Journal of Organometallic Chemistry, 280 (1985) 159–164
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PREPARATION AND ^{13}C NMR CHARACTERIZATION OF γ,γ'-DISUBSTITUTED ALLYLLITHIUM COMPOUNDS

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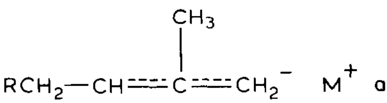
(Received February 28th, 1984; in revised form July 23rd, 1984)

Summary

Two γ,γ'-disubstituted derivatives of allyllithium have been prepared by the classical transmetallation route between phenyllithium and allyltriphenyltin derivatives. These compounds substituted with methyl and ethyl groups or methyl and neopentyl groups in the γ-position were studied by ^{13}C NMR in diethyl ether and tetrahydrofuran. The results are compared with those previously reported for monosubstitution. Charge distributions are not greatly different but the *trans* configuration is more stable in the disubstituted derivatives.

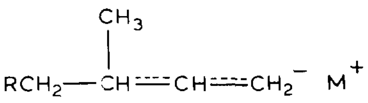
Introduction

Although the preparation and characterization of allyllithium and a number of β- or γ-alkyl-substituted derivatives have been adequately described in the literature [1–7], γ,γ'-disubstituted derivatives have not. Alkyl-substituted allyl anion pairs are important intermediates in the anionic polymerization of diene monomers. In the polymerization of isoprene, for example, two different active centers can in principle occur:



$RCH_2{-}CH\overset{\cdots}{=}\overset{\displaystyle CH_3}{\overset{|}{C}}\overset{\cdots}{=}CH_2^- \; M^+$ and

(a)



$RCH_2{-}\overset{\displaystyle CH_3}{\overset{|}{CH}}\overset{\cdots}{=}CH\overset{\cdots}{=}CH_2^- \; M^+$

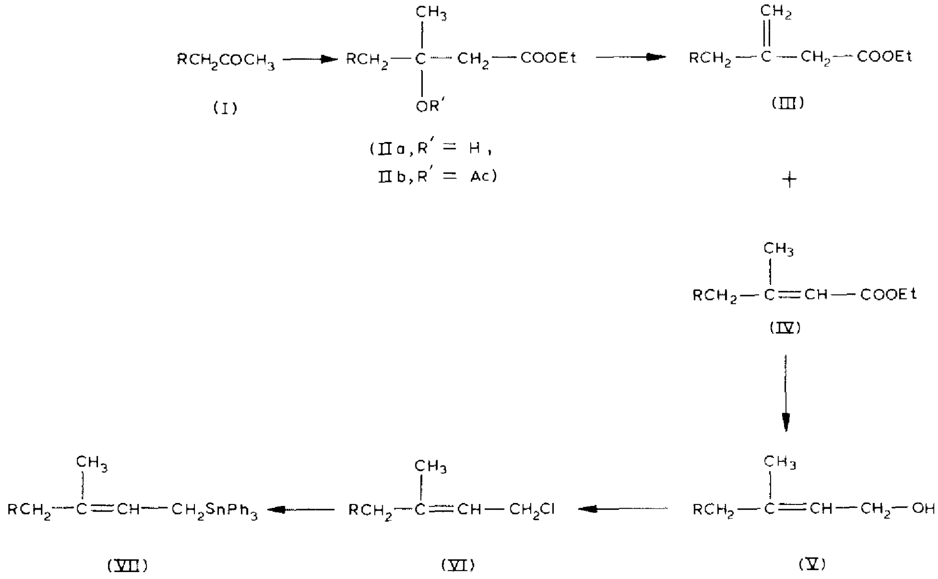
(b)

where R is the polymer chain. Type **a** centers are formed by 4,1 addition of a monomer molecule to a preceding active center and type **b** by 1,4 addition. Type **a** on further monomer addition become 4,3 or 4,1 in-chain units dependent on the position of attack (γ or α respectively). Type **b** in a similar manner produce 1,2 or 1,4 units in the polymer chain (1,4 and 4,1 are indistinguishable in the chain). In polar solvents generally, polymers formed are high in vinyl unsaturation, the

0022-328X/85/$03.30

presence of both 4,3 and 1,2 units indicating that both types of active center coexist during polymerization. It is of interest to know their relative proportions and for this purpose characterization of shorter chain analogs with R a simple alkyl group rather than a polymer chain are useful for identification purposes. A knowledge of their configurational preference (*cis* or *trans*) is also useful in investigations of stereospecificity in diene polymerization [8].

Compounds of type **a** (R = s- or t-butyl) have been prepared in high yield by direct addition of s- or t-butyllithium to isoprene in benzene for the mode of addition is overwhelmingly 4,1 [9] in this solvent. Corresponding type **b** anion pairs cannot be prepared in this simple way. It is, therefore, necessary to use other methods to produce these compounds. Direct metallation of the corresponding 2-olefin although easily achieved by potassium compounds [10] requires the presence of complexing agents such as tetramethylethylenediamine with alkyllithiums [6]. Their presence could affect the configurational preference of the lithium compounds. Metallation processes suffer also from the disadvantage that with **b** type 2-olefins, both α- and γ-methyl groups are susceptible to attack so that a mixture of products can be formed. Transmetallation between phenyllithium and allyltriphenyltin compounds does, however, enable the required lithium compounds to be prepared directly in diethyl ether or even in pentane [1]. The general route followed to prepare the tin compounds was shown in Scheme 1.



SCHEME 1

Exploratory experiments were carried out on commercially available 1-chloro-3-methyl-2-butene (VI, R = H, Eastman). Later experiments used 1-chloro-3-methyl-2-pentene (VI, R = CH_3) and 1-chloro-3,5,5 trimethyl-2-hexene (VI, R = t-C_4H_9). The latter compound yields the 1,4 analog of the 4,1 product from t-butyllithium and isoprene which has been previously investigated in detail as a model for polymerization systems [8,11].

Experimental

(a) Preparation of 1-chloro-3,5,5-trimethyl-2-hexene

46.5 g (0.41 mol) of 4,4-dimethyl-2-pentanone (prepared by a Grignard reaction of methyl iodide, Mg and CuCl on mesityl oxide) was treated with 0.35 g $HgCl_2$, 30.0 g of activated Zn and 73.5 g (0.44 mol) of ethylbromoacetate to give 55.8 g of crude hydroxyester IIa. This was dissolved in 100 ml of CH_2Cl_2, treated with 30 ml of acetyl chloride and a few drops of pyridine and left overnight. The product was extracted with ether to give 57.3 g of crude acetoxyester IIb which was refluxed with 5.0 g Na in 150 ml of ethanol for 15 min. After cooling, the product was extracted with ether giving on work-up a dark brown product which was fractionated retaining the fraction (50.0 g) distilling at 100°C at 15–18 torr. A doublet at 4.8 ppm in the ^1H NMR spectrum indicated that unwanted ester III was also present. The product was therefore dissolved in 150 ml CH_2Cl_2, cooled to 0°C and bromine added dropwise. When most of the unwanted ester had reacted (GLC) the mixture was poured into cold water and extracted with CH_2Cl_2. Work-up gave a dark yellow product fractioned at 99–100°C (15–18 torr) to give 40.2 g (0.22 mol, 54%) of ester IV. IR: ν_{max} 1715, 1640 cm^{-1}; NMR δ_{TMS} (in CCl_4): 0.98 (s, 9H, t-But); 1.25 (t, 3H, J 7 Hz, ester CH_3); 2.63(*E*), 2.03 *Z*) (s, 2H, CH_2); 1.93(*Z*), 2.18(*E*) (d, 3H,C(CH_3)=); 4.04 (q, 2H, J 7 Hz, CH_2); 5.48(*E*), 5.65(*Z*(s, 1H olefinic).

20 g (0.11 mol) of ester IV were treated with 1.5 g $LiAlH_4$ in 180 ml of ether at reflux for 30 min. Work-up gave 15.3 g of crude alcohol V. (IR: ν_{max} 3330 (OH), 1610, 1005 cm^{-1} (C=C)). 27.7 g of crude alcohol was treated with 7 ml PCl_3 at 0°C in 80 ml DMF. The mixture was left at 0°C for 15 min and room temperature for 30 min. After addition of water the product was extracted with ether to give 25.7 g of crude chloride VI which on distillation gave 22.7 g (0.14 mol, 70%) of pure chloride b.p. 77–78°C, 15–18 torr; NMR δ_{TMS} in CCl_4: 0.93 (s, 9H t-But); 1.78 (s, 3H,(CH_3)C=C); 1.95(*E*), 2.03(*Z*) (s, 2H, CH_2); 3.99 (d, 2H, J 7 Hz, CH_2Cl); 5.36 (t, 1H, J 7 Hz, olefinic).

(b) Preparation of 1-chloro-3-methyl-2-pentene

This chloride was prepared from 2-butanone using a similar procedure. The Reformatsky reaction was however modified using 85 g (0.7 mol) ethyl chloroacetate 20 g Mg, 1 g $HgCl_2$ in a mixture of 55 ml ether, 75 ml benzene and 50 g (0.69 mol) of 2-butanone. This reaction proceeds violently initially, care is required in its use. 94.7 g (0.59 mol 85%) of hydroxy ester was obtained b.p. 90–91°C, 13–15 torr.

The chlorination step was also modified [12] since PCl_3 gave a poor yield. 12 g (0.12 mol) of the unsaturated alcohol in 10 ml DMF were added to 19 g of Cl_2HC-$N(CH_3)_2$ in 50 ml DMF and 1 g LiCl at 0°C. The mixture was agitated at room temperature for 30 min. After addition of water the product was extracted with ether. Distillation gave 11.3 g (0.095 mol, 79%) of pure chloride b.p. 52°C, 15–18 torr. NMR δ_{TMS} in CCl_4: 1.05 (t, 3H, CH_3CH_2); 1.73 (s, 3H, CH_3C=C); 2.08 (m, 2H, CH_3CH_2); 3.98 (d, 2H, J 7 Hz, CH_2Cl); 5.38 (t, 1H, olefinic).

(c) Preparation of tin compounds

These were prepared according to Seyferth and Hauser [1]. The reaction with 20 g (0.17 mol) of 1-chloro-3-methyl-2-pentene gave 44 g of crude product, recrystallized from hexane to give 28 g (0.065 mol, 38%) of pure product. NMR δ_{TMS} in benzene:

0.85 (t, 3H, CH_3–CH_2); 1.42(*E*), 1.60(*Z*), (s, 3H, CH_3C=C); 1.9 (q, 2H, CH_3CH_2); 2.28 (d, 2H, CH_2–Sn); 5.48 (t, 1H, olefinic). The reaction with 20 g (0.125 mol) of 1-chloro-3,5,5-trimethyl-2-hexene gave 35 g of crude product, recrystallized from hexane to give 24.5 g (0.051 mol, 41%) of pure product. NMR, δ_{TMS} in CCl_4: 0.75(*E*), 0.88(*Z*), (s, 9H, $(CH_3)_3$); 1.53(*E*), 1.70(*Z*) (s, 3H, CH_3C=C); 1.80 (s, 2H, CH_2-t-Bu); 2.33 (d, 2H, CH_2–Sn); 5.37 (t, 1H, CH=).

Transmetallation with phenyllithium [1] was carried out in diethyl ether at 10°C. A two-fold excess of phenyllithium was found to be necessary to remove tin compounds. Attempts to carry out the reaction in tetrahydrofuran failed, so that for characterization in this solvent, the ether was removed as far as possible in vacuo at low temperature and replaced by tetrahydrofuran. All manipulations were carried out in vacuum systems. The samples after removal of precipitated tetraphenyltin were transferred to NMR tubes and examined by ^{13}C NMR as described previously for other substituted allylic ion pairs.

Results and discussion

NMR results are summarized in Table 1, a typical spectrum being given in Fig. 1. The lithium compounds show the usual large upfield shift compared to the parent olefin of the γ-carbon plus a smaller downfield shift of the signal from the α-carbon. The major difference from the many allylic lithium compounds described earlier is the *trans* configurational preference. In either ether or tetrahydrofuran, about 80–85% of both γ-methyl substituted allyllithium compounds is in the *trans* configuration.

In comparison the β-methyl-substituted analog (a, R = t-Bu) is 75% *cis* in diethyl ether and > 95% *cis* in tetrahydrofuran [11]. Some γ-monosubstituted derivatives of allyllithium are known whose configurational preference at least in diethyl ether is *trans* (γ-neopentyl [11], γ-propyl [7]) but this changes to *cis* in a stronger solvating

TABLE 1

^{13}C CHEMICAL SHIFTS OF γ-γ′-DISUBSTITUTED ALLYLLITHIUM $RCH_2C(CH_3)CHCH_2M$ AND THE PARENT 2-OLEFINS (T −20°C, c ~ 0.5 M)

Solvent	Substituents		C(7)	C(6)	C(5)	C(4)	C(3)	C(2)	C(1)
Ether	R = CH_3	t	–	15.8 [a]	13.0	33.0	137.4	117.3	13.3
	M = H	c	–	22.9	12.6	24.9	137.6	118.4	13.0
Ether	R = CH_3	t	–	16.1	14.7	34.2	111.6	133.7	20.6
	M = Li	c	–	23.6	12.2	25.6	[b]	134.7	[b]
THF	R = CH_3	t	–	16.1	15.6	35.1	94.9	137.8	25.8
	M = Li	c	–	24.5	12.6	26.4	[b]	138.6	[b]
THF	R = t-Bu	t	18.7	30.4	32.1	54.2	134.3	122.5	13.5
	M = H	c	26.8	30.8	33.5	45.5	134.8	122.3	14.7
Ether	R = t-Bu	t	20.1	30.2	33.6	55.5	104.8	138.8	23.6
	M = Li	c	27.5	31.1	35.5	46.3	[b]	137.7	[b]
THF	R = t-Bu	t	20.7	30.2	34.2	57.3	89.5	142.5	27.9
	M = Li	c	29.0	31.3	36.3	48.0	[b]		[b]

[a] In THF, peak obscured by solvent in ether. [b] C(1)C(3) signals are probably close to those of the *trans* compound which are noticeably broadened. [c] Numbering from M, C(6) correponds to the γ-methyl group when R = CH_3, C(7) when R = t-Bu

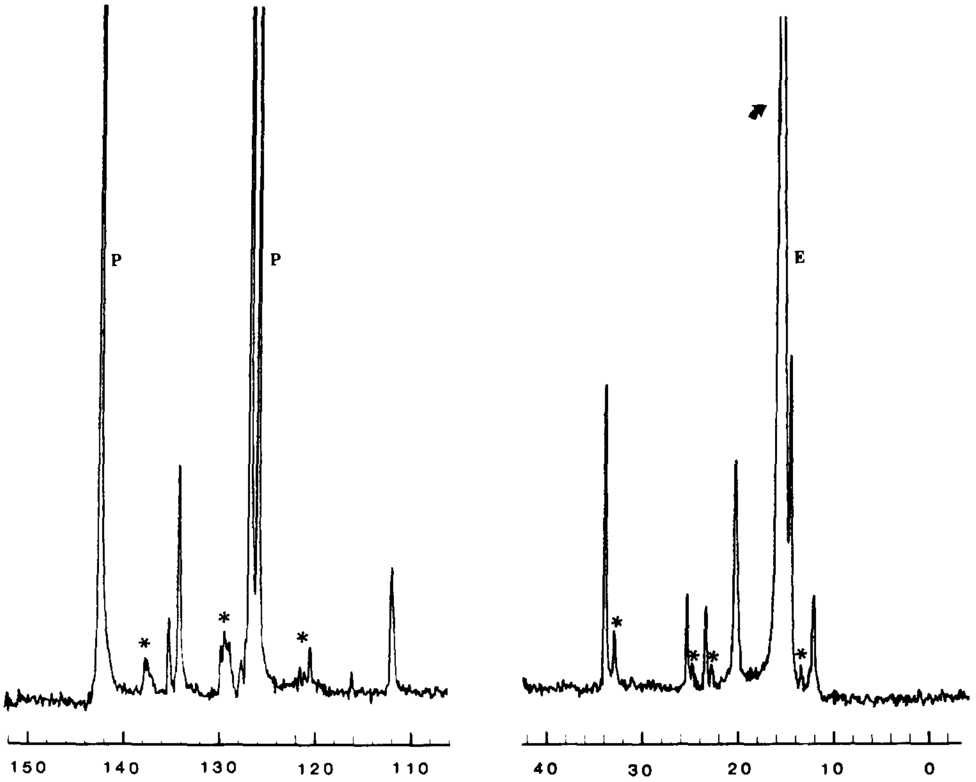


Fig. 1. ^{13}C NMR spectrum of $CH_3CH_2C(CH_3)CHCH_2Li$ in diethyl ether. P = excess phenyllithium, E = diethyl ether, *side products not destroyed by H_2O. Arrow indicates 16.1 ppm signal only fully resolved in deuterated ether.

solvent such as tetrahydrofuran. The only one reported with *trans* preference in tetrahydrofuran involves direct γ-substitution with a bulky t-butyl group [7], i.e., where steric problems are likely to be severe in the *cis* form. It is conceivable that the different configurational preferences in the two solvents are caused by different states of aggregation. In diethyl ether, for example, type **a** compounds show evidence for aggregation at concentrations greater than 3×10^{-3} M [13]. No change in *cis/trans* ratio could be detected, however, in the concentration range 1.5×10^{-3} to 0.4 M, so that in this case at least the explanation lies elsewhere. Ion-pair aggregation will only occur at higher concentrations in better solvating solvents such as THF but cannot be excluded completely at the concentrations necessary for ^{13}C NMR experiments. In its absence the ion pairs will be of the contact type since the equivalent conductance of substituted allyllithium compounds in dilute solutions in THF is very low [14,15]. The increase in reactivity with counter-ion size is also in agreement with this conclusion.

The *cis* configurational preference normally found for other γ-monoalkyl-substituted allylic anions has been ascribed to various causes; hydrogen bonding between alkyl groups and the terminal carbon [7]; interaction of the dipole of the alkyl group with the allylic system [17]; or 1,4-electronic interaction in the *cis*-isomer

[18]. The latter explanation which involves hyperconjugation of, for example, a methyl group to the allylic system seems the most plausible. Compounds of the type under investigation having two γ-alkyl substituents would, on this scheme, be stabilized in both configurations. A stronger hyperconjugation of the methyl than a methylene group would then give some preferential stabilization to the *trans* form. Alternatively in the absence of a strong difference in stabilization between *cis* and *trans* forms steric hindrance of a *cis*-alkyl group could tend to favor the *trans* form.

The chemical shifts of the allylic carbon atoms are in the regions expected of charge delocalized anions. The charge density at α- and γ-carbons can be estimated in the manner used previously for mono-γ-substituted derivatives [11]. The results are similar i.e., 24% (diethyl ether) and 34% (tetrahydrofuran) charge delocalized to the γ-carbon, not significantly different from the compounds studied earlier. In both cases the relative results may be influenced by the different aggregation states in the two solvents. The major effect overall, however, on chemical shifts at the γ-carbon for example is likely to be charge for they are 30–40 ppm to higher field than expected of an sp^2 hybridized carbon at this position. It is unlikely that other causes, including aggregation could account for such large changes.

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