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STRUCTURE, THERMAL STABILITY AND DECOMPOSITION OF BIS-ALLYL-ZINC COMPOUNDS

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Summary

The structure, thermal stability and decomposition of solutions of diallylzinc (I), bis(2-methylallyl)zinc (II), bis(3-methylallyl)zinc (III) and bis(3,3-dimethylallyl)zinc (IV) in deuterated solvents, have been investigated by ^{1}H NMR and by kinetic measurements at temperatures between —125 and +180°C. At room temperature I, II, III and IV are dynamic systems and are best described as being rapidly equilibrating mixtures of all isomeric σ-allyl forms; the NMR spectra are averages weighted according to the relative concentrations of the respective forms. I displays a ^{1}H NMR spectrum of a static σ-allyl system only below —125°C and II only below —115°C. At temperatures above 100°C the thermal decomposition of I—IV results in coupling of the allyl groups, decomposition via radicals being the major process. The coupled products exhibit CIDNP, in which the multiplet polarisations confirm a decomposition via randomly diffusing allyl radicals. In the allyl radicals $CH_2CR^1CR^2R^3$ an alternating spin density was proved experimentally. The thermal stability decreases in the order I > II > III > IV.

Introduction

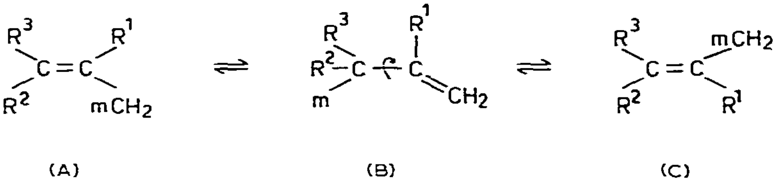
Like many organic derivatives of some main group metals, certain organozinc compounds may be used as effective reagents for addition to olefins [1]. For example, bis(3-methylallyl)zinc (III) [3], and di-t-butylzinc (V) [2], add to olefins under mild conditions (at temperatures between 20 and 60°C, and between —20 and 75°C, respectively). At higher temperatures decomposition takes place. With the exception of V [4], little is known about the thermal stability of these reactive alkenyl- and alkyl-zinc compounds or of their mode of decomposition. Since it is important to understand the mechanism by which zinc—carbon σ-bonds are broken, we have investigated the thermal stability and decomposition of diallylzinc (I), bis(2-methylallyl)zinc (II), bis(3-methylallyl)zinc (III), and bis-(3,3-dimethylallyl)zinc (IV), in deuterated hydrocarbons.

Results and discussion

1. General remarks on ^1H NMR spectra of bis(allyl)zinc compounds

Many allylmetal compounds are fluxional systems. The limiting forms of such organometallic compounds may be delocalized (π-allyl or anionic species) or σ-allyl structures [5]. Delocalized allylmetal compounds may be distinguished from σ-allyls by their IR or Raman spectra, especially in the range of the C=C valence vibrations [5]. The IR spectra [5—8] of bis-allyl-zinc compounds I—IV in solution confirm that these compounds are of the σ-allyl type in the liquid state (cf. experimental part).

In earlier papers Roberts and coworkers [9—12] studied the behaviour of allylmagnesium compounds by ^{1}H NMR and showed that even at temperatures below —120°C allylmagnesium halides and diallylmagnesium interconvert rapidly ($\tau < 0.001$ s) between the isomeric forms (A), (B) and (C) (Scheme 1). In the ^{1}H NMR spectra the observed chemical shifts are average values, weighted according to the relative concentrations of the isomers (A), (B), and (C). Thiele and coworkers [6,7] investigated the allyl zinc compounds I—III at room temperatures and obtained ^{1}H NMR spectra typical of dynamic allyl systems. We have now studied in detail the ^{1}H NMR spectra of I—IV in the temperature range from —125 to 180°C. We find that Scheme 1 can also be used to explain the spectra of I—IV. For example, I ($R^1 = R^2 = R^3 = H$) displays an AX_4 ^{1}H NMR spectrum between —40 and 100°C, showing the four α and γ protons to be magnetically equivalent with respect to the β proton and coupled to it with ^3J 10.8 Hz. The resonances of I in an ethereal solution broaden at temperatures below —20°C: below —120°C a spectrum of an $AMNX_2$ spin system is observed, which is assigned to the static σ-allyl form of I. Coalescence is observed at $T_C \approx -75$°C (at 80 MHz). Below —110°C the ^{1}H NMR spectrum of II displays an ABM_3X_2 spectral pattern, characteristic for a static σ-bis(2-methylallyl)zinc compound, whereas above +15°C ($T_c \approx -55$°C) II rapidly rearranges and displays a spectrum of an A_4X_3 system. Evidently, the rate constants for exchange in the allylzinc compounds are lower than for the corresponding magnesium compounds, for which the slow exchange limit could not be reached even at temperatures below —120°C [12].



SCHEME 1

The ^{1}H NMR spectra of III ($R^1 = R^2 = H$, $R^3 = CH_3$) and IV ($R^1 = H$, $R^2 = R^3 = CH_3$) are just what would be expected for bis(3-methylallyl)zinc and bis-(3,3-dimethylallyl)zinc, respectively. Nevertheless III and IV must be considered to be rapidly equilibrating mixtures of the *cis*- and *trans*-isomers (A) and (C), with undetectable amounts of (B). This is indicated by the 270 MHz ^{1}H NMR spectra of III at 30°C. The analysis of these spectra confirms a vicinal olefin coupling $^3J(H,H)$ 12.4 Hz. This value may be considered as an average of that expected for a *cis*-($^3J \sim 10$ Hz) and a *trans*-($^3J \sim 16$ Hz)-olefin hydrogen coupling. There is also evidence of a fast exchange (A) $\rightleftharpoons$ (C) in the ^{1}H NMR spectra of IV. In the 60 MHz spectra of IV a temperature dependence of the methyl proton signals was observed similar to that of 3,3-dimethylallylmagnesium bromide [11b]. At temperatures below 25°C the two chemically non-equivalent methyl groups give a symmetrical doublet. On raising the temperature, the signals broaden, and above 50°C a single signal is observed. On the other hand no changes in form or position of the signals are observed in cooling from 25 to —90°C. In III the average vinyl coupling and in IV the equivalence of the methyl groups is seen to be due to very rapid incursion of (B) in which there is more or less free rotation about the central single C—C bond. Since the interconversion between the allylic isomers is rapid, the chemical shifts and coupling constants of the protons in III and IV are an average of the isomer forms (A), (B) and (C), weighted according to their relative concentrations. If there were appreciable amounts of the thermodynamically less stable isomers (B) with a bond between metal and a secondary or tertiary carbon atom existing in equilibrium with the primary isomers (A) and (C), a decrease in temperature should cause an increase in the amounts of the stable isomers, producing changes in the chemical shifts of the methylene groups. Since no measurable changes occur on reducing the temperatures to —90°C, III and IV must exist almost exclusively as the primary isomers (A) and (C).

2. *Nuclear polarisation (CIDNP)*

The bis-allyl-zinc compounds I—IV, dissolved in hydrocarbons, decompose rapidly at temperatures above 100°C with half-lives of the order of several minutes. The reaction products are unsaturated hydrocarbons. Alkyl radicals have found to be involved in the decomposition of V [4] and hence homolysis of zinc—carbon σ-bonds might be expected to be significant in the decomposition of the bis-allyl-zinc compounds. The ^{1}H NMR spectra were therefore examined for evidence of chemically induced dynamic nuclear polarisation (CIDNP), which is particularly sensitive for identifying radical pathways in chemical reactions [13]. Kaptein's rule for the multiplet effect [14] can be applied for interpretation of the polarisation of the reaction product R′—R″.

$$\Gamma(\mathrm{R'{-}R''}) = \mu \cdot \epsilon \cdot a_i \cdot a_j \cdot J_{ij} \cdot \sigma_{ij} \qquad \begin{matrix} \Gamma > 0\text{: } E/A \\ \Gamma < 0\text{: } A/E \end{matrix} \qquad (1)$$

Γ describes the phase of the polarised multiplet and is positive for E/A and negative for A/E.

μ is positive for triplet precursors IT > or pair formation by free radical encounters IF > and is negative for radical pair precursors in the singlet state IS >.

ε is positive for a recombination or disproportionation product and negative for escape or transfer reaction products.

a_i and a_j are the isotropic hyperfine coupling constants (h.f.c.) of nuclei i and j in the radicals R′ and R″, the polarisation of which is observed in the diamagnetic product R′—R″.

J_{ij} is the indirect nuclear spin coupling constant.
σ_{ij} is positive if the coupled nuclei reside in the same radical and is negative if i and j reside in different radicals.

Although CIDNP was first detected in the reaction of n-butyllithium with n-butyl bromide in hexane [15], the great majority of CIDNP effects have been reported in absence of organometallic compounds [16]. CIDNP studies involving metal—carbon bonds have been reported relatively infrequently. This may be due to inherent difficulties with the detection of CIDNP in these systems, especially for products from pairs involving metal-centred radicals with extremely short electron spin—spin relaxation times (T_2(electron) $\leqslant 10^{-9}$ s) or with large g-factor differences. More recently, however, nuclear polarisations have been detected in reactions of organometallic compounds involving not only the main group metals Li [15], Na [17], Mg [4], Sn [18] and Pb [19], but also sub-group metals such as Zn [4], Hg [4,20], and Au [21,22].

3. *Thermolysis of bis-allyl-zinc compounds*

3.1. *Diallylzinc (I) and bis(2-methylallyl)zinc (II)*

^{1}H NMR spectra of I in cyclododecane-d_{24} are shown in Fig. 1(a) before and (b) during the thermal decomposition at T 153° C. The resonances in (b) at ±5.7, 5 and 2 show a pure A/E multiplet polarisation and are assigned to the olefin and methylene protons of hexa-1,5-diene (VI). VI is the sole reaction product in the decomposition of I as confirmed by GC analysis. For allyl radicals (conjugated π-systems) we assume alternating spin densities [23]. Thus, the h.f.c. $a(\mathrm{H}_\alpha)$ (i.e., the h.f.c. constant over one bond from the formal radical center) is negative, while $a(\mathrm{H}_\beta)$ (two bonds) is assumed to be positive. In VI the indirect spin coupling constants ^3J is positive and ^4J is negative [24]. From eq. 1, the A/E polarisations indicate in each case that $\Gamma < 0$, proving a free radical reaction (IF > precursors). Further support for IF > precursors is given by the fact that the fine structure of the low field polarised multiplet of VI fits well with the corresponding multiplet in propene calculated by a CIDNP computer simula-

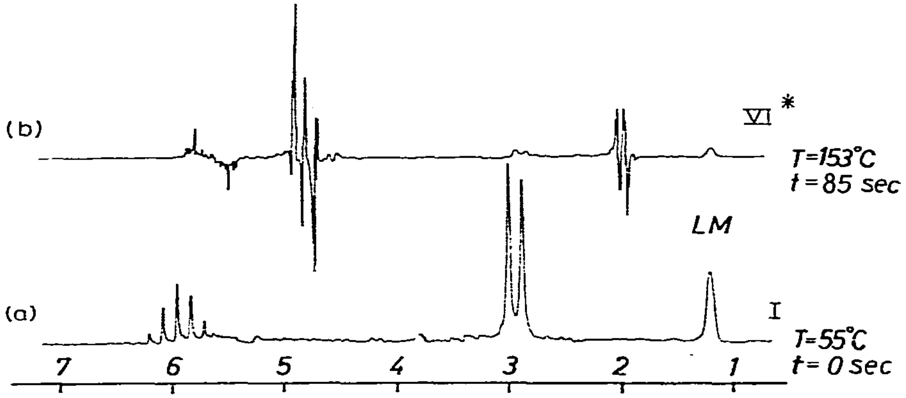


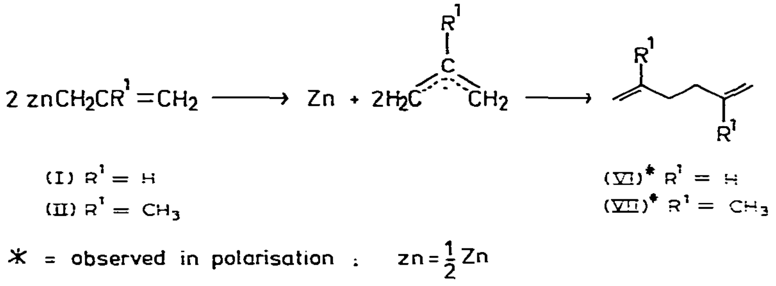
Fig. 1. 90 MHz ^{1}H NMR spectra of I: (a) at 55°C, (b) at 153°C after 85 s. The vertical display in (b) is reduced by a factor 8. The assignment is given in full in the experimental part.

tion with similar parameters [25]. The enhancement factors V of VI have been estimated from the equation:

$$V = I(t)/I_0(t) \times (t/T_1)$$

which was used by Fischer and coworkers [26]. We find V to be of the order of several hundreds. From kinetic measurements the decomposition of I was found to be first order in the temperature range from 120 to 150°C. In I the half-life time $\tau_{1/2}$ is 40, 80 and 122 s at temperatures 143, 135, and 130°C, respectively. From these data the Arrhenius activation energy for the decomposition of I was calculated to be $E_a = 29.0 \pm 3$ kcal mol^{-1}.

The decomposition of II proceeds in the same manner as that of I. 2,5-dimethylhexa-1,5-diene (VII) is the sole reaction product, and is characterised by spectra with enhanced A/E multiplet polarisations ($V \sim 200$) in the double bond region as well as in the methyl region (cf. Fig. 2). Analysis of the multiplet polarisations shows that uncorrelated 2-methylallyl radicals are precursors for the reaction product VII. Again, the decomposition of II is first order and half-life time at 130°C is $\tau_{1/2}$ 90 s, indicating I to be slightly more stable than II. Thus the main mode of decomposition of both I ($R^1 = R^2 = R^3 = H$) and II ($R^1 = CH_3$, $R^2 = R^3 = H$) in the temperature range $100 \leqslant T \leqslant 150$°C is a radical pathway as summarised in Scheme 2. At lower temperatures the rates of decomposition of



SCHEME 2

I and II are too slow to be detected by CIDNP. However, since VI and VII, resrespectively, occur as sole reaction products at temperatures between 50 and

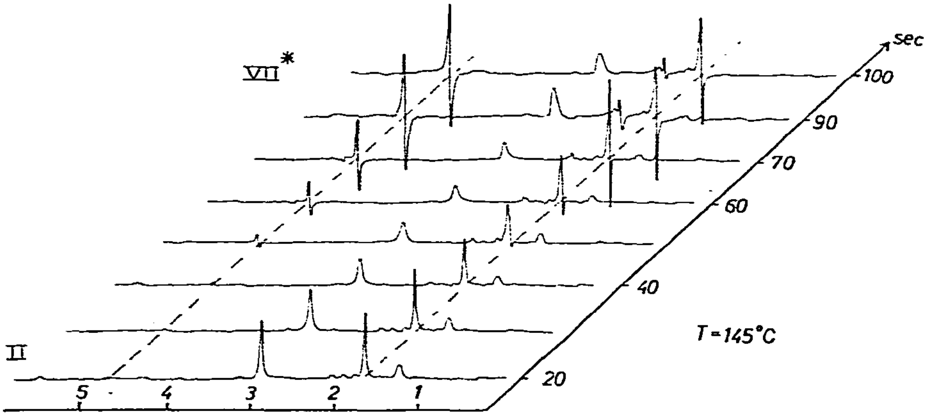
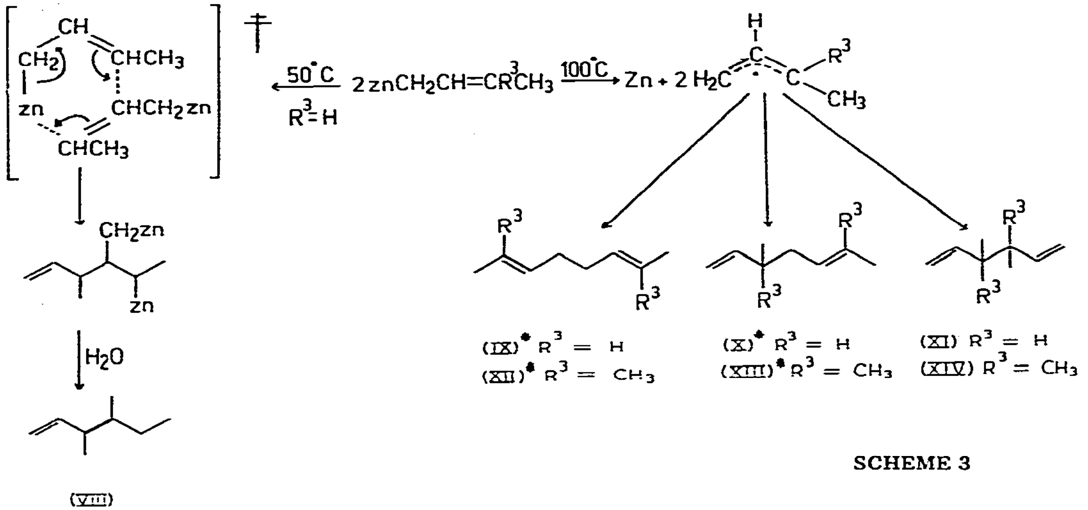


Fig. 2. 90 MHz ^{1}H NMR spectra of II at 145°C recorded at 10 s intervals.

100°C, it is likely that the same radical mechanism for the decomposition is operating in this temperature range as well.

3.2. *Bis(3-methylallyl)zinc (III) and bis(3,3-dimethylallyl)zinc (IV)*

The thermal stability of III has been investigated earlier [3,27] and from product analysis two reaction pathways for the decomposition of III have been proposed (cf. Scheme 3, R^2 = H). One involves the addition of zinc—carbon bonds to the double bonds of alkenyl rests leading (after hydrolysis) to 3,4-dimethylhexene-1 (VIII). This organometallic dimerisation is believed to occur via a six-membered cyclic transition state and seems to be the predominate pathway at temperatures around 50°C. Additional decomposition via radical formation cannot be ruled out; this is believed to become the major process at higher temperatures. At 100°C the reaction products are octa-2,6-diene (IX) (19.2% *trans,trans*, 19.5% *trans,cis*, and 11.2% *cis,cis*), 3-methylhepta-1,5-diene (X) (20.5% *trans*, 14.3% *cis*) and 3,4-dimethylhexa-1,5-diene (XI) (6.2%) as identified by GC and GC/MS analysis [27]. The formation of these products IX, X and XI can be explained by a homolytic decomposition of III. This is confirmed by the ^{1}H NMR spectra recorded at 270 MHz during the decomposition of III at 100°C. Polarised resonances of IX and X (cf. Fig. 3) were detected, giving direct proof of a decomposition pathway via 3-methylallyl radicals in the high temperature range.



SCHEME 3

Even at temperatures as low as 50°C, the decomposition of IV leads to 2,7-dimethylocta-2,6-diene (XII), 2,3,3-trimethylhepta-2,6-diene (XIII) and 3,3,4,4-tetramethyl-1,5-hexadiene (XIV). The product distribution does not change significantly on increasing the temperature, in contrast to the decomposition of III. At 100°C we obtain XII (55%), XIII (34.9%) and XIV 10.1%) as identified by GC and NMR spectroscopy. At temperatures above 85°C A/E multiplet polarisations of these products are observed in the NMR spectra recorded during the decomposition of IV. The A/E type multiplet polarisations are analysed by the Kaptein rule (eq. 1). For the parameters J and a_i in eq. 1 the following holds $^2J > 0$, $^3J > 0$, and $^4J < 0$ in IX—XIV [24] and for the differently substituted

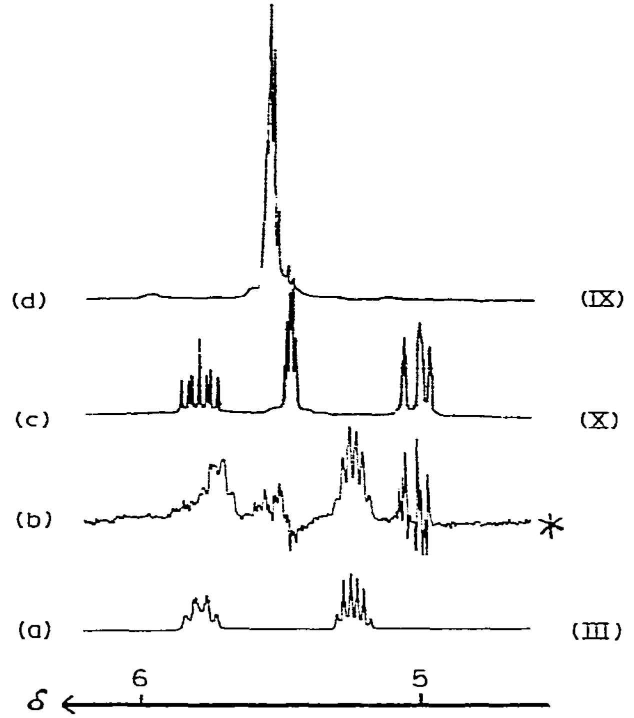


Fig. 3. Olefin part in the 270 MHz ^{1}H NMR spectra: (a) III at 25°C, (b) III at 100°C during the thermal decomposition, (c) X (*trans*) at 25°C, and (d) IX (*trans,trans*) at 25°C.

allyl radicals $\overbrace{CH_2{-}CH{-}CR^2R^3}^{\cdot}$ alternating h.f.c. constants in these conjugated π-electron systems are assumed [23] ($a(H_\alpha) < 0$, $a(H_\beta) > 0$, $a(H_\gamma) < 0$ and $a(H_\delta) > 0$). With these parameters eq. 1 uniformly predicts IF > precursors for XII, XIII, XIV and IX, X in the decomposition of IV and III, respectively. The reaction mechanism for the decomposition of III ($R^1 = R^2 = H$, $R^3 = CH_3$) and IV ($R^1 = H$, $R^2 = R^3 = CH_3$) is summarised in Scheme 3. According to Schemes 2 and 3 the decomposition of the bis-allyl-zinc compounds I—IV proceeds predominantly by a IF > pair radical process at least at sufficiently elevated temperatures. The same is true for the decomposition of tertiary alkylzinc compounds [4]. In the decomposition of the alkenylmetals I—IV the IF > type polarisation may be generated either by random encounter pairs or by geminate IF > pairs. The latter may be due to the pair substitution sequence

$$\overline{R'\cdot\cdot ZnR''}^{\,IS>} \xrightarrow{k} \overline{Zn + R'\cdot + \cdot R''}^{\,IF>}$$

[28]. This substitution process would take place if the electron spin—spin phase coherence in the pair $R'\cdot\cdot ZnR''$ is lost rapidly as consequence of short T_2(electron) (T_2(electron) $\leqslant 10^{-8}$ s) or large Δg values ($(\frac{1}{2}\Delta g\,\beta H_0)^{-1} < 10^{-8}$ s) in metal centred radicals or if the fragmentation rate constant k for the pair substitution is high ($k^{-1} < 10^{-10}$ s). In the thermal decomposition of alkylmercury compounds the IF >-type polarisation from geminate pairs plays at most only a minor part [4]. However, for alkenylzinc compounds we expect a longer phase coherence than for the corresponding mercury compounds as well as a smaller fragmenta-

tion rate constant k. The latter is due to higher dissociation energies for the fragmentation of organic zinc radicals than for organomercury radicals [4]. Therefore, we conclude that the IF $>$ polarisation in IX, X, XII, XIII and XIV is generated predominantly by random encounter pairs, but geminate IF $>$ pairs cannot be ruled out.

The decomposition of III and IV is first order, like that of I and II. The half-life times at 130°C are $\tau_{1/2}$ (I) 122 s, $\tau_{1/2}$ (II) 90 s, $\tau_{1/2}$ (III) $\approx$ 40 s (estimated value) and $\tau_{1/2}$ (IV) $\approx$ 25 s. The latter is very similar to the half life time of the tertiary alkylzinc compound V. Thus, the thermal stability decreases in the order I $>$ II $>$ III $>$ IV $\approx$ V. This stability series and the observed product distribution is best interpreted in terms of the radical decomposition of I—IV proceeding to a significant extent via the more reactive form (B), in which the metal is bound to a primary, secondary or tertiary carbon atom.

Experimental

1. Spectroscopy

The NMR spectra were recorded on Bruker WP60, WP80, WH90 and WH270 FT spectrometers, which (except for the WP60 and WP80) were equipped with a Nicolet 12K (36K) computer and a 600K Diablo Disk. Small flip angles ($\sim$20°C) were chosen in order to prevent distortion of the ^{1}H NMR CIDNP spectra by the pulse technique [29]. The procedures of recording and evaluation were similar to those described in ref. [4]. All chemical shifts were derived relative to the residual proton signals of the deuterated solvents and then converted to the TMS scale.

(a) Allylzinc compounds

NMR [*]. I in cyclododecane-d_{24} at 60°C $\delta(CH_2)$ 2.94, d, ^3J 10.8, δ(CH) 5.95, quin.; II in cyclododecane-d_{24} at 60°C $\delta(CH_2)$ 2.90 broadened s; $\delta(CH_3)$ 1.68(br). s, $^4J < 1$; III in toluene-d_8 at 30°C $\delta(CH_2)$ 1.11, d, d, quar.; ^3J 8.6, ^4J 1.2, ^5J 1; δ(CH) 5.55, d, tr, quar, ^3J 12.4, ^3J 8.6, ^4J 1.7; δ(CH) 5.01, d, quar, tr. ^3J 12.4, ^3J 6.3, ^4J 1.2; $\delta(CH_3)$ 1.51, d, d, tr, ^3J 6.3, ^4J 1.7, ^5J 1; IV in toluene-d_8 at 35°C, 60 MHz, $\delta(CH_2)$ 0.97, d, sep, ^3J 8.8, ^5J 0.75; δ(CH) 5.32, tr, sep, ^3J 8.8, ^4J 1.3; $\delta(CH_3)$ 1.48(br) s.

IR. I in THF ν(C=C) 1602 cm^{-1}, II in THF ν(C=C) 1604 cm^{-1}, III in THF ν(C=C) 1625 and 1640 cm^{-1}, IV in THF ν(C=C) 1656 cm^{-1}.

(b) Products [**]

NMR. VI in benzene-d_6 δ(C(1)H *cis*) 4.95, d, ^3J +11.6; δ(C(1) H *trans*) 4.98, d, ^3J +15.1 A/E; δ(C(2)H) 5.73, m, A/E; δ(C(3)H_2) 1.98, m, A/E. VII in benzene-d_6 δ(C(1)H_2) 4.78 (br). s, A/E; δ(C(2)CH_3) 1.61, m. A/E; δ(C(3)H_2) 2.07, (br) s., A/E. IX (*trans,trans*) in benzene-d_6 $\delta(CH_3)$ 1.54, $^3J > 0$, A/E; δ(HC=CH) 5.36, 5.32, 5.24, m, not assigned A/E; $\delta(CH_2)$ 1.98 (br) s. X (*trans*) in benzene-d_6 (C(1)H *cis*) 4.87, d, ^3J +11.4, δ(C(1)H *trans*) 4.92, d. ^3J +15.5 A/E; δ(C(2)H) 5.69, m, A/E; δ(C(3)H) 1.51, m; δ(C(3)CH_3) 0.95, d, ^3J +6.5

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[*] s = singlet, d = doublet, tr = triplet, quar = quartet, quin = quintet; δ(ppm) and J(Hz).

[**] C(i) denotes the carbon atom number (i) in the corresponding product.

A/E; $\delta(C(4)H_2)$ 1.98; $\delta(C(5)H)$ and $\delta(C(6)H)$ 5.35 and 5.44, m, not assigned A/E; $\delta(C(7)H_3)$ 1.60, d, ^3J +5.5 A/E. XII in toluene-d_8 $\delta(CH_3)$ 1.63, A/E; $\delta(CH_3)$ 1.76, A/E. $\delta(C(3)H)$ 5.25, m, A/E; $\delta(C(4)H_2)$ 2.18, m, A/E. XIII in toluene-d_8 $\delta(CH_3)$ 1.63, A/E; $\delta(CH_3)$ 1.76, A/E; $\delta(C(3)H)$ 5.25, m, A/E; $\delta(C(4)H_2)$ 2.08, d, ^3J +8.4, A/E; $\delta(C(5)CH_3)$ 1.03, A/E; $\delta(C(6)H)$ 5.88, m, A/E; $\delta(C(7)H\ \textit{cis})$ 5.00, d, ^3J +11, A/E; $\delta(C(7)H\ \textit{trans})$ 4.97, d, ^3J +16, A/E. 14 in toluene-d_8 $\delta(C(1)H\ \textit{cis})$ 4.95, d, ^3J +11, $\delta(C(1)H\ \textit{trans})$ 4.95, d, ^3J +16.5, A/E; $\delta(C(2)H)$ 5.83, m, A/E; $\delta(CH_3)$ 1.08.

(c) Isotropic hyperfine coupling constants h.f.c., in allyl radicals

Allyl radicals $CH_2{=}CH\dot{C}H_2$: $a(CH_2)$ —13.93, $a(CH_2)$ —14.93 (two CH_2 protons, one of each CH_2 groups, signs determined by CIDNP, amounts of the splitting parameters in Gauss from ref. 30); $a(CH)$ +4.06 G.

2-Methylallyl radical $CH_2{=}C(CH_3)\dot{C}H_2$; $a(CH_2) < 0$; $a(CH_3) < 0$. Crotyl radical $CH_2{=}CH\dot{C}HCH_3 \rightleftharpoons CH(CH_3){=}CH\dot{C}H_2$; $a(CH_2) < 0$; $a(CH)$, $a(C(CH_3)) > 0$. 3,3-Dimethylallyl radical $CH_2{=}CH\dot{C}(CH_3)_2 \rightleftharpoons C(CH_3)_2{=}CH\dot{C}H_2$; $a(CH_2) < 0$, $a(CH)$, $a(C(CH_3)_2 > 0$.

2. *Preparative thermolysis*

The preparative thermolysis of III at 50 and 100° C is described in ref. 3, 27. The preparative thermolysis of IV at 50°C yielded: XII 58.5% (GC), XII 30.9% (GC), XIV 10.6% (GC); at 100°C the product distribution was: XII 54.7%, XIII 35.0%, XIV 10.3% evaluated from GC and ^1H NMR experiments. GC data: column 53 m Squalan (glass); 0.25 temperature 200 -80 -200°C; gas 0.5 atm N_2; detector FID; probe volume 0.2 μl; recorder 1 cm min^{-1} ABIMED; retention index I(XII) 970.31, I(XIII) 883.45, I(XIV) 894.90

3. *Organozinc compounds*

The compounds I, II, III, and IV were prepared according to references 2, 6, 7 and 27. The samples I—IV were dissolved in the commercial perdeuterated solvents benzene-d_6, toluene-d_8 and cyclododecane-d_{24} and mixtures (4/1) of diethyl ether-d_{10} and THF-d_8, which had been dried and purified. All NMR tubes were sealed under purified argon. The IR experiments of I—IV were performed by Dr. K. Seevogel and will be published elsewhere.

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