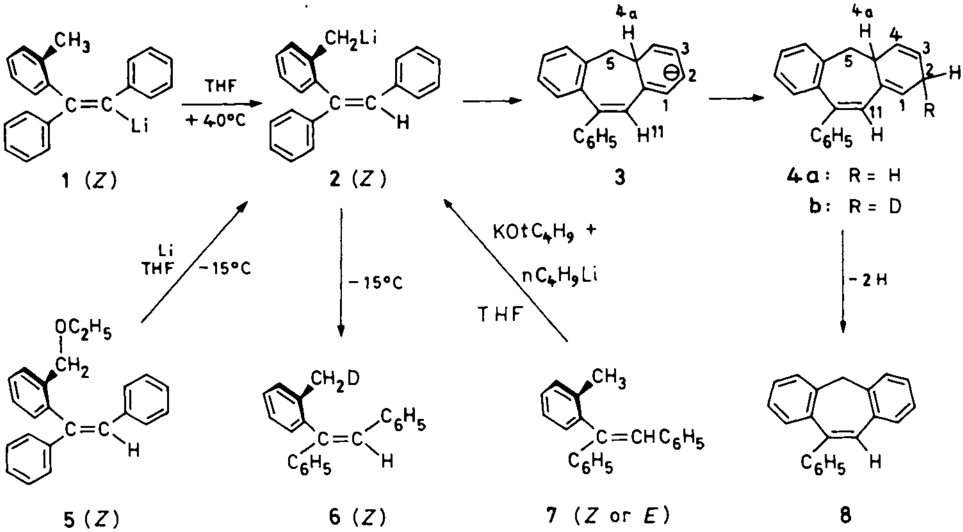
Anticipating the structure of the cyclohexadienide anion **3**, it is convenient to rationalize its formation by proton transfer from the methyl group in **1** to the vinylic position. The resulting benzyllithium derivative **2** would then give rise to the formation of **3** by nucleophilic aromatic addition. However, from related studies[2] it appeared probable that the *E*-isomer of **2** should be the primary product of isomerization; an intramolecular proton transfer in **1** with direct formation of **2** is difficult to visualize for geometrical reasons. Could trace amounts of the parent olefin **7** of either lithium compound possibly mediate the conversion of **1** to **2** by an intermolecular mechanism, as had been found earlier[3] for a vinyl-to-allyl transmetallation? A control experiment performed by addition of two equivalents of **7** to **1** revealed no noticeable rate alteration. Therefore, the isomerization of **1** is not catalysed by **7**, but involvement of **7** in a later step after the rate-determining one cannot be excluded and will be demonstrated on a related object[2].



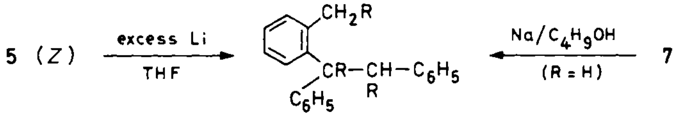
^{1}H-NMR spectral assignments in the cyclohexadienide **3** were hampered by low resolution of the deeply coloured THF solutions and by further rearrangement to give **10** (see Section B). Nevertheless, variable-temperature spectra revealed clear coalescence phenomena (at 60 MHz, see Exp. Part and Discussion) for the pair of diastereotopic CH_2-5 protons at ca. +30°C as well as for the olefinic 2- and 4-H at ca. +10°C. The chemical shifts assigned to 1- and 3-H agreed very well with those for the non-charged positions in cycloheptadienide[4,5] and cyclohexadienide[5] anions, whereas, compared to such reference anions, 2- and 4-H showed ca. 1 ppm smaller upfield shifts possibly because of more extensive charge delocalization and hence, smaller charge densities.

Protolysis of **3** resulted in immediate colour discharge and dramatic ^{1}H NMR spectral simplification. Although lack of resolved splitting patterns precluded detailed assignments, the proposed structure **4a** is quite compatible with NMR data of the unsubstituted[6] and 3,6-disubstituted[7] 1,4-cyclohexadienes. Thus, a narrow five-proton multiplet at δ ca. 2.8 is reasonably attributed to the 4a-hydrogen coinciding with the CH_2-5 and CH_2-2 absorptions; the upfield flank of this signal was missing in **4b** obtained by deuteriolysis of **3**. A broad olefinic signal of intensity three at δ = 5.7 accounts for 1-, 3-, and 4-H with the deceptive spectral simplicity noted before⁶⁾. The presence of two methylene and only one methine groups in **4a** became definitely clear from the ^{13}C NMR spectra, ruling out all possible isomers with a terminal olefinic CH_2 group as well as those in which a quarternary carbon atom had been protonated. All of the expected eleven tertiary and five quarternary aromatic and olefinic carbon atoms were observed with the aid of off-resonance decoupling.

The carbon skeleton of **4a** had to be established by chemical means. Dehydrogenation by chloranil produced solely **8** which was identical with samples of certified structure¹⁾.

The intermediacy of **2** had hitherto been speculative; **2** was suspected to escape detection because of rapid cyclization to **3** under the rearrangement conditions of **1** (at or above room temperature). We therefore sought to generate **2** by an independent route. Since the benzyl ether **5** had previously¹⁾ been shown to possess the *Z*-configuration necessary to form **2** directly, we reasoned that reductive ether cleavage of **5** might produce **2** at much lower temperatures. Furthermore, although cyclization to **3** could still be rapid, there might be a chance to trap **2** by deuteriolysis particularly in diethyl ether (in which solvent the rearrangement of **1** did not occur).

Indeed, treatment of **5** in diethyl ether with lithium metal for 0.5 h at −15 °C gave, after deuteriolysis, a mixture of **4b**, **6**, and *Z*-**7**. Only **4b** was isolated if the same experiment was run in THF for 1.5 h at −15 °C, proving that the cyclization step was not rate-determining during the slower conversion of **1** to **3**. This ether cleavage is recommended as the safest route to prepare pure **4a** by the application of lithium in stoichiometric amounts. Use of a large excess of lithium at −10 to 0 °C resulted in reduction of the double bond to give, after hydrolysis, **9a** which was independently prepared from **7**. The intermediacy of a trilithio compound was shown by deuteriolysis to **9b**.

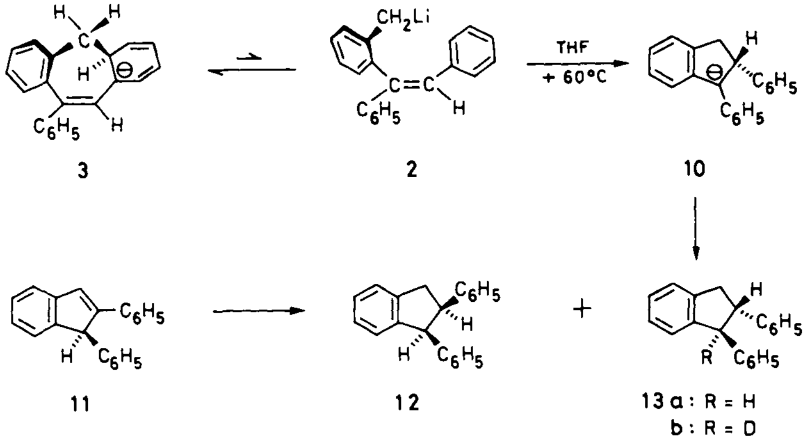


9a: R = H, 9b: R = D

Additional evidence for **2** was obtained by deprotonation of the olefin **7** in THF with n-butyllithium and an equimolar amount of potassium *tert*-butoxide (see ref.¹⁾ for the action of catalytic amounts in hexane). Quenching of such solutions of **3** with deuterium oxide led to the expected **4b**.

B. Five-membered Ring Closure

The cyclohexadienide **3** of Section A obviously is thermodynamically more stable than the benzyllithium derivative **2**. Charge delocalization in **2** is probably confined to just one aromatic nucleus because of the *ortho*-effect[1]; on the other hand, the degree of anionic resonance stabilization in **3** might be considerable although it is not known whether a sufficiently large fragment of **3** shows the necessary coplanarity.



3 **2** **10**

11 **12** **13a**: R = H
b: R = D

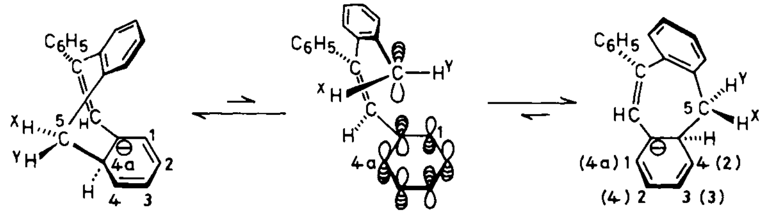
Nevertheless, **3** can by ring-opening return to **2** with reimbursement of aromatic stability and then take the chance of entering a thermodynamic termination reaction: Prolonged heating of **3** to +60°C gave clear spectral evidence for the final indanide **10** stabilized by benzylhydryl resonance but formed *via* a relatively large energy barrier. The brown THF solution showed two aromatic protons at high NMR field, indicating strong charge delocalization.

Quenching of **10** with water or deuterium oxide led to the pure *trans*-isomers **13a** and **b**, respectively. **13a** and its *cis*-isomer **12** are both known; since stereochemical assignments had not been made, both isomers were independently prepared from **11** and purified for unequivocal identification by virtue of the smaller vicinal coupling constant $^3J_{MX}$ in the complete ^1H NMR analysis of **13a**. Deprotonation experiments on **13a** offered no indication that the final ring closure might be reversible.

C. Discussion

The cyclization of resonance-stabilized carbanions to give seven-membered rings has ample precedence[4,5,8]. However, **3** appears to be a rarely encountered case where aromatic stability has to be sacrificed during ring closure. Although carbanionic attack on phenyl moieties to give 3-[9], 4-[9], 5-[9,10], and 6-membered rings[11] is well known, it is usually found with highly reactive "carbanions" in non-polar solvents. Whereas some of the numerous compounds produced from a cyclohexadienide related to **3** may indicate carbanionic elimination[12], none of them corresponded to the formal 1,5-migration across the anionic ring in **3**. Therefore, the reversible addition in THF of the benzyllithium moiety to the aromatic nucleus in **2** is thought to be due to a special geometric situation.

A closer view of the diastereotopomerization of **3** is given in **14**–**16**. At suitable temperatures, NMR coalescences should be observed for protons at positions 1/4a and 2/4, whereas 3-H should remain unperturbed; as far as recognizable from the poorly resolved spectra, these expectations have been confirmed. If classified as a concerted, suprafacial sigmatropic [1,5]-carbon shift[13], the interconversion of **14** and **16** is an allowed process with retention of configuration; the transition state picture **15** illustrates the participating frontier orbitals, and the interchange of the benzylic protons H^x and H^y was correctly observed in the NMR spectra. However, **14** and **16** might interconvert with **2** as an intermediate rather than a transition state **15**; this process may formally be described as an 8π-electrocyclic conversion[13]. A clear distinction should be possible by retention or loss of the ^3J coupling constant between $H^{x,y}$ and $H^{1,4a}$. The poor spectral quality precluded such an analysis and does perhaps indicate a biradical intermediate related to **15** as a further mechanistic possibility.



14 (**3**) **15** (or **2**) **16** (**3**)

At any rate, a rapid equilibrium between **2** and **3** (**14**, **16**) is a reasonable working hypothesis. The formation of **2** from **5** at −15°C has shown that its cyclization was rapid in THF and measurably slower in diethyl ether (as demonstrated by quenching to give **6**). Such solvent dependence suggests this process to be promoted by increasing ionization.

A discussion of the formation of **2** from **1** will be given subsequently[2]. The final 6π-electrocyclization to **10** requires no special comment.

We wish to thank Mr. *H. Huber* for maintenance of the NMR spectrometer HA-60-IL donated by the *Stiftung Volkswagenwerk.*

Experimental Part

Preparations of the starting materials and descriptions of most of the equipment used in these investigations have been given preciously[1]. The ^{13}C NMR spectra were obtained at 20.151 MHz on a Bruker WP-80 spectrometer.

Lithium 4a,5-dihydro-10-phenyl-2H-dibenzo[a,d]cyclohepten-2-ide (**3**): 260 mg of **1**, prepared[1] in pentane and dried in vacuo, was dissolved in 1.0 ml of [D$_8$]THF. After an incubation period at 24°C of 87 h, the ^{1}H NMR spectra taken at a probe temperature of −5°C did not change down to −31°C, except for line broadening: δ = 7.3 to 6.4 (broad m, aromatic H), 6.22 (s, 11-H), 5.70 (m with prominent t structure, *J* ca. 7 Hz, 1- and 3-H), 4.97 and 4.30 (2 broad m, 4- and 2-H, coalesced at +24°C with δ = 4.63), 3.03 (broad s, 4a-H, not observable above

+20 °C), 2.92 and 2.17 (2 broad m, CH_2-5, coalesced at +38 °C with δ = 2.57). – Only signals of **4a** and a trace of **7** could be detected after hydrolysis.

4a,5-Dihydro-10-phenyl-2H-dibenzo[a,d]cycloheptene (**4**)

a) *From* **1**: A larger-scale preparation of **3** in THF was performed as above. The crude oil obtained in 85% yield by hydrolysis at −70 °C and ether extraction was found to be contaminated by **7** and **13a**; pure **4a** was more conveniently prepared by route b) as described below. – ^{1}H-NMR (CCl_4 or [D_8]THF at +24 or −31 °C): δ = 7.18, 7.09, and 6.92 (s and 2 m, aromatic H), 6.38 (s, 11-H), 5.72 (broadened s, 1-, 3-, and 4-H), 2.87 and 2.73 (m, 4a-H, CH_2-5, and CH_2-2, intensity at δ 2.73 reduced after deuteriolysis to **4b**).

b) *From* **5** *in THF:* **5** (3.20 mmol)[1)] in 15 ml of anhydrous THF was stirred at −15 (±5) °C with 50 mg of lithium ribbon cut into small pieces. After 10 min the solution turned deeply blue and assumed a more scarlet colour during 80 min at −15 °C. The anion was quenched at −40 °C with 5 ml of methanol and the crude product (0.92 g containing only a trace of **7**) isolated by work-up with ether and water. Crystallization from ethanol yielded 60% of colourless needles of **4a** with m.p. 100 – 101 °C. – IR (KBr): 3045, 3015, 2925, 2840, 2805 (CH); 1613 (CC); 1596, 1486, 1443, 964, 900, 774, 748, 700, 685 cm^{-1}. – UV (cyclohexane): λ_{max} (lg ε) = 313 (sh 4.18), 298 (4.33), 241 nm (4.22). – ^{1}H NMR ($DCCl_3$): As above in a). – ^{13}C NMR ($DCCl_3$, multiplicities given for off-resonance decoupling): δ = 146.7, 142.7, 139.0, 138.2, and 137.5 (5 s, 5 quat-C); 134.2, 131.5, and 130.2 (3 d, 3 CH), 129.4 (d, 2 *o* or *m*-CH), 128.6 (d, CH), 128.0 (d, 2 *m*- or *o*-CH); 127.1, 126.9, 126.7, 125.7, and 122.9 (5 d, 5 CH); 43.9 (t, CH_2), 39.1 (d, aliph. CH), 27.5 (t, CH_2).

$C_{21}H_{18}$ (270.4) Calcd. C 93.29 H 6.71 Found C 93.24 H 6.95

Quenching with deuterium oxide produced only **4b** (see above); under similar conditions a large excess of lithium led to **9** (see below).

c) *From* **5** *in diethyl ether:* The scarlet solution obtained from **5** in anhydrous diethyl ether as above in b) was quenched with deuterium oxide after 45 min at −15 °C. The ethereal layer yielded **4b** as a mixture with *Z*-**6** (δ = 1.98, t with $^2J_{HD}$ = 2 Hz) and some non-deuterated *Z*-olefin **7** (s at δ = 2.00 in CCl_4).

d) *From* **7**: Potassium *tert*-butoxide (3.7 mmol) and 1.00 g of **7** were stirred for 1 h with n-butyllithium (4 mmol) in hexane. After addition of 40 ml of anhydrous THF at −50 °C, aliqouts of the dark scarlet solution were quenched with deuterium oxide at the end of 1 h at −20 °C and 10 h at +25 °C. In either case a mixture of **4b** and **7** was secured in quantitative yield.

Structural Proof of **4a**: 320 mg of **4a** and 400 mg of chloranil were heated in 10 ml of toluene on a steam-bath for 90 min. The ethereal solution was repeatedly extracted with dilute aqueous sodium hydroxide, washed, and dried over calcium chloride to yield 95% of crude **8**. After one recrystallization from ethanol, the sample had m.p. 105 – 108 °C and showed IR and ^{1}H NMR spectra identical with those of an authentic specimen[1)]; mixed m.p. without depression.

1-(2-Methylphenyl)-1,2-diphenylethane (**9**)

a) *From* **5**: The benzyl ether **5** (980 mg) and 200 mg of lithium were stirred in 50 ml of anhydrous THF at 0 °C for 1 h. Part of the scarlet-blue solution was hydrolyzed to give a mixture containing predominantly **9a**. The second aliquot was quenched with deuterium oxide; the washed and dried ether layer yielded **9b**; ^{1}H NMR (CCl_4): δ = 3.23 (broad s, CHD), 2.03 (s, CH_3 with overlaid CH_2D feature).

b) *From* **7**: 3.7 mmol of *Z*-**7** and 4.8 mmol of sodium were refluxed in 30 ml of *tert*-butyl alcohol overnight. Aqueous work-up with extraction by ether yielded 44% of pure, colourless **9a**, m.p. 58 – 58.5 °C (from ethanol). – IR (KBr): 3065, 3025, 2950 (CH); 1600, 1499, 1456, 1448; 761, 753, 732, 700 cm^{-1}. – ^1H NMR (CCl_4): δ = 6.95 (mc, 14 aromat. H), 4.28 (t, ^3J = 7.5 Hz, *tert*-H), 3.23 (d, ^3J = 7.5 Hz, CH_2), 2.00 (s, CH_3).

$C_{21}H_{20}$ (272.4) Calcd. C 92.60 H 7.40 Found C 92.24 H 7.27

Lithium 1,2-diphenylindan-1-ide (**10**): A THF solution (20 ml) of the anion **3** (6.2 mmol from 1.70 g of crystalline **1**) was prepared as above and heated to + 60 °C for 22 h; prolongation of the reaction period caused no further spectral changes of the brown solution in which all **3** had been converted to **10**. – ^1H NMR ([D_8]THF): δ = 7.00 and 6.42 (2 mc, aromat. H), 5.60 (mc, 2 aromat. H), 3.80 (dd, ^3J = 10 Hz and 2 Hz, 2-H), 3.23 (dd, ^3J = 10 and ^2J = 15 Hz, 3-H), 2.38 (dd, ^3J = 2 and ^2J = 15 Hz, 3-H).

trans-1,2-Diphenylindan (**13**): The THF solution of **10** described above was hydrolyzed and extracted with ether to give 86% of a crude oil. The *Z*-olefin **7** present as an impurity was destroyed by heating on a steam-bath with 1.0 ml of hydrogen peroxide (30%) in 15 ml of acetic acid. This solution was poured on water, extracted with ether, and the washed and dried ether layer filtered through a short column of basic Al_2O_3 (act. I). Recrystallisation of the eluated material yielded 30% of colourless needles of **13a** with m.p. 122 – 123 °C (lit.[14] 123 – 124.5 °C). – IR (KBr): 3030, 2915 (CH); 1495, 1450, 768, 743, 697 cm^{-1}. – ^1H NMR (CCl_4): δ = 7.0 (mc, 12 aromat. H), 6.57 (m, 2 aromat. H), 4.5741(7) (d, X-part of ABMX, 1-H), 3.9228(8) (q, M-part, 2-H), 3.302(2) and 3.182(2) (A and B interchangeable, CH_2-3); ABMX spectral simulation: $^2J_{AB}$ = –15.9(1), $^3J_{AM}$ or $^3J_{BM}$ = +8.2(1) or 7.7(1), $^4J_{AX}$ = $^4J_{BX}$ = –0.2(1), $^3J_{MX}$ = +7.89(6) Hz; uncertainties in the last digit are shown in parentheses.

After deuteriolysis of **10** and similar work-up, the ^1H NMR spectrum of **13b** was identical except for the absence of the d at δ 4.57 and a triplet feature at δ 3.92.

$C_{21}H_{18}$ (270.4) Calcd. C 93.29 H 6.71 Found C 93.34 H 6.61

Structural Proof of **13a** *and cis-1,2-Diphenylindan* (**12**): 1,2,3-Triphenyl-2-propanol was prepared[15,16] from ethyl benzoate and benzylmagnesium chloride and dehydrated[14] to a mixture of *Z*- and *E*-1,2,3-triphenylpropene. Subsequent bromination[15] produced 36% of 1,2-diphenylindene (**11**) with m.p. 174 – 178 °C (lit.[15] 177 – 178 °C). This material was reduced with sodium in boiling pentanol[14] and the product after acidic work-up crystallized from 1-propanol to give 60% of pure **13a**, m.p. 122 – 123 °C, no depression by admixture of the preceding sample from **10**, identical IR and ^1H NMR spectra.

The mother liquor was distilled at 150 – 170 °C/0.001 Torr and the distillate crystallized from ethanol to yield pure **12** with m.p. 83 – 84 °C (lit.[14] 89 °C). – IR (KBr): 3020, 1470, 1450, 743, 697 cm^{-1}. – ^1H NMR (CCl_4): δ = 7.05 (s + m, 14 aromat. H), 4.318(2) (broad d, X-part of ABMX, 1-H), 3.499(4) (m, M-part, 2-H), 3.332(5) and 3.184(7) (m, AB-part, CH_2-3); ABMX spectral simulation: $^2J_{AB}$ = –16.0(5), $^3J_{AM}$ = 10.0(3), $^3J_{BM}$ = 8.2(3), $^4J_{AX}$ = 1.0(4), $^4J_{BX}$ = –0.4(4), $^3J_{MX}$ = 9.8(2) Hz.

$C_{21}H_{18}$ (270.4) Calcd. C 93.29 H 6.71 Found C 93.20 H 6.78

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1) *R. Knorr, E. Lattke,* and *E. Räpple,* Chem. Ber. **114**, 1581 (1981), preceding paper.

2) *E. Lattke* and *R. Knorr,* Chem. Ber. **114**, 1600 (1981), following paper.

3) *R. Knorr* and *E. Lattke,* Tetrahedron Lett. **1977**, 4655.

4) *R. B. Bates, W. H. Deines, D. A. McCombs,* and *D. E. Potter,* J. Am. Chem. Soc. **91**, 4608 (1969).

5) *H. Kloosterziel* and *J. A. A. van Drunen,* Rec. Trav. Chim. Pays-Bas **88**, 1084 (1969); **89**, 368 (1970).

6) *W. Auf der Heyde* and *W. Lüttke,* Chem. Ber. **111**, 2384 (1978).

[7] *M. C. Grossel, A. K. Cheetham,* and *J. M. Newsam,* Tetrahedron Lett. **1978**, 5229; *M. C. Grossel, A. K. Cheetham, D. A. O. Hope, K. P. Lam,* and *M. J. Perkins,* ibid. **1979**, 1351.

[8] *R. B. Bates, S. Brenner, W. H. Deines, D. A. McCombs,* and *D. E. Potter,* J. Am. Chem. Soc. **92**, 6345 (1970).

[9] *J. A. Bertrand, E. Grovenstein, P. Lu,* and *D. Van Derveer,* J. Am. Chem. Soc. **98**, 7835 (1976), and references cited therein.

[10] *H. Pines,* Acc. Chem. Res. **7**, 155 (1974); *D. Margerison* and *V. A. Nyss,* J. Chem. Soc. C **1968**, 3065.

[11] *S. Brenner* and *E. Dunkelblum,* Tetrahedron Lett. **1973**, 2487, with references to the earlier literature.

[12] *S. W. Staley* and *J. P. Erdman,* J. Am. Chem. Soc. **92**, 3832 (1970).

[13] *R. B. Woodward* and *R. Hoffmann,* Angew. Chem. **81**, 797 (1969); Angew. Chem., Int. Ed. Engl. **8**, 781 (1969).

[14] *E. Bergmann* and *H. Weiß,* Liebigs Ann. Chem. **480**, 64 (1930).

[15] *A. Orechoff,* Ber. Dtsch. Chem. Ges. **47**, 89 (1914).

[16] *A. Klages* and *S. Heilmann,* Ber. Dtsch. Chem. Ges. **37**, 1447 (1904), p. 1456.

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