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NEOPENTYLALLYLLITHIUM

IV. REACTIONS IN ETHER SOLVENTS

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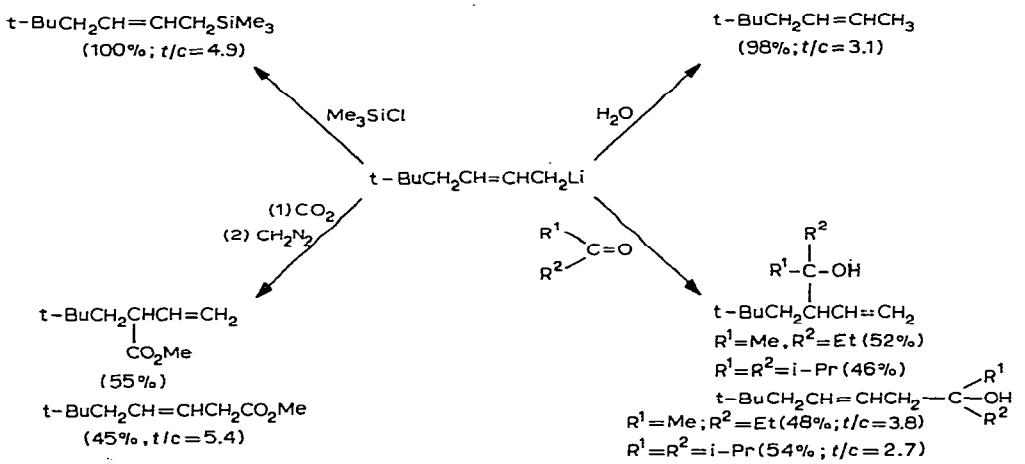
SUMMARY

Protolysis and ketone addition reactions are reported for neopentylallyllithium in THF solvent. The yield of the *trans*-C_8H_{16} olefin is essentially constant for protolysis with the following active hydrogen compounds: water, tert-butanol, 1-hexyne, cyclopentadiene, fluorene, and triphenylmethane. The relative yields of the *cis*- and α-neopentallyl isomers apparently depend on the steric bulk as well as the strength of the acid. The degree of allylic rearrangement observed from a series of ketones also is a function of the size of the ketone.

In this paper we present the results of several reactions involving neopentylallyllithium (NpALi), the 1,4-addition product of tert-butyllithium and 1,3-butadiene. We have previously shown that NpALi exists as aggregated, covalent forms in hydrocarbon solvents[1], and as largely delocalized ion pairs in THF[2]. In another paper, we

SCHEME 1. REACTIONS OF NpALi IN HYDROCARBON SOLVENT (n-PENTANE)



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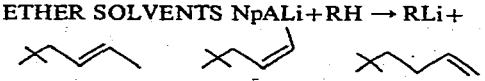
examined some typical reactions of NpALi in hydrocarbon media[3]. It was shown that protolysis and silylation (coupling with $ClSiMe_3$) proceed with little or no allylic rearrangement, while substantial amounts of rearranged products are obtained from reactions with carbon dioxide, ketones and butadiene (Scheme 1).

There is a considerable literature on reactions of this type[4], but the data reported in Part II of the Series[3] represent the first systematic study in hydrocarbon media. Since NpALi is a new compound, we thought that a parallel study of its chemistry in ether solvents would be necessary in order to appreciate the previous results.

TABLE 1

PROTOLYSIS OF NpALi IN ETHER SOLVENTS NpALi+RH → RLi+



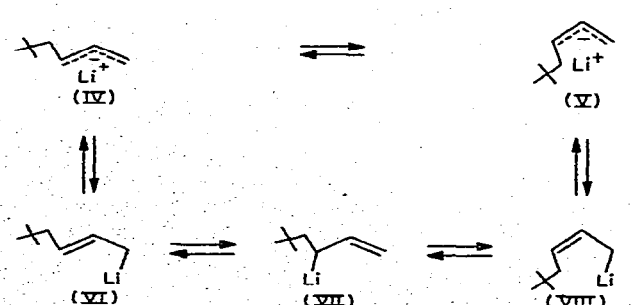
(I) (II) (III)

RH	*Solvent*	*I* (%)	*II* (%)	*III* (%)
H_2O	THF	49.4	36.9	13.7
t-BuOH	THF	48.4	20.8	30.8
n-$C_4H_9C{\equiv}C{-}H$	THF	43.4	21.1	35.4
Cyclopentadiene	THF	44.9	35.5	19.6
Fluorene	THF	43.1	49.7	7.2
$(C_6H_5)_3CH$	THF	43.8	55.3	0.9
H_2O	Et_2O	68.0	21.0	11.0
EtOH	THF/DME[a]	40	30	30
EtOH	DME[b]	43	37	20
EtOH	Diglyme[b]	43	32	25

[a] Solvent ratio 2.5/1. [b] 11 ml added to 50 ml pentane.

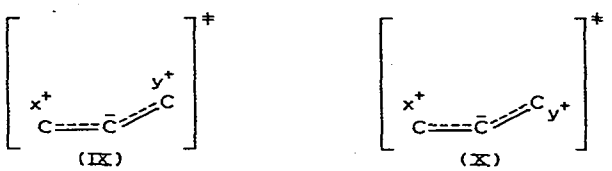
Protolysis of NpALi in donor solvents

Table 1 shows the results of several reactions of NpALi in donor solvents with active hydrogen compounds. In each case, NpALi was prepared in n-pentane[3] and a number of moles of ether added which was at least ten times the number of moles of NpALi. The solution was allowed to stand for 30 min at 0°C and the active hydrogen compound added through a syringe cap. On the basis of our PMR data[2], extensive *cis/trans* isomerization of NpALi would have occurred at 0°C. In THF, a ratio of



isomers of approximately 1.3 *cis*/1.0 *trans* would result. At this temperature, we postulate that the principle species are ion pairs (IV) and (V), but that covalent forms (VI)–(VIII) may provide the mechanism for *cis*/*trans* isomerization.

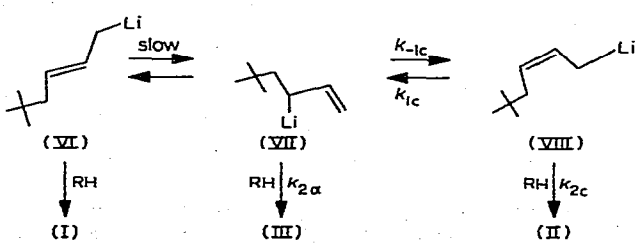
The data in THF, DME, and diglyme shown in Table 1 show two features when contrasted to the results in pentane solvent[3]. First, we note that much larger quantities of the 1-alkene (III) are usually produced, and second, we note that in THF the yield of (III) decreases in the series 1-hexyne > t-butanol > cyclopentadiene > water > fluorene > triphenylmethane. More striking is the constancy of the yield of the *trans* product and of the ratio (I)/(II)+(III). We recall that the ratio of *trans*/*cis* isomers of NpALi in THF at 0°C is approximately 0.77[2]. One is tempted to conclude that protolysis of the *trans* form of NpALi occurs with retention of geometrical configuration, but that the *cis* form may yield either (II) or rearranged (III), depending on the nature of the active hydrogen compound. Two rationalizations of such a position are possible. In one, we may assume that the transition state involves an incipient allyl carbanion of the type proposed by Anh[5], where x^+ and y^+ are the



(IX) (X)

leaving and entering groups (Li^+ and H^+ respectively)*. Anh's arguments show that *anti* transition states such as (X) must involve synchronous leaving and entering of x and y respectively, while *syn* transition states (IX) are allowed only for non-synchronous processes. Thus, the data in Table 1 suggest that the *trans* isomer of NpALi is prevented for some reason from participating in either (IX) or (X) and therefore that *rearrangement* involving this isomer is not possible.

The second rationalization of the data in Table 1 is a kinetic one. We recall that *cis*/*trans* isomerization in THF is slow on the NMR time scale[2]. If we furthermore assume that formation of the α-neopentylallyl isomer (VII) is possible (for some unknown reason) only from the *cis* isomer (VIII), then the relative amounts of products



* The stereochemistry of allylic rearrangements has been investigated in some detail for reactions of Grignard reagents with ketones, aldehydes, epoxides, etc.[4]. The conclusion of Felkin is that these are S_E2, rather than S_Ei, processes[4c]. However, no corresponding information is available for protolysis reactions[4d].

(II) and (III) will depend on the rate constants k_{1c}, k_{-1c}, k_{2c}, and $k_{2\alpha}$*, whereas the yield of (I) would be determined only by the equilibrium concentration of (VI).

The change in the (II)/(IV) ratio as the active hydrogen compound is changed may be interpreted in terms of a change in $k_{2\alpha}$ *vs.* k_{2c} due to steric effects or to a change in the "acidity" of the proton donor.

Obviously, these rationalizations are speculative and further information on this matter is required**.

TABLE 2

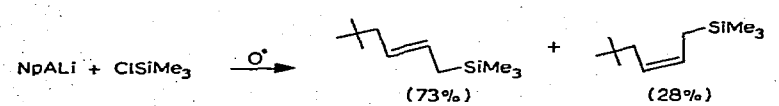
CARBONYL ADDITION REACTIONS OF NpALi IN THF

Substrate	*R*	*Products (relative %)*		
		t-BuCH$_2$(H)C=C(H)CH$_2$R	t-BuCH$_2$(H)C=C(CH$_2$R)H	t-BuCH$_2$CH(R)CH=CH$_2$
$C_2H_5CCH_3$ (O)	$C_2H_5C(OH)CH_3$	12.8 (IXa)	8.9 (Xa)	78.3[a] (XIa)
CH_3C-i-C_3H_7 (O)	$CH_3C(OH)$-i-C_3H_7	11.6 (IXb)	11.2 (Xb)	77.2[a] (XIb)
$(i\text{-}C_4H_9)_2C{=}O$	$(i\text{-}C_4H_9)_2COH$	4.3 (IXc)	11.7 (Xc)	84.0 (XIc)
$(i\text{-}C_3H_7)_2C{=}O$	$(i\text{-}C_3H_7)_2COH$	11.7 (IXd)	22.6 (Xd)	65.7 (XId)
$(t\text{-}C_4H_9)_2C{=}O$	$(t\text{-}C_4H_9)_2COH$	56.9 (IXe)	43.1 (Xe)	

[a] Two diastereomers found in approximately equal quantities.

Reactions with other substrates

Two types of reactions will be reported in this paper, *viz.*, reaction with chlorotrimethylsilane and addition to carbonyl compounds. As we have seen previously[3], coupling of NpALi with Me_3SiCl involves no allylic rearrangement. The



* We may extend the arguments used in refs. 2 and 6 as follows. Assume that of the two instantaneous conformations of (VII), one having a *cis* and one a *trans* precursor, only the former may react at an appreciable rate with proton donors. Thus, the system appears to be "semi-dynamic" in its protolysis reactions.

** Some comment may be in order concerning the data in Table 1 in diethyl ether. We note that the products obtained from hydrolysis are more similar to those obtained in n-pentane than in the other ether solvents. This is consistent with the PMR data[2] which indicate that the *cis/trans* ratio is approximately 0.3 and that *cis/trans* isomerization does not occur at 0°C. It is interesting that the sum of the yields of (II) and (III) represent approximately 0.3 of the yield of the *trans* compound.

same result is obtained in THF, only *cis* and *trans* primary isomers are produced. The absence of any rearranged product may be ascribed to a steric effect in the concerted transition state[7,8].

Table 2 shows the results of several carbonyl addition reactions of NpALi in THF. As in the case of protolysis reactions, the allyllithium reagent was allowed to equilibrate for 30 min at 0°C before the addition of the ketone. In accordance with other work[4] we find that the yield of α-neopentylallyl isomer decreases when a very bulky ketone (di-tert-butyl) is used. Also we note that there is no obvious preference for either the *cis* or *trans* primary isomer in the reaction products. As we have expressed in an earlier paper, the *cis* preference observed for crotyllithium and crotyl Grignard reactions does not apply to allyl metals which have bulky γ-substituents. In fact, the use of reaction product distributions to ascertain the relative stability of allylic carbanion conformations is not a reliable method. Further work on the structure and reaction mechanisms of allyl metal compounds is in progress.

EXPERIMENTAL

All reactions involving organometallic compounds were carried out in rigorously dried apparatus under an atmosphere of dry, oxygen free nitrogen. Identification of compounds was verified by collecting samples by preparative GLC followed by spectrometric verification of structure (PMR, mass and IR spectroscopy) (see Table 3).

Protonation

NpALi (46 mmol) was prepared as described previously[3], then cooled to −70°C and dry THF (50 ml) was added. The ether solution was allowed to warm to 0°C and held at this temperature for 0.5 h. To this solution was added a slight excess of the proton donor (50 mmol). The reaction mixture was stirred for a further 0.5 h, during which time it attained room temperature. Water (50 ml) was added and the ether layer was separated and dried. Most of the THF was removed on a spinning band column and the pot residue, containing the mixture of hydrocarbons, was subjected to GLC analysis on an EDO-1 column at 25°C[6]. Spectral parameters of the C_8H_{16} olefin isomers are shown in Table 3 (b.p. 99–102°).

Control experiments

The results of two control experiments have shown that NpALi does not metalate THF solvent at an appreciable rate at 0°C. NpALi in THF-d_8 held at this temperature in the PMR probe showed no increase in free olefin resonances at τ 4.2–4.5 for periods of 1 to 2 h. In another type of experiment, a solution containing 0.10 mol of NpALi was held below −70°C during the addition of 125 ml of dry THF. After approximately 5 min an excess of deuterium oxide was added. A second solution containing NpALi/THF in the same ratio as the first solution was allowed to warm to 0°C for a period of 1 h, following which it also was quenched with D_2O. The C_8-olefin fractions from the two batches were collected by spinning band distillation and a mass spectrum obtained for each fraction. The ratios of the mass 112/113 peaks (parent ions) of the two fractions were found to be equal within experimental error. Substantial THF cleavage at 0°C would have resulted in an increase in the mass 112 peak at the expense of the 113 peak.

TABLE 3

DERIVATIVES OF NEOPENTYLALLYLLITHIUM[a]

Formula of derivative	*Elemental analysis found (calcd.) (%)*		*Spectral data*[b]
	C	*H*	
$t\text{-}Bu\overset{1}{C}H_2\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}H_2\overset{5}{S}i(\overset{6}{C}H_3)_3$	71.68 (71.74)	13.18 (13.04)	IR: 1658 (w, C=C); 1250 (s, $SiMe_3$); 967 (m, *trans*-CH=CH); 855 (s, br, Si–C); 690 (w, *cis*-CH=CH). PMR: 5.25 (m, H-3, H-4); 8.08 (d, H-2); 8.62 (d, H-5); 9.12 (s, H-1); 10.00 (s, H-6). MS: parent ion *m/e* 184; $M-CH_3$, 169; $M-C_4H_9$, 127.
$t\text{-}Bu\overset{1}{C}H_2\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}H_2\overset{5}{C}O_2\overset{6}{C}H_3$[c]	70.19 (70.59)	10.72 (10.59)	IR: 1745 (s, C=O); 1655 (w, C=C); 970 (m, *trans*-CH=CH); 787 (m, *cis*-CH=CH). PMR: 4.54 (m, H-3, H-4); 6.38 (s, H-6); 7.00 (d, H-5); 8.12 (d, H-2); 9.12 (s, H-1). MS: parent ion *m/e* 170; $M-CH_3$, 155; $M-O-CH_3$, 139; $M-C_4H_8$, 114.
$t\text{-}Bu\overset{1}{C}H_2\overset{2}{C}H(\overset{3}{C}O_2\overset{6}{C}H_3)(\overset{4}{C}H{=}\overset{5}{C}H_2)$[c]	70.72 (70.59)	11.11 (10.59)	IR: 1742 (s, C=O); 1637 (m, C=C); 1154 (s, C–O–C); 990, 917 (m, $CH{=}CH_2$). PMR: 4.38 (m, H-4); 5.05 (m, H-5); 6.40 (s, H-6); 6.9 (m, H-3); 8.16 and 8.68 (non-equivalent H-2); $J_{22}=14$; $J_{23}=8$; $J_{23}=4$; 9.10 (s, H-1). MS: weak parent ion; $M-CH_3$, 155; $M-OCH_3$, 139; $M-C_4H_8$, 114; $M-C_4H_9$; 113.
$t\text{-}Bu\overset{1}{C}H_2\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}H_2\overset{5}{C}(OH)(\overset{6}{C}H_3)(\overset{7}{C}H_2\overset{8}{C}H_3)$ (IXa, Xa)	78.10 (78.26)	12.92 (13.04)	IR: 3378 (s, br, OH); 1639 (w, C=C); 975 (m, *trans*-CH=CH); 750 (w, *cis*-CH=CH). PMR: 4.45 (m, H-3, H-4); 7.81 (m, H-5); 8.0 (OH); 8.10 (d, H-2); 8.52 (m, H-7); 8.85 (s, H-6); 9.0–9.1 (s, H-1; t, H-8). MS: weak parent ion $M-CH_3$, 169; $M-H_2O$, 166; $M-CH_3$, H_2O, 151; $M-C_2H_5$, 155; $M-C_2H_5$, H_2O, 137.
$t\text{-}Bu\overset{1}{C}H_2\overset{2}{C}H(\overset{3}{C}H{=}\overset{4}{C}H_2)(\overset{6}{C}H_3)(\overset{7}{C}H_2\overset{8}{C}H_3)$ (XIa)	78.47 (78.26)	13.28 (13.04)	IR: 3470 (s, br, OH); 1635 (m, C=C); 1006 (s), 914 (s), $CH{=}CH_2$. PMR: 4.35 (m, H-4); 4.83 (m, H-5); 7.80 (t, H-3); 8.13 (s, OH); 8.4–8.8 (m, H-2, H-7); 8.89, 8.94 (s, H-6 on two diastereomers); 9.1 (s, H-1; t, H-8). MS: weak parent ion, 184; $M-CH_3$, 169; $M-H_2O$, 166; $M-C_2H_5$, 155; $M-CH_3$, H_2O, 151; $M-C_2H_5$, H_2O, 137; other peaks at 112, 110, 109.
$t\text{-}Bu\overset{1}{C}H_2\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}H_2\overset{5}{C}(OH)(\overset{6}{C}H_3)(\overset{7}{C}H\overset{8}{C}H_3)(CH_3)$ (IXb, Xb)	78.18[d] (78.79)	12.50[d] (13.13)	IR: 3436 (s, br, OH); 1626 (w, C=C); 973 (s, *trans*-CH=CH); 743 (w, *cis*-CH=CH). PMR: 4.50 (m, H-3, H-4); 7.85 (m, H-5); 8.17 (m, H-2); 8.3–8.7 (m, H-7, OH); 8.7–9.3 (m, H-1, H-6, H-8).
$t\text{-}Bu\overset{1}{C}H_2\overset{2}{C}H(\overset{3}{C}H{=}\overset{4}{C}H_2)(\overset{6}{C}H_3)(\overset{7}{C}H\overset{8}{C}H_3)(CH_3)$	78.20[d] (78.79)	12.98[d] (13.13)	IR: 3484 (s, br, OH); 1637 (m, C=C); 910, 1000 (s, $CH{=}CH_2$). PMR: 4.39 (m, H-4); 4.97 (m, H-5); 7.90 (t, H-3); 8.1–8.8 (m, H-2, H-7); 8.8 (OH); 9.0–9.2 (m, H-1, H-6, H-8).

(IXc, Xc)			
t-Bu^{1}CH$_2^{2}$CHC(OH)(CH$_2^{6}$CHCH$_3^{8}$)$_2$ $\vert_{4}$ $\vert_{7}$ CH=CH$_2^{5}$ CH$_3$	80.20 (80.31)	13.37 (13.39)	IR: 3690 (s, sp, OH); 1634 (m, C=C); 919, 1005 (m, CH=CH$_2$). PMR: 4.60 (m, H-4); 4.80 (m, H-5); 7.80 (t, H-3); 8.25 (m, H-7); 8.5–9.0 (m, H-2, H-6), 9.06 (s, OH); 9.14 (d, H-8); 9.16 (s, H-1).
(XIc)			
t-Bu^{1}CH$_2^{2}$CH=^{3}CH^{4}CH$_2^{5}$C(OH)(C$_6$H$_5$)$_2$[c]	85.93 (85.71)	8.72 (8.84)	IR: 3508 (m), 3425 (sh), OH; 1644 (w, C=C); 1592 (m, aromatic C=C); 970 (m, *trans*-CH=CH). PMR: 2.2–2.8 (m, aromatic protons); 5.50 (m, H-3, H-4); 7.14 (d, H-5); 8.03 (s, OH); 8.30 (d, H-2); 9.17 (s, *cis*-H-1); 9.23 (s, *trans*-H-1).
t-Bu^{1}CH$_2^{2}$CH=^{3}CH^{4}CH$_2^{5}$C(OH)(CH^{6}CH$_3^{7}$)$_2$ $\vert_{7}$ CH$_3$	79.85 (79.65)	13.02 (13.27)	IR: 3510 (m, OH); 1630 (w, C=C); 970 (m, *trans*-CH=CH); 727 (w, *cis*-CH=CH). PMR: 4.44 (m, H-3, H-4); 7.65 (d, H-5); 7.84–8.20 (m, H-2, H-6); 8.67 (s, OH); 8.90–9.16 (m, H-1, H-7).
(IXd, Xd)			
t-Bu^{1}CH$_2^{2}$CHC(OH)(CH^{6}CH$_3^{7}$)$_2$ $\vert_{4}$ $\vert_{7}$ CH=CH$_2^{5}$ CH$_3$	79.49 (79.65)	13.11 (13.27)	IR: 3508 (m, OH); 1620 (m, C=C); 1005, 917 (m, CH=CH$_2$). PMR: 4.12 (m, H-4); 4.77 (m, H-5); 7.26 (t, H-3); 7.88 (septet, H-6); 8.18 (s, OH); 9.0 (m, nonequivalent H-2); 8.88–9.08 (m, H-1, H-7).
(XId)			
t-Bu^{1}CH$_2^{2}$CH=^{3}CH^{4}CH$_2^{5}$C(OH)(t-Bu^{6})$_2$	80.54 (80.31)	13.44 (13.39)	IR: 3521 (m, sp, OH); 1634 (w, C=C); 1389, 1366 (s, t-Bu); 975 (m, *trans*-CH=CH); 719 (w, *cis*-CH=CH). PMR: 4.46 (m, H-3, H-4); 7.49 (d, H-5); 7.97 (overlapping d, *cis* and *trans* H-2); 8.32 (s, OH); 8.88 (s, H-6); 9.09 (s, H-1).
(IXe, Xe)			
t-Bu^{1}CH$_2^{2}$CH=^{3}CH^{4}CH$_3^{5}$	—	—	IR: 1636 (w, C=C); 1393, 1364 (m, t-Bu); 972 (s, *trans*-CH=CH); 681 (w, *cis*-CH=CH). PMR: 5.45 (m, H-3, H-4); 8.16 (t, H-2); 8.37 (t, H-5); 9.10 (s, *cis*-H-1); 9.12 (s, *trans*-H-1). MS: parent ion: 112; from hydrolysis with D_2O 113.
t-Bu^{1}CH$_2^{2}$CH$_2^{3}$CH=^{4}CH$_2^{5}$	—	—	IR: 1641 (m, C=C); 1393, 1364 (m, t-Bu); 991 (m), 910 (s), CH=CH$_2$. PMR: 5.33 (m, H-4); 4.83 (H-5); 7.96 (m, H-3); 8.72 (m, H-2); 9.10 (s, H-1).

[a] Analytical data for *cis* and *trans* isomers of primary derivatives obtained from mixtures collected by preparative GLC. Identification of *cis* isomer confirmed by PMR integration, carbon–hydrogen data, and relative GLC retention times (ref. 4b). The weak absorption of the *cis*-CH=CH group is not a reliable diagnostic tool. [b] IR (liquid film, cm^{-1}): w, weak; m, medium; s, strong; br, broad; sp, sharp; (sh), shoulder. PMR ($CDCl_3$) τ (ppm): s, singlet; d, doublet; t, triplet; m, multiplet. MS: 70 eV spectra, heated liquid inlet. [c] Ref. 3. [d] Reinjection on GLC of 3-methyl-2-butanone adduct showed the presence of decomposition products apparently due to high temperatures which were required in the collection process.

Reaction with chlorotrimethylsilane

Reaction with chlorotrimethylsilane was carried out as described before[2,6]. Only a trace amount of a silane tentatively identified as the α-neopentylallyl isomer was found. Silane isomers were separated with a SE-30 GLC column at 150°C. Yield: 80% (Table 3).

Addition to ketones

The THF solution of the adduct was prepared as described above and the ketone (50 mmol) added after the solution had stirred at 0°C for 0.6 h. The reaction mixture was allowed to warm to room temperature and stirred for another 0.5 h. Water (50 ml) was added, the ether layer separated and dried, and the solution concentrated by evaporation. Yields were 60–75% in each case studied. Distillation of the tertiary carbinols at 18 mmHg resulted in some thermal decomposition of the derivatives labeled (X) and (IX) in Table 2. Preparative GLC was successfully accomplished using either a $10' \times \frac{1}{4}''$ SE-30 column or, preferably, a $10' \times \frac{1}{4}''$ Carbowax 20 M column. In each case, examination of the crude reaction mixture after evaporation of most of the solvent showed significant amounts of only the compounds listed in Table 2 with retention times always in the order: (XI)<(IX)<(X). Also usually present was a small quantity of the tertiary alcohol formed by reaction of excess tert-butyllithium with the appropriate ketone (approximately 10% of total GLC area). Table 3 is a compilation of spectral data for the various derivatives prepared in this and in previous work[3].

Boiling points of some isomers listed in Tables 2 and 3 are as follows: (XIb) 115°/18 mmHg; (XIc) 147–150°/18 mmHg; (XId) 135–138°/18 mmHg; (XIe) 161–163°/18 mmHg. The methyl esters of the carboxylic acids shown in Table 3 boiled at 150°/34 mmHg.

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