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1,($\omega - 1$)-Dienes: solvent controlled unilateral or bilateral metalation

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Abstract

In hexane, i.e. under heterogeneous conditions, 1,($\omega - 1$)-dienes readily undergo double deprotonation to give bis(allylmetal) intermediates. In tetrahydrofuran at −75 or −50 °C, however, only monometalation occurs with dienes having chains of up to 12 carbon atoms. The practical potential of such selective monosubstitution reactions is demonstrated by two novel pheromone syntheses.

Introduction

Aggregate formation may retard but can also accelerate organometallic processes [1]. In particular, it can promote di- and poly-metalation. Thus, when heated to 240 °C solid tetrameric methyllithium undergoes disproportionation to afford dilithiomethane and methane [2] whereas the same reagent is too inert to attack paraffinic hydrocarbons even at high temperatures [3]. Treatment of benzyllithium with ethyllithium at 75 °C produces mainly di-, at 95 °C tri- and tetra-lithiotoluene [4]. Recently, numerous di- or poly-metalated hydrocarbons have been reported [5]. Although the second deprotonation step can always be assumed to occur within a mixed aggregate [1] and hence under quasi-intramolecular conditions, it is generally found to be slower than the first hydrogen–metal exchange. Therefore successful dimetalation usually requires prolonged reaction times and use of an excess of the reagent. Under special circumstances, however, the second hydrogen–metal exchange may occur even faster than the first. Such an exceptional situation is encountered when ferrocene is treated with tert-butyllithium in tetrahydrofuran (THF) [6]. The reaction leads directly and almost quantitatively to the 1,1′-dilithio derivative. On the other hand, clean conversion into the monolithio compound can be achieved if diethyl ether is employed as the solvent [7].

We describe below novel procedures that allow selective mono- or di-metalations of 1,($\omega - 1$)-diene to be carried out, the solvent again being the crucial variable. In tetrahydrofuran the second deprotonation is found to be considerably slower than the first, and so the reaction stops at the monometalation stage. In contrast, only dimetalated derivatives are generated if hexane is used as the solvent. Apparently,

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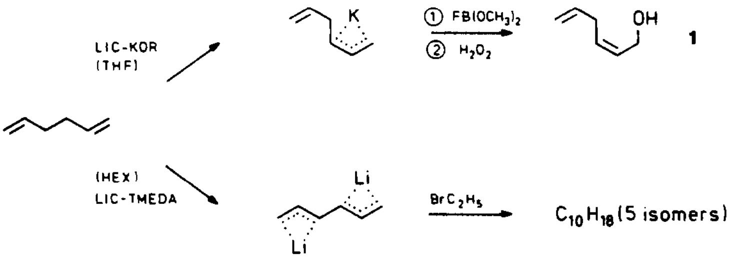
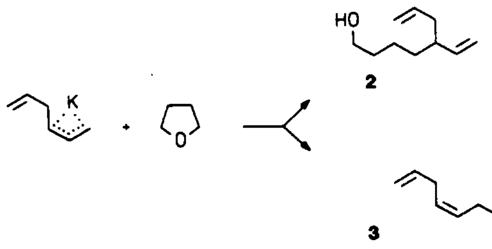
the non-polar medium favors the complexation of the metal with an intramolecularly available olefinic moiety and so accelerates the second deprotonation [8].

Results and discussion

We recognized this solvent effect for the first time when we treated 1,5-hexadiene with two equivalents of potassium-tert-butoxide-activated [8] butyllithium ("LIC-KOR") in THF at −75 °C. Despite the use of an excess of this reagent, only a monosubstituted product, (*Z*)-2,5-hexadien-1-ol (**1**, 63%), was obtained after trapping of the organometallic intermediate with fluorodimethoxyboron [9] and subsequent oxidation *. This was particularly surprising since Bates et al. [10] had previously accomplished a rapid double metalation of 1,5-hexadiene by using two equivalents of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine-activated butyllithium (LIC-TMEDA) in hexane (HEX).



Besides hexadienol **1**, two by-products, 5-vinyl-7-octen-1-ol (**2**, 6%) and (*Z*)-6,9-decadien-1-ol (**3**, 4%) were formed. They must have arisen from an unprecedented addition reaction of the allyl-type organometallic intermediate to the THF solvent. Previously only organocopper reagents [13] and the push-pull couples [14] triphenylboron or triphenylaluminium and triphenylmethylsodium had been found to promote the ring opening of cyclic ethers.



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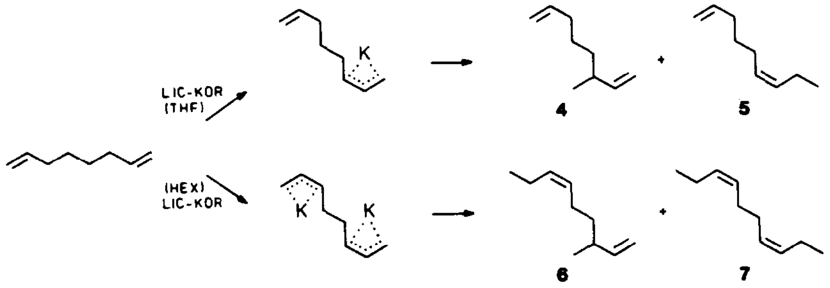
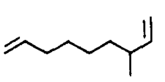
* The surprising *endo* stereoselectivity of 2-alkenyl-potassium compounds and the more or less complete regioselectivity of their reactions with electrophiles have been explicitly considered in previous articles [8,11,12]. (If generated with the LIC-KOR superbase, the organometallic intermediates contain also some lithium species. For simplicity, however, we depict them as pure potassium compounds.)

The LIC-KOR metalation of the homologous 1,7-octadiene was studied in detail. In THF, the reaction once again did not proceed beyond the mono-metalated species irrespective of whether butyllithium and potassium tert-butoxide were used in stoichiometric amounts or in excess. A 1 : 5 mixture of 3-methyl-1,7-octadiene (**4**, 9%) and (*Z*)-1,6-nonadiene (**5**, 55%) was invariably isolated. On the other hand, use of the same reagent in hexane generated exclusively the dimetalated species (having the *endo,endo* configuration) even when the substrate was employed in a fourfold excess. Trapping with methyl iodide gave a mixture of (*Z*)-3-methyl-1,6-nonadiene (**6**, 16%) and (3Z,7Z)-3,7-decadiene (**7**, 34%).



1,8-Nonadiene and 1,9-decadiene exhibited the same solvent dependent selectivity for mono- or di-metalation. In tetrahydrofuran solution 3-methyl-1,8-nonadiene (**8**, 11%) and (*Z*)-3,9-decadiene (**9**, 56%) or 3-methyl-1,9-decadiene (**10**, 11%) and (*Z*)-3,10-undecadiene (**11**, 60%) were obtained, whereas in hexane suspension (*Z*)-3-methyl-1,7-decadiene (**12**, 17%) and (3Z,8Z)-3,8-undecadiene (**13**, 30%) or (*Z*)-3-methyl-1,8-undecadiene (**14**, 14%) and (3Z,9Z)-3,9-dodecadiene (**15**, 26%) were produced.



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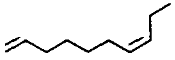

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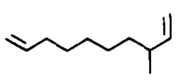

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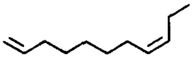

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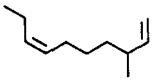

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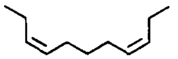

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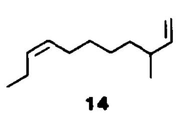

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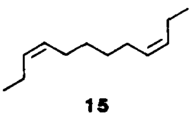

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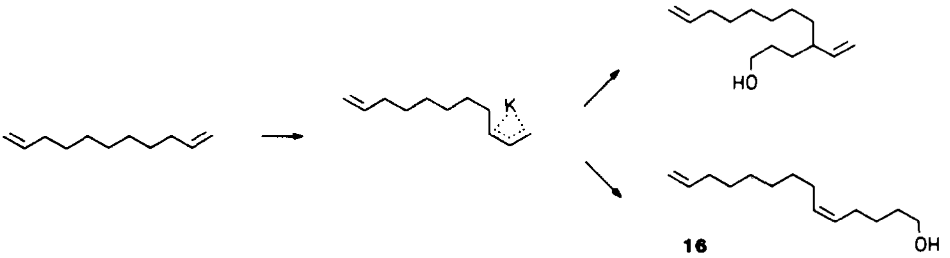
All 1,(*ω* − 1)-dienes can, of course, be forced into dimetalation if an excess of the superbasic reagent is used in a paraffinic medium. In THF, however, the selectivity for monometalation depends on the deactivation of an olefinic bond by a nearby allyl-type organometallic moiety. This effect should vanish with sufficient distance between the double bond and the latter moiety. We decided to find out at what chain length of the diene the control over mono- vs. di-metalation is lost. 1,11-Dodecadiene appears to mark this turning point.

The selectivity achieved with 1,10-undecadiene was still satisfactory. Monometalation followed by metal-assisted *endo–exo* equilibration [15], condensation with 2-(3-iodopropanoxy)-tetrahydropyran, acid-catalyzed acetal hydrolysis, and elimination of the regioisomeric by-product by fractional crystallization at low temperatures gave (*Z*)-5,13-tetradecadien-1-ol (**16**) in an overall yield of 17%. The latter compound as well as its acetate are major constituents of the mandibular secretion of carpenter moth (*Cossus cossus*) larvae [16].



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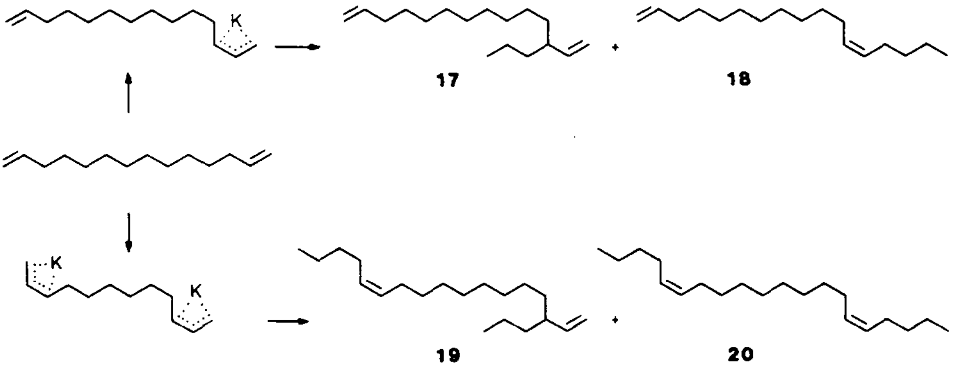
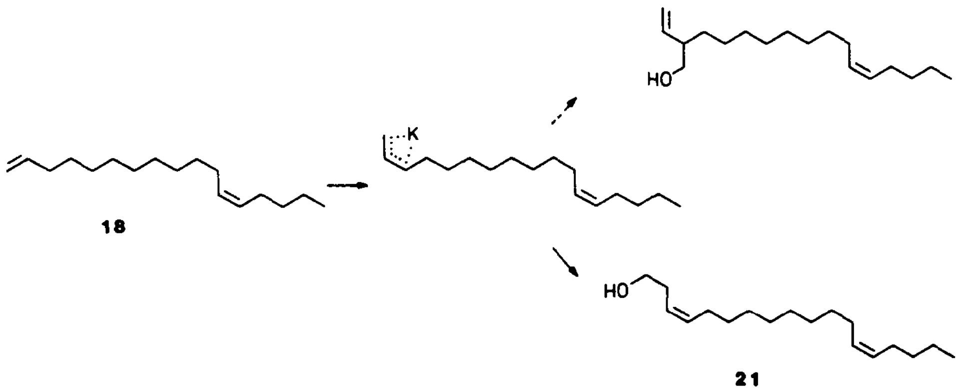
In the case of 1,13-tetradecadiene extensive dimetalation proved to be unavoidable whatever the reaction conditions. Metalation in THF by the standard procedure and subsequent condensation with propyl iodide gave four main products: 3-propyl-1,13-tetradecadiene (**17**, 7%), (*Z*)-5,16-heptadecadiene (**18**, 33%), (*Z*)-3-propyl-1,12-heptadecadiene (**19**, 3%) and (5*Z*,15*Z*)-5,15-icosadiene (**20**, 5%).



17 **18** **19** **20**

It was possible to separate and to purify the major component **18** by preparative gas chromatography. Nevertheless its preparation by *cis* selective [17] Wittig reaction was found to be more satisfactory. Diene **18** contains three allylic and hence activated positions. At first sight one might expect these three methylene groups to show identical reactivity. However, when the relative thermodynamical stability (basicity) [18] of the resulting allylmetal species is considered, it becomes obvious that the site adjacent to the vinyl group should be attacked preferentially if not exclusively. This was indeed found to be the case. Metalation of diene **18** and subsequent treatment with paraformaldehyde gave, after neutralisation, a 2 : 3 mixture of regioisomeric alcohols. The major product, (3*Z*,13*Z*)-3,13-octadiene-1-ol

(**21**), was isolated after distillation and repetitive crystallization in an overall yield of 22%. The corresponding acetate has been previously identified as the sex attraction of the peach tree borer moth *Sanninoidea exitiosa* [19].



The latter example illustrates that our findings have a novel and valuable synthetic potential. Two consecutive monometalations using superbasic reagents allow elongation or functionalization of 1,($\omega - 1$)-diene chains first on one side of the molecule and then on the other.

Experimental

1. General

Unless otherwise specified, ^{1}H-NMR spectra were recorded at 80 MHz or, where indicated by an asterisk, at 360 MHz, and ^{13}C-NMR spectra at 90.6 MHz. Mass spectra were obtained under electron impact at a 70 eV ionization potential and at a source temperature of 150 °C or, where indicated by an asterisk, 180 °C.

For further details, see earlier paper (e.g., ref. 20).

2. Starting materials

(a) 1,10-Undecadiene and 1,13-tetradecadiene were supplied by Wiley Organics (formerly Chemical Samples), Columbus, Ohio.

(b) (*Z*)-5,16-Heptadecadiene (**18**): Triphenyl-11-dodecenylphosphonium iodide, prepared by the dropwise addition of 10-undecenyl iodide [21] (14.0 g, 50 mmol) to a solution of triphenylphosphoniumethanide [22] in THF (0.10 L) at −75 °C, was vigorously stirred with potassium amide (50 mmol) in refluxing liquid ammonia (0.10 L) for 1 h. The ammonia was then allowed to evaporate through a mercury seal and the solid material was suspended in toluene (50 mL). At −75 °C, pentanal (5.3 mL, 4.3 g, 50 mmol in 5 mL of toluene) was added dropwise during 10 min. The solvent was evaporated at 25 °C under reduced pressure and the residue thoroughly extracted with hexane (5×0.10 L). The combined organic layers were concentrated to one fourth of the volume, cooled to −20 °C (deep-freeze) and filtered through a layer of silica gel. Distillation gave 6.15 g (52%) of **18**; b.p. 150–153 °C/0.2 mmHg. ^{1}H-NMR: 5.75 (1H, ddt, *J* 17, 10, 7); 5.33 (2H, t, *J* 5); 4.97 (1H, d, *J* 17); 4.92 (1H, d, *J* 10); 2.0 (6H, m); 1.3 (18H, m); 0.90 (3H, t, *J* 6). MS: 236 (62%, M^+), 55

(100%). Analysis. Found: C, 85.94; H, 13.95. $C_{17}H_{32}$ (236.44) calc.: C, 86.36; H, 23.64%.

3. Dimetalation reactions

(a) 1,7-Octadiene derivatives: A mixture of 1,7-octadiene (9.1 mL, 6.6 g, 60 mmol), butyllithium (120 mmol) and potassium tert-butoxide (13.5 g, 120 mmol) in hexane (0.15 L) was stirred vigorously for 3 days at 25°C. It was then cooled to −75°C and precooled THF (0.15 L) was added and then methyl iodide (10.0 mL, 22.8 g, 161 mmol) was introduced dropwise. After evaporation of the solvent, the residue was distilled under reduced pressure; b.p. 80–96°C/86 mmHg; 4.15 g. Analytical gas chromatography (2 m, 10% silicon rubber UCC-W, 80 → 200°C) showed that the products **6** and **7** were present in a 1:4 ratio. They were separated by preparative gas chromatography (6 m, 10% Apiezon L, 125°C). **6**: ^{1}H-NMR: 5.6 (3H, m); 5.0 (2H, m); 2.0 (5H, m); 1.3 (2H, m); 0.9 (6H, m). MS: 138 (5% M^+), 69 (39%), 68 (100%). Analysis. Found: C, 86.81; H, 13.26. $C_{10}H_{18}$ (138.25) calc.: C, 86.88; H, 13.12%. **7**: ^{1}H-NMR (CCl_4, 60 MHz): 5.4 (4H, m); 2.1 (8H, m); 0.96 (6H, t, *J* 7). MS: 138 (9%, M^+), 69 (100%), 68 (75%). Analysis. Found: C, 86.81; H 13.26. $C_{10}H_{18}$ (138.25) calc.: C, 86.88; H, 13.12%.

(b) 1,8-Nonadiene derivatives: A similar procedure, but without the addition of THF as a cosolvent prior to the trapping with methyl iodide, yielded **12** and **13** in a 1:1.8 ratio; 47%; separation was by preparative gas chromatography (3 m, 8% silicon rubber SE-30, 140°C). **12**: b.p. 179–180°C; n_D^{20} 1.4380. ^{1}H-NMR*: 5.72 (1H, ddd, *J* 17.3, 10.0, 7.5); 5.4 (2H, m); 4.98 (1H, dm, *J* 17.6); 4.93 (1H, dm, *J* 10.5); 2.1 (5H, m); 1.3 (4H, m); 1.01 (3H, d, *J* 6.8); 0.98 (3H, t, *J* 7.4). Analysis. Found: C, 87.04; H, 13.14. $C_{11}H_{20}$ (152.28) calc.: C, 86.76; H 13.24%. **13**: b.p. 187–188°C; n_D^{20} 1.4441. ^{1}H-NMR*: 5.4 (4H, m); 2.1 (8H, m); 1.4 (2H, m); 0.98 (6H, t, *J* 7.6). Analysis. Found: C, 86.96; H, 13.11. $C_{11}H_{20}$ (152.28) calc.: C, 86.76; H, 13.24%.

(c) 1,9-Decadiene derivatives: An procedure analogous to that described above (Section 3b) yielded **14** and **15** in a 1:1.9 ratio; 40% yield; separation by preparative gas chromatography (3 m, 8% silicon rubber SE-30, 130°C). **14**: ^{1}H-NMR*: 5.69 (1H, ddd, *J* 17.0, 10.0, 7.3); 5.3 (2H, m); 4.95 (1H, dm, *J* 17.2); 4.91 (1H, dm, *J* ~ 10); 2.1 (5H, m); 1.3 (6H, m); 0.98 (3H, d, *J* ~ 7); 0.96 (3H, t, *J* 7.5). Analysis. Found: C, 86.26; H, 13.79. $C_{12}H_{22}$ (166.31) calc.: C, 86.67; H, 13.33%. **15**: b.p. 209–211°C; n_D^{20} 1.4476. ^{1}H-NMR*: 5.4 (4H, m); 2.1 (8H, m); 1.4 (4H, m); 0.98 (6 H, t, *J* 7.5). Analysis. Found: C, 86.13; H, 13.67. $C_{12}H_{22}$ (166.31) calc.: C, 86.67; H, 13.33%.

4. Monometalation reactions

(a) 1,5-Hexadiene derivatives: Precooled (−75°C) THF, 1,5-hexadiene (11.9 mL, 8.2 g, 100 mmol) and then potassium tert-butoxide (11.2 g, 100 mmol) were added to commercial butyllithium (100 mmol) from which the solvent (hexane) had been stripped off. The mixture was stirred until a homogeneous solution was obtained and then kept for 24 h at −75°C. Treatment with fluoromethoxyborane [9] (100 mmol) and alkaline hydrogen peroxide followed by partial evaporation of the organic solvent, extraction with hexane (5 × 50 mL), washing of the extract with water (2 × 25 mL), and then distillation gave two crude fractions (4.5 g, b.p. 58–59°C/10 mmHg, and 1.8 g, b.p. 90–160°C/10 mmHg) which contained **1**

(63%), **2** (6%) and **3** (4%). The pure products were isolated by preparative gas chromatography (3 m, 20% Carbowax 20M, 150 or 210 °C). **1**: ^{1}H-NMR*: 5.82 (1H, ddt, *J* 17.2, 10.5, 6.6); 5.70 (1H, dtt, *J* 10.9, 6.2, 1.3); 5.58 (1H, dtt, *J* 11.0, 7.4, 1.2); 5.06 (1H, dq, *J* 17.1, 1.8); 5.01 (1H, dq, *J* 10.0, 1.4); 4.21 (2H, dd, *J* 7.0, 1.0); 2.85 (2H, t, broad, *J* 6.6); 1.70 (1H, s, broad). MS*: 98 (2%, M^+), 57 (100%). Analysis. Found: C, 73.35; H 10.39. $C_6H_{10}O$ (98.15) calc.: C, 73.43; H, 10.27%. **2**: ^{1}H-NMR*: 5.76 (1H, ddt, *J* 16.8, 10.0, 6.9); 5.58 (1H, ddd, *J* 17.2, 10.5, 8.0); 5.0 (4H, m); 3.65 (2H, t, *J* 6.5); 2.1 (3H, m); 1.5 (3H, m); 1.4 (2H, m); 1.3 (2H, m). MS*: 154 (3%, M^+), 67 (100%). Analysis. Found: C, 78.10; H, 11.82. $C_{10}H_{18}O$ (154.25) calc.: C, 77.87; H, 11.76%. **3**: ^{1}H-NMR*: 5.83 (1H, ddt, *J* 17.0, 10.1, 6.5); 5.45 (2H, symm. m); 5.03 (1H, dq, *J* 17.5, 1.8); 4.99 (1H, dq, *J* 9.7, 1.6); 3.67 (2H, d, *J* 6.7); 2.76 (2H, tq, *J* 4.9, 1.5); 2.03 (2H, symm. m, q-like, *J* ~ 6.7); 1.59 (2H, pent, *J* 7.0); 1.4 (5H, m). MS*: 136 (2%, $M^+ - H_2O$), 79 (100%). Analysis. Found: C, 78.01; 11.91. $C_{10}H_{18}O$ (154.25) calc.: C, 77.87; H, 11.76%.

(b) 1,7-Octadiene derivatives: Similarly 1,7-octadiene (50 mmol) was metalated during 10 h at −50 °C and the organometallic intermediated was trapped with methyl iodide (50 mmol). Products **4** (9%) and **5** (55%) were isolated by extraction and distillation and purified by preparative gas chromatography (3 m, 15% SE-30, 70 °C). **4**: ^{1}H-NMR: 5.7 (2H, m); 5.0 (4H, m); 2.0 (3H, m); 1.3 (4H, m); 0.97 (3H, d, *J* 7). **5**: ^{1}H-NMR*: 5.83 (1H, ddt, *J* 17.2, 10.5, 6.7); 5.36 (2H, symm. m, like δ 5.37, 1H, dt, *J* ~ 11.7 and δ 5.34, 1H, dt, *J* ~ 11.7); 5.01 (1H, dq, *J* 17.0, 1.3); 4.95 (1H, dq, *J* 10.0, 1.3); 2.06 (4H, symm. m, like δ 2.08, 2H, q, *J* ~ 7 and δ 2.04, 2H, q, *J* ~ 7); 1.47 (2H, pent, *J* 7.5); 0.99 (3H, t, *J* 7.3). MS: 124 (0.2%, M^+), 41 (100%). Analysis. Found: C, 86.80; H, 13.21. C_9H_{16} (124.23) calc.: C, 87.02; H, 12.98%.

(c) 1,8-Nonadiene derivatives: By the procedure described above (Section 4a), **8** and **9** were obtained in a 1 : 5.1 ratio and with 67% yield. **8**: b.p. 154–156 °C; n_D^{20} 1.4299. ^{1}H-NMR*: 5.81 (1H, ddt, *J* 17.0, 10.4, 6.7); 5.69 (1H, ddd, *J* 17.2, 10.1, 7.5); 4.90 (1H, dm, *J* ~ 18); 4.94 (1H, dm, *J* ~ 16); 4.93 (1H, dm, *J* ~ 10); 4.90 (1H, dm, *J* ~ 10); 2.1 (3H, m); 1.3 (6H, m); 0.98 (3H, d, *J* 6.7). Analysis. Found: C, 87.06; H, 12.95. $C_{10}H_{18}$ (138.26) calc.: C, 86.88; H, 13.12%. **9**: b.p. 165–168 °C; n_D^{20} 1.4368. ^{1}H-NMR*: 5.83 (1H, ddt, *J* 17.0, 10.3, 6.5); 5.4 (2H, m); 5.02 (1H, dm, *J* 17.2); 4.96 (1H, dm, *J* 10.2); 2.1 (6H, m); 1.4 H (4H, m); 0.98 (3H, t, *J* 7.5). Analysis. Found: C, 87.09; H, 13.07. $C_{10}H_{18}$ (138.26) calc.: C, 86.88; H, 13.12%.

(d) 1,9-Decadiene derivatives: By the procedure described above (Section 4a), **10** and **11** were obtained in a 1 : 5.5 ratio and with 71% yield. **10**: b.p. 181–182 °C; n_D^{20} 1.4335. ^{1}H-NMR*: 5.81 (1H, ddt, *J* 17.0, 10.2, 6.7); 5.69 (1H, ddd, *J* 17.0, 10.2, 6.7); 5.69 (1H, ddd, *J* 17.4, 10.5, 7.5); 5.01 (1H, dm, *J* ~ 18); 4.95 (1H, dm, *J* ~ 18); 4.94 (1H, dm, *J* ~ 10); 4.91 (1H, dm, *J* ~ 11); 2.1 (3H, m); 1.4 (2H, m); 1.3 (6H, m, narrow); 0.97 (3H, d, *J* 6.5). Analysis. Found: C, 87.04; H, 13.08. $C_{11}H_{20}$ (152.28) calc.: C, 86.76; H, 13.24%. **11**: b.p. 188–189 °C; n_D^{20} 1.4404. ^{1}H-NMR*: 5.83 (1H, ddt, *J* 17.0, 10.2, 6.7); 5.4 (2H, m); 5.03 (1H, dm, *J* 17.0); 4.96 (1H, dm, *J* 10.1); 2.07 (6H, pent-like m); 1.4 (6H, m); 0.98 (3H, t, *J* 7.4). Analysis. Found: C, 87.14; H, 12.93. $C_{11}H_{20}$ (152.28) calc.: C, 86.76; H, 13.24%.

(e) 1,13-Tetradecadiene derivatives: Product **17** and **18** and the by-products **19** and **20** were characterized only from their mass spectra, relative gas chromatographic retention times and the ^{1}H-NMR spectrum of the crude mixture. The structure assignments are thus tentative.

5. *Pheromones*

(a) (*Z*)-5,13-Tetradecadien-1-ol (**16**): The metalation of 1,10-undecadiene (10 mmol) was carried out as described before (Section 4a and 4b). The reaction mixture was treated with 2-(3-iodopropanoxy)tetrahydropyran [19] (2.7 g, 10 mmol) and then, evaporated to dryness, and the residue neutralized with ethereal hydrogen chloride and dissolved in refluxing ethanol (25 mL) containing *p*-toluenesulfonic acid (25 mg). After 30 min the solvent was evaporated off and the residue distilled. The crude product (0.84 g, **16** and its regioisomer in a 5 : 2 ratio) was repeatedly crystallized from little pentane at −75 °C to afford 17% of pure **16**. ^{1}H-NMR: 5.5 (3H, m); 5.0 (2H, m); 3.64 (2H, t, *J* 6); 2.0 (6H, m); 1.4 (13H, m). ^{13}C-NMR: 139, 130, 129, 114, 63, 34, 32 (2C), 30, 29, 27 (2C), 26. MS: 210 (8%, M^+), 67 (100%). Analysis. Found: C, 80.11; H, 12.30. $C_{14}H_{26}O$ (210.36) calc.: C, 79.94; H, 12.46%.

In order to obtain a maximum *cis/trans* ratio (96 : 4 before crystallization) after reasonably short equilibrium times, catalysis with allylmagnesium bromide (0.1–0.5 mmol) is advisable. Alcoholates may, however, make the magnesium reagent inefficient. In such case, metalation with trimethylsilylmethylpotassium [20] rather than with butyllithium and potassium tert-butoxide proved to be advantageous. This reagent was also used for the metalation of 1,13-tetradecadiene (see below).

(b) (3*Z*,13*Z*)-3,13-Octadecadien-1-ol (**21**) and its acetate: A solution of (*Z*)-1,12-heptadecadiene (**18**, 2.4 g, 10 mmol) and trimethylsilylpotassium (10 mmol) in THF (20 mL) was kept for 15 h at −55 °C, then a catalytic amount of allylmagnesium chloride (0.2 mmol in 0.5 mL of THF) was added and the mixture stored for 10 h at −45 °C before a small quantity was withdrawn and was treated with chlorotrimethylsilane. GLC (40 m, Carbowax, 20M, 160 °C) showed two peaks in a 98 : 2 ratio, and these were tentatively assigned to the (3*Z*,13*Z*) and (3*E*,13*Z*) stereoisomers. The bulk of the reaction mixture was stirred for 1 h at −75 °C with paraformaldehyde and the mixture then allowed to warm to 25 °C. The solvent was evaporated and the residue partitioned between hexane (50 mL) and water (10 mL). The organic layer contained product **21**, which was purified by several crystallizations from hexane at −75 °C. ^{1}H-NMR: 5.4 (4H, m); 3.63 (2H, t, *J* 7); 2.32 (2H, q, *J* 7); 2.0 (6H, m); 1.73 (1H, s); 1.3 (16H, m); 0.90 (3H, t, *J* 6). MS: 266 (35%, M^+), 55 (100%). Analysis. Found: C, 80.96; H, 13.09. $C_{18}H_{34}O$ (266.47) calc.: C, 81.13; H, 12.86%.

The most convenient way to prepare the acetate [19] is to add acetic anhydride after the organometallic intermediate has reacted with the formaldehyde (as evidenced by decolorization of the solution).

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