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Activated alkyl- and allyl-alkali metal reagents: Contrasting behaviour towards ethylene

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Abstract

Ethylene, hex-1-ene and (+)-α-pinene were readily metallated in methylcyclohexane with the system $^{n}BuLi/LiK(OCH_2CH_2NMe_2)_2$. The regioselectivity of the reaction of metallated hex-1-ene and (+)-α-pinene with CO_2 could be substantially modified by the addition of $Mg(OCH_2CH_2OEt)_2$. Addition of the latter also solubilizes the organometallic reagents. The allylmetallic products from the metallation of hex-1-ene and α-pinene added to ethylene under mild conditions. Whereas up to four molecules of ethylene added to metallated hex-1-ene, only one or two, depending on the reactant ratios, added to metallated α-pinene. Similar reactions involving use of a variety of other strong bases such as $^{n}BuLi/^{t}C_5H_{11}OK$ and ^{n}BuM (M = Li, Na, K), with and without added TMEDA, indicated that the presence of a tertiary amine, apart from assisting the metallation reaction, is essential for the occurrence of the addition.

1. Introduction

The addition of organometallic compounds to unactivated carbon–carbon double bonds is well documented [1] and is of fundamental importance in the polymerization of olefins by the Ziegler–Natta [2] or anionic processes [3]. For organometallic derivatives of the alkali metals, addition generally occurs only if there are no allylic hydrogens present; otherwise allylic metallation takes place preferentially. Exceptions to this are only observed when the potential allylmetal is a high energy species, as in the case where the allylic proton is at a bridgehead position [4].

Two types of reaction have been observed between alkali metal organometallics and ethylene, namely metallation and addition. Metallation of ethylene at 1 atm pressure is reported to occur with n-pentylsodium [5] or with the reagent system n-butyllithium/potassium tert-butoxide in the presence of TMEDA [6*,9*]. In the absence of TMEDA, the latter system is reported to be unreactive towards ethylene while, for simple organolithium compounds, addition to ethylene occurs in the presence of a Lewis base such as THF or TMEDA [1a,2]. The allylmetal formed by Lickor metallation of 2,3-dimethylbut-2-ene in THF has been observed to add to ethylene [10], and a similar addition with 1-phenylcyclopropylpotassium has also been reported [11]. The ethylene in these cases was formed by base cleavage of THF [1a,2]. In the case of other unsaturated hydrocarbons with no allylic hydrogens, metallation at the olefinic position is effected by organosodium reagents, especially in the presence of sodium or potassium alkoxides [4], while an examination of the literature reveals that vinylic metallations using an organolithium/potassium alkoxide combination are successful only when a functional group is also present [12].

Our interest in the modification of organometallic reagents by metal alkoxides [13] led us to examine aspects of the metallation reaction and the chemistry of the products formed, and in particular the reaction with ethylene. The initial investigations have centred on metallations of hex-1-ene and (+)-α-pinene. The former was used to evaluate the extent and regioselectivity of metallation, whereas the latter was chosen because of its chemical interest. The use of bicyclo[3.1.1]-heptane derivatives as chiral auxiliaries and as synthetic reagents is well known, and α-pinene is prob-

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* Reference number with asterisk indicates a note in the list of references.

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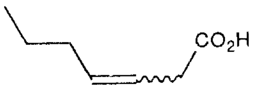
ably the most readily available representative of this class [14,15]. Since the metallation of (+)-α-pinene using a number of strong bases, and subsequent reactions with substrates such as Me_3SiCl, Bu_3SnCl, $B(OMe)_2X$ *etc.*, have been reported previously [16], we have concentrated more on the ethylene addition reaction as a means of extending the chemistry of α-pinene and its homologues.

2. Results and discussion

In view of the known effect of tertiary amines in promoting the metallation reaction [17], we chose to employ alkoxides derived from 2-dimethylaminoethanol in conjunction with n-butyllithium. The simple alkoxides $NaOCH_2CH_2NMe_2$ (**1**) and $KOCH_2CH_2NMe_2$ (**2**) were found to be insoluble in methylcyclohexane (MCH), but acceptable concentrations could be obtained by using the double alkoxide, $LiK(OCH_2CH_2NMe_2)_2$ (**3**). Although it could be argued that the presence of the lithium alkoxide might reduce the effectiveness of the butyllithium/metal alkoxide system as a metallating agent, it should be borne in mind that lithium alkoxides are an inevitable component in the reactions of conventional Lickor reagents.

Hex-1-ene was found to be readily metallated by ^{n}BuLi/**3**, and the extent of metallation was determined by carbonation, the regioselectivity of which could be varied to a certain degree by the prior addition of $Mg(OCH_2CH_2OEt)_2$ (**4**). The magnesium alkoxide was preferred to alternative magnesium compounds since it is known to provide hydrocarbon-soluble reagents [13b,18].

We see from the results presented in Table 1 that, for maximum yields of the acids (*E*)- and (*Z*)-hept-3-enoic acid (**5**) and 2-propylbut-3-enoic acid (**6**), a 1 : 1 stoichiometry of ^{n}BuLi to K is required (compare entries 1 and 3). The reaction time was not optimized, but it appears that the metallation is essentially complete within 3 h. Addition to the γ position becomes more significant when **4** is present (compare entries 1–5), and is comparable to the corresponding reactions with allyl Grignard reagents [19]. In the absence of **4** (Entry 2) or when the ratio of **3** to **4** is 2 : 1 (entry 5), substantially more terminal acids are obtained. We can thus infer that a species with substantial organomagnesium character is formed after addition of the magnesium alkoxide, and it is to be expected that similar additives derived from other metals will also cause alterations in stereo- and regiochemical behaviour. Such differences have indeed already been observed for allylmetal reagents prepared by other routes [20]. The use of $KOCMe_2Et$ instead of **3** appears to give slightly lower yields, (entries 9 and 10). We observed little or no drop in yield when longer metallation times were used. This implies that the organometallic formed does not react to any significant extent with the aminoalkoxide. While TMEDA is known to react slowly with organolithiums to give low yields of metallated products [21], in our case the negative charge on the alkoxide, and possibly the inferior metallating ability of the allylmetals formed compared with alkylmetals, could be expected to further minimize this side-reaction.



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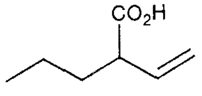

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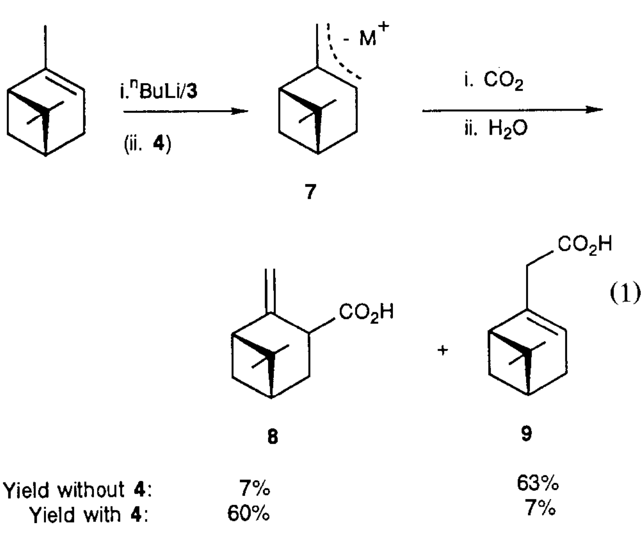
A similar picture holds for α-pinene. Metallation and subsequent carbonation gives approximately 70% of acids **8** and **9** (eqn. (1)). In the presence of **4** the ratio of **8** to **9** is 9 : 1 whereas in its absence the ratio is reversed.

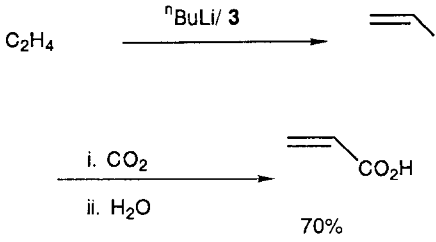
TABLE 1. Metallation of hex-1-ene and product distribution after carbonation

Entry	Hex-1-ene (mmol)	^{n}BuLi (mmol)	$LiK(OR)_2$ (mmol)	**4** (mmol)	Metallation time (h)	Total yield (%)	Ratio **5** : **6**
1	30	20	10	20	20	30	10 : 90
2	30	20	20	0	20	65	49 : 51
3	30	20	20	20	24	70	16 : 84
4	30	20	20	40	3	66	6 : 94
5	15	10	20	10	20	39	41 : 59
6 [a]	30	20	20	20	2	56	20 : 80
7 [a]	30	20	20	20	20	53	17 : 83
8 [b]	30	20	20	20	24	55	13 : 87
9	30	20	20 [c]	20	72	34	15 : 85
10 [b]	30	20	20 [c]	20	72	54	13 : 87

[a] ^{n}BuLi first added to solution of **3** followed by hex-1-ene. [b] Metallation with ice cooling instead of dry ice/acetone. [c] $KOCEtMe_2$.



Having established the effectiveness of ^{n}BuLi/**3** as a metallating agent, we turned our attention to the reaction of the product organometallics with ethylene. As mentioned above, ^{n}BuLi/^{t}BuOK is reported to be unreactive towards ethylene, whereas addition of TMEDA causes metallation [9]. Metallation of ethylene at 1 atm pressure is also effected by ^{n}BuLi/**3**, a 70% yield of acrylic acid being obtained after carbonation. No addition product, *i.e.* heptanoic acid, was detected (eqn. (2)).



(2)

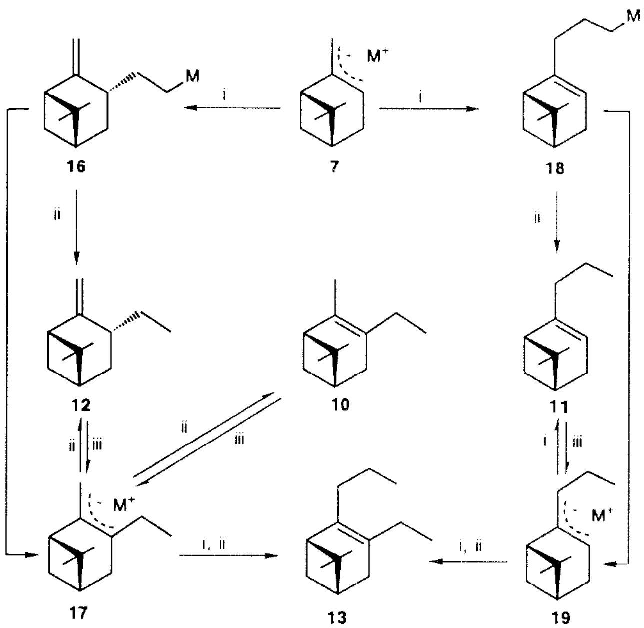
In the case of the reaction of ethylene with metallated hex-1-ene, GC analysis of the hydrolyzed product mixture indicated the presence of a number of components in groups corresponding to C_8, C_{10}, C_{12}, and C_{14} hydrocarbons, while no uptake of gas was observed in the presence of **4**. The complex nature of the product mixture led us to try the analogous reaction with α-pinene. Addition did indeed occur slowly, reaction times were generally 3–6 days at 1 atm and room temperature, and hydrolysis gave up to four products that were isolated by preparative GC. On the basis of analytical and ^{1}H and ^{13}C NMR data, structures **10–13** are proposed (Scheme 1).

Compounds **11** and **12** arise from the addition of ethylene to either of the two ends of the allylmetal, **7**, to give **16** or **18**, which are then protonated by excess α-pinene or by the product allylic hydrocarbons, while **10** is most probably formed by isomerization of **12**. (The analogous isomerization of β- to the thermodynamically more favourable α-pinene is known to be induced by organosodium compounds [22].) Metallation of any of the monoaddition products and subsequent addition of ethylene followed by protonation would give **13**.

TABLE 2. Metallation of α-pinene and distribution of ethylene addition products

Entry	α-Pinene (mmol)	Base (mmol)	Time (days)	Total yield [a] (%)	**10**:**11**:**12** comp.
1	30	^{n}BuLi(20)/**3**(20)	7	95	48:13:16 [b]
2	20	^{n}BuLi(20)/**3**(20)	5	76	40:17:7 [c]
3	80	^{n}BuLi(20)/**3**(20)	5	95	28:22:50
4	100	^{n}BuLi(15)/**3**(15)	1	60	13:9:77
5	100	^{n}BuLi(15)/**3**(15)	4	130	22:11:67
6	500	^{n}BuLi(50)/**3**(50)	1 [d]	170	9:19:73
7	100	^{n}BuLi(15)/**14**(15)	5	165	12:23:65
8	100	^{n}BuLi(15)/**15**(15)	9	Trace	–
9	100	^{n}BuLi(15)/**15**(15)/TMEDA(30)	3	160	9:12:79
10	100	^{n}BuLi(15)/TMEDA(15)	3	16	0:8:92
11	100	^{n}Bu$_2$Hg/Na(15)/TMEDA(15)	4	210	71:4:25
12	100	^{n}Bu$_2$Hg/K(15)	3	0	–
13	100	^{n}Bu$_2$Hg/K(15)/TMEDA(15)	6	230	22:10:68

[a] By GC. Yields are given on the basis of the amount of metallating agent used. [b] 23% of **13** also produced. [c] 36% of **13** also produced. [d] At 3 atm. **14** = LiK(OCH$_2$CH$_2$N^{i}Pr$_2$)$_2$; **15** = KOCMe$_2$Et.



Scheme 1. i. C_2H_4; ii. protonation by an allylic hydrocarbon, or, in the case of entries 1 and 2 (Table 2), in the aqueous work-up, iii. metallation by organoalkali metal species.

Several features of interest arising from the results given in Table 2 may be noted. Firstly, since metallation of α-pinene is considered to occur predominantly at the C-10 methyl group, addition of ethylene occurs mainly with allylic rearrangement and, in this respect, is reminiscent of the ene reaction [23]. It is worth noting that the addition reaction seems to be facile only with allylmetallics; addition of alkyl-, aryl- or vinylmetallics, where it occurs at all, usually requires a high pressure of olefin [3].

Secondly, although the immediate product of addition should be the organometallics **16** and **18**, no evidence of metallation of ethylene or addition of ethylene to the terminally metallated position was found. In those runs in which the reaction was quenched with CO_2, no acrylic acid or acid corresponding to organometallics such as **16** or **18** was detected. The major proportion of the acid formed was **9**, with **8** as the most significant minor product, and the yields were typically in the range 30–50% based on the quantity of metallating agent used. It therefore seems that **16** and **18** rapidly metallate any available site either intra- or intermolecularly to give an allylmetal derivative (*e.g.* 7, **17** or **18**). The regeneration of **7** suggests that the production of ethylated pinenes could be made to be catalytic in metallating agent but, in fact, only up to about two cycles were observed indicating that the regeneration or the reactivity of **7** was somehow adversely affected. From the yields of acids after carbonation, it seems that some of the loss of activity is due to side-reactions of the intermediate non-allylic carbanions, possibly with the aminoalkoxide (or TMEDA [21]). Metallation of the amine additive by allylic carbanions is not expected to be significant. Indeed, metallation of α-pinene with ^{n}BuLi/**3** and carbonation after 3 days gave the same yield of acids as with carbonation of the fresh reaction mixture. A further factor that may be responsible for the loss of activity is that an unfavourable change in aggregation is occurring as the essentially heterogeneous reaction progresses.

Addition of two ethylene molecules to give **13** is only important when stoichiometric or near stoichiometric ratios of the reactants are employed (entries 1 and 2). According to Scheme 1, the second addition proceeds by way of the allylic species **17** or **19**. The latter could arise either by intramolecular rearrangement of **16** or **18**, or indirectly *via* **12** or **11**. The species **16** and **18**, have sp^3 carbanionic centres and should be strong metallating agents capable of rapidly metallating α-pinene if its concentration were relatively high, and thus leading to the hydrocarbons **12** or **11**. The subsequent thermodynamically favourable isomerization of **12** to **10** is presumably promoted in this case by allylmetal. Here, the equilibria most likely favour the hydrocarbons and, consequently, the amount of **17** present, and its ethylene addition product, will be small. On the other hand, if the concentration of α-pinene is low, as in the case of entry 1 or entry 2, direct rearrangement of **16** or **18** to **17** or **19**, respectively, while perhaps slower than the indirect route, could be a much more significant process and would explain the higher proportions of **13** and **10** that are observed in these cases.

Of particular significance is the fact that essentially no addition occurs in the absence of tertiary amine (entries 8 and 12) even though it is not essential for metallation, as shown above for hex-1-ene and previously for α-pinene by other workers [16]. The reason for this requirement is not clear and needs further examination to determine whether the role of amine is to activate directly the allylmetal towards addition of ethylene or indirectly by promoting de-aggregation of the organometallic species. The nature of the metal is seen to influence both the yield and the product composition. With lithium alone as the metal, only a low yield is obtained (entry 10), although this may reflect, at least partly, a lower yield of metallation. The highest yields were obtained with the systems ^{n}BuNa/TMEDA and ^{n}BuK/TMEDA (entries 11 and 13), but while with the latter the product ratio was similar to that obtained using ^{n}BuLi/**3** (compare entries 5 and 13), with the former there was extensive isomerization to **10** (entry 11). Possibly the intermediate **16** metallates α-pinene more rapidly than **12** when ^{n}BuK is used to generate **7**, whereas the reverse applies for ^{n}BuNa.

Only one of the two possible diastereoisomers of **12** appears to be formed since, although we have not determined which one is formed (the structure given above for **12** is expected from steric considerations to be the more likely), the ^{13}C NMR spectrum gave just 12 signals.

The addition of ethylene to metallated α-pinene may be compared to the reaction with ethyl iodide where the major product is **11** (85% of the product) and **12** is the minor (10%) [24*]. A further 3% is due to an accompanying peak in the GC and which is perhaps due to the C-3 epimer of **12**. Treatment of the metallated α-pinene with a large excess of **4** before reaction with EtI changes this composition only slightly (74% **11**, 26% **12**). On the other hand, metallation of α-pinene by ^{n}BuLi/**3** followed by reaction with diethyl sulphate gave a much higher percentage of **12** (56% **11**, 42% **12**, 2% unknown).

3. Experimental section

All reactions with air-sensitive reagents were carried out under pure argon. Nuclear magnetic resonance spectra (NMR) were recorded on a Varian FT80 instrument. Gas-liquid chromatography (GLC) was carried on a Pye Unicam GCV chromatograph with Apiezon L on Chromosorb GAW/BMCS analytical and preparative columns. GLC yields were estimated by use of an internal standard (decalin) and also from the total of the peak areas of unreacted pinene and the reaction products. Both methods gave comparable results. Elemental analyses were performed at NCSR, "Democritos", Athens. Magnesium 2-ethoxyethoxide was prepared as described previously [18]. All other reagents were obtained commercially.

3.1. Preparation of [$LiOCH_2CH_2NMe_2 \cdot KOCH_2CH_2NMe_2$] (3)

Potassium metal (8.5 g, 220 mmol), cut into pieces under dry methylcyclohexane (MCH), was covered with 80 ml of MCH in a three-necked flask equipped with a pressure-equalizing dropping funnel and condenser. A solution of 2-dimethylaminoethanol (35.7 g, 400 mmol) in MCH (120 ml) was added during 20 min. (The reaction is fairly mild and no cooling is necessary). After the addition, and when the rate of evolution of hydrogen had decreased substantially, the mixture was heated under reflux for 3–4 h until all the metal had been consumed. On cooling, a white crystalline mass began to separate out. Before the mixture had cooled completely to room temperature, lithium metal pieces (1.4 g, 200 mmol) were added. A mildly exothermic reaction ensued. After 30 min, heating was again applied and continued until the metal remaining ceased to float on the surface (indicating that the excess of potassium metal had been displaced by the lithium) and then for a further 2 h to ensure completion. The solution formed was stable for long periods under an inert atmosphere and at temperatures above *ca.* 20°C. (At lower temperatures alkoxide precipitates out on standing for several days.) The concentration was determined by hydrolyzing an aliquot (1.00 ml) and titrating against 0.100 N HCl using methyl red indicator to give total organic and inorganic base concentration. The total alkoxide concentration is one-half of this and was typically 1.7 N. The potassium and lithium concentrations were assumed to be equal and thus one-half of the alkoxide concentration.

$KOCEtMe_2$ was prepared by addition of $EtMe_2COH$ (19.0 g, 215 mmol) in MCH (60 ml) to potassium metal pieces (9.5 g, 240 mg atom) covered with MCH (60 ml). (The reaction is very mild and the addition may be carried out fairly rapidly). After the addition, the reaction mixture was heated under reflux. After a while, a thick white precipitate formed (presumed to be an alkoxide/alcohol aggregate). This redissolved on further heating which was stopped after 2 h. No precipitate formed on cooling. Titration of a hydrolyzed aliquot against 0.100 N HCl indicated an alkoxide concentration of 1.64 N.

3.2. Metallation of ethylene and carbonation

The metallation was carried out under an atmosphere of ethylene. A solution of **3** (23 ml, 0.87 N, 20 mmol) was cooled in ice and ^{n}BuLi (11.5 ml, 1.8 N, 21 mmol) added during 20 min. Ethylene was passed through the suspension for 2 h after which it became orange-red. The mixture was poured onto crushed dry ice in Et_2O and allowed to warm to room temperature. Water was added and volatiles removed by rotary evaporation. The aqueous solution was extracted with 2 × 50 ml toluene and 2 × 50 ml hexane and then acidified with 20% H_2SO_4. The organic fraction was extracted with 4 × 75 ml Et_2O, dried over anhydrous $MgSO_4$, filtered, and concentrated by evaporation under reduced pressure at room temperature to give an oil, which gave a ^{1}H NMR spectrum identical to that of propenoic acid [25]. Yield 1.0 g (70%).

3.3. Metallation of hex-1-ene and carbonation, (entry 1)

Hex-1-ene (3.8 ml, 30 mmol) and **3** (12.0 ml of a MCH solution 1.7 N in alkoxide; 10 mmol of **3**) were cooled in a dry ice/acetone bath. ^{n}BuLi (10.5 ml of a 1.9 N MCH solution; 20 mmol) was added over 15 min and the reaction mixture (an orange-brown suspension) then allowed to warm slowly to room temperature. After stirring at room temperature for 60 h, $Mg(OCH_2CH_2OEt)_2$ (4.1 g, 20 mmol) was added and stirring continued for 24 h to give a brownish solution. The solution was poured onto crushed dry ice/Et_2O. When this had warmed to room temperature, water was added and the mixture then evaporated to dryness. The residue was acidified with a little 20% H_2SO_4 and extracted with Et_2O (3 × 50 ml); the extracts were concentrated and stirred overnight with aq. Na_2CO_3. The aqueous layer was separated, washed with 2 × 50 ml toluene and 2 × 50 ml hexane, acidified as before, extracted with 4 × 50 ml dichloromethane, dried over $MgSO_4$, and filtered and concentrated to a small volume. The remaining solution was left to evaporate in a preweighed beaker overnight. ^{1}H NMR of the residual oil indicated a yield of 1.4 g of acids (after allowing for a small amount of residual ethoxyethanol) (55%), of which 8% was (*E*)- and (*Z*)-hept-3-enoic acid (**5**) and 47% was 2-propylbut-3-enoic acid (**6**). The composition was inferred from the ^{1}H NMR spectrum by integration of the olefinic and allylic proton regions [26]. The remaining entries in Table 1 were carried out analogously using the conditions reported. Anal. Found: C, 65.42; H, 9.35. $C_7H_{12}O_2$ calcd.: C, 65.60; H, 9.44.

3.4. *Metallation of α-pinene and carbonation*

α-Pinene (3.1 ml, 2.7 g, 20 mmol) and **3** (31 ml of MCH solution 0.65 N in **3**, 20 mmol) were cooled in ice and ^{n}BuLi (11.5 ml of 1.9 N MCH solution, 22 mmol) added over 20 min. An orange suspension formed. After 16 h stirring at room temperature, $Mg(OCH_2CH_2OEt)_2$ (4.1 g, 20 mmol) was added and stirring continued for 24 h, when a clear solution was obtained. Carbonation and subsequent work-up was as described above for the reaction with hex-1-ene, care being taken to use only the minimum amount of cold 5% H_2SO_4 in the acidification steps. Yield of acids 2.4 g (67%) [28]. ^{1}H NMR indicated a composition of 90% **8** and 10% **9** by integration of the olefinic proton region (**8**: 4.8 (m, 1H); 5.0 (m, 1H). 9: 5.4 (m, 1H)). The ratio was confirmed by esterification with Me_2SO_4 followed by GC. Anal. for **8** + **9**: Found: C, 73.17; H, 8.83. $C_{11}H_{16}O_2$: calcd.: C, 73.30; H, 8.95%.

A similar reaction without addition of $Mg(OCH_2CH_2OEt)_2$ gave 70% of the acids (composition 10% **8** and 90% **9**).

3.5. *Addition of ethylene to metallated hex-1-ene*

A solution of **3** (23 ml, 0.86 N, 20 mmol), and hex-1-ene (6.5 ml, 50 mmol) were cooled in ice and ^{n}BuLi (11 ml, 1.8 N, 20 mmol) added during 20 min. After 1 h stirring at room temperature, the argon atmosphere was replaced by ethylene by a freeze/thaw cycle and stirring continued at 1 atm for 6 days. The mixture was hydrolyzed, and the organic components extracted with hexane. The extract was dried over anhydrous $MgSO_4$, and than examined by GC (without removal of solvents). A very complex chromatogram was obtained, with groups of peaks appearing at regular intervals after that due to hexene, and assumed to be from isomeric octenes, decenes, dodecenes and possibly tetradecenes.

3.6. *Addition of ethylene to metallated α-pinene*

Details are given for entry 3 of Table 2. A mixture of *α*-pinene (11.0 g, 81 mmol) and **3** (23 ml, 0.88 N, 20 mmol) was cooled in ice and ^{n}BuLi (11.8 ml, 1.8 N, 21 mmol) was added during 20 min. The orange-yellow suspension was stirred overnight and the argon atmosphere then replaced by ethylene by a freeze/thaw cycle. Stirring was continued for 5 days under a 1 atm pressure of ethylene. The suspension turned brown during this time. The reaction was quenched with 50% aqueous isopropanol and the products extracted with 4 × 50 ml hexane. After drying over anhydrous Na_2SO_4, the extract was filtered and concentrated under reduced pressure to leave an oil, GLC analysis of which indicated the presence of three components other than starting material (estimated GC yield of products: 95% based on quantity of metallating agent used). Fractional distillation at 78–80°C/10 mm gave 2.6 g of a colourless liquid (79%). Preparative gas chromatography and subsequent NMR analysis showed the product to be a mixture of **10**, **11** and **12** in the ratio 28 : 21 : 51. The experiments corresponding to the remaining entries in Table 2 were carried out in a similar fashion using the quantities shown in the Table. Metallations other than with ^{n}BuLi/**3** were carried out as described below. ^{1}H NMR ($CDCl_3$, ppm from internal TMS): **10**: 0.77 (s, 3H); 1.0 (m, 5H); 1.22 (s, 3H); 1.60 (br.s, 3H); 2.1 (m, 6H). **11**: 0.82 (s, 3H); 1.26 (s, 3H); 1.1 (br.m, 7H); 2.1 (m, 6H); 5.2 (m, 1H). **12**: 0.75 (s, 3H); 1.0 (m, 5H); 1.23 (s, 3H); 1.9 (m, 5H); 4.7 (m, 2H). **13**: 0.76 (s, 3H); 1.23 (s, 3H); 1.1 (m, 9H); 2.1 (m, 9H). ^{13}C NMR ($CDCl_3$, ppm from internal TMS; multiplicities from off-resonance spectra and assignments in parentheses; superscripts denote assignments that may need to be reversed): **10**: 12.9 (q, C-12); 18.7 (q, C-9); 20.7 (q, C-10); 24.1 (C-11); 26.5 (q, C-8); 32.3 (t, C-7)^{a}; 34.6 (t, C-4)^{a}; 38.8 (s, C-6); 41.4 (d, C-5); 48.1 (d, C-1); 127.3 (s, C-3); 135.2 (s, C-2). **11**: 14.0 (q, C-12); 20.5 (t, C-11); 21.3 (q, C-8); 26.5 (q, C-9); 31.5 (t, C-4)^{b}; 31.8 (t, C-7)^{b}; 39.4 (t, C-10); 41.3 (d, C-5); 41.4 (s, C-6); 46.2 (s, C-1); 115.9 (d, C-3); 148.6 (s, C-2). **12** 12.4 (q, C-12); 21.7 (q, C-9); 26.1 (q, C-8); 28.9 (t, C-7); 30.8 (t, C-11); 35.4 (t, C-4); 36.9 (d, C-3); 40.4 (s, C-6); 41.5 (d, C-5); 52.8 (d, C-1); 107.8 (d, C-10); 156.1 (s, C-2). **13**: 13.4 (q, C-14)^{c}; 14.3 (q, C-12)^{c}; 21.2 (t, C-11); 21.2 (q, C-9); 23.9 (t, C-13); 226.5 (q, C-8); 32.6 (t, C-7); 34.6 (t, C-4)^{d}; 34.9 (t, C-10)^{d}; 38.7 (s, C-6); 41.3 (d, C-5); 46.4 (d, C-1);

127.7 (s, C-3); 139.7 (s, C-2). The ^1H and ^{13}C NMR data for **11** agree with those reported [14c].

Anal. **10**, **11** and **12**: Found **10**: C, 87.65; H, 12.20. Found **11**: C, 87.67; H, 12.18. Found **12**: C, 87.58; H, 12.34. $C_{12}H_{20}$ calcd.: C, 87.73; H, 12.27%. Anal. **13** $C_{14}H_{24}$: C calcd.: 87.42; H, 12.58%. Found: C, 87.30; H, 12.69.

3.7. *Metallation of α-pinene with ^nBuLi and $KOCEtMe_2$*

A solution of $KOCEtMe_2$ in MCH (9.5 ml, 1.64 N, 15 mmol) and α-pinene (16 ml, 100 mmol) was cooled in ice and ^nBuLi (9.0 ml, 1.8 N, 16 mmol) added over 20 min. The mixture was stirred overnight at room temperature before use.

3.8. *Metallation of α-pinene with ^nBuLi, $KOCEtMe_2$ and TMEDA*

A solution of $KOCEtMe_2$ in MCH (9.5 ml, 1.64 N, 15 mmol), α-pinene (16 ml, 100 mmol) and TMEDA (4.5 ml, 30 mmol) was cooled in ice and ^nBuLi (9.0 ml, 1.8 N, 16 mmol) added over 20 min. The mixture was stirred for 2 h at room temperature before use.

3.9. *Metallation of α-pinene with ^nBuLi and TMEDA*

^nBuLi (9.0 ml, 1.8 N, 16 mmol), α-pinene (16 ml, 100 mmol) and TMEDA (4.5 ml, 30 mmol) were stirred together at room temperature for 60 h before use.

3.10. *Metallation of α-pinene with ^nBuNa and TMEDA*

Sodium (0.35 g, 15 mmol), $(^nBu)_2Hg$ (2.5 g, 8 mmol). TMEDA (2.3 ml, 15 mmol), α-pinene (16 ml, 100 mmol) and MCH (15 ml) were stirred together at room temperature for 2 days before use.

3.11. *Metallation of α-pinene with ^nBuK and TMEDA*

Potassium (0.6 g, 15 mmol), $(^nBu)_2Hg$ (2.5 g, 8 mmol), TMEDA (2.3 ml, 15 mmol), α-pinene (16 ml, 100 mmol) and MCH (15 ml) were stirred at room temperature for 24 h before use.

3.12. *Metallation of α-pinene with ^nBuK*

Potassium (0.6 g, 15 mmol), $(^nBu)_2Hg$ (2.5 g, 8 mmol), α-pinene (16 ml, 100 mmol) and MCH (15 ml) were stirred at room temperature for 36 h before use.

3.13. *Reaction of metallated α-pinene with EtI*

A solution of **3** (12 ml, 0.85 N, 10 mmol) and α-pinene (1.6 ml, 10 mmol) was cooled in ice and ^nBuLi (5.5 ml, 1.8 N, 10 mmol) added dropwise. After overnight stirring at room temperature, the mixture was cooled in ice and quenched with an excess of EtI. The mixture was hydrolyzed and the products extracted with 2 × 50 ml hexane. The combined extracts were washed with cold dilute H_2SO_4 and saturated aqueous $NaHCO_3$, dried over Na_2SO_4, filtered, concentrated, and distilled under reduced pressure (75–80°C/10 mm). Yield of **11** and **12** was 52%. The ratio of **11** to **12** was 85 : 12, the remainder being a small unidentified component, possibly the C-3 epimer of **12**.

3.14. *Reaction of metallated α-pinene with Et_2SO_4*

The reaction was carried as with EtI, the reaction being quenched with excess Et_2SO_4. Yield was 60%, composition 56% **11**, 42% **12** and 2% unknown.

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