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3-NEOPENTYLALLYLLITHIUM

II. REACTIONS IN HYDROCARBON MEDIA

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SUMMARY

Product distributions are reported for several reactions in hydrocarbon solvent of 3-neopentylallyllithium, the 1,4-addition product of tert-butyllithium and 1,3-butadiene. Protolysis with several agents yields predominately the "normal" products [(Ia) and (Ib)] with less than 6% of the terminal olefin observed. The ratio of the *cis/trans* isomers [(Ia) and (Ib)] parallels the ratio of the lithiated forms before protolysis. Reaction with chlorotrimethylsilane also shows no "rearranged" product. Carboxylation and ketone addition reactions, however, proceed with marked rearrangement unless the ketone is very hindered. Di-tert-butyl ketone and benzophenone give no rearranged product. Addition of a second mole of butadiene also results in predominant (60%) rearrangement of the neopentylallyl group. Bromination with molecular bromine and 1,2-dibromoethane yields a mixture of dibromo-derivatives in the former case and C_{16}-diolefin coupling products in the later case. Tentative mechanisms for protolysis and addition reactions are discussed.

INTRODUCTION

The mechanisms of electrophilic substitution reactions, particularly those which involve organometallic substrates, continue to receive much attention[1]. When the reacting organometal is of the allylic type, the number of mechanistic possibilities expands considerably, depending on the nature of the metal atom, the type of substituents on the allylic moiety, the solvents, etc.

If the metal allyl is σ-bonded and not "dynamic"[2], three transition state geometries have been proposed in which the carbon–metal bond retains some degree of covalency. Scheme 1 illustrates these three mechanisms, S_E2, S_Ei, and S_Ec**. Each may be modified to account for allylic rearrangement (S_E2', S_Ei', and S_Ec'). Abraham and Hill have discussed several cases which illustrate the transition from S_E2 to S_Ec[1a].

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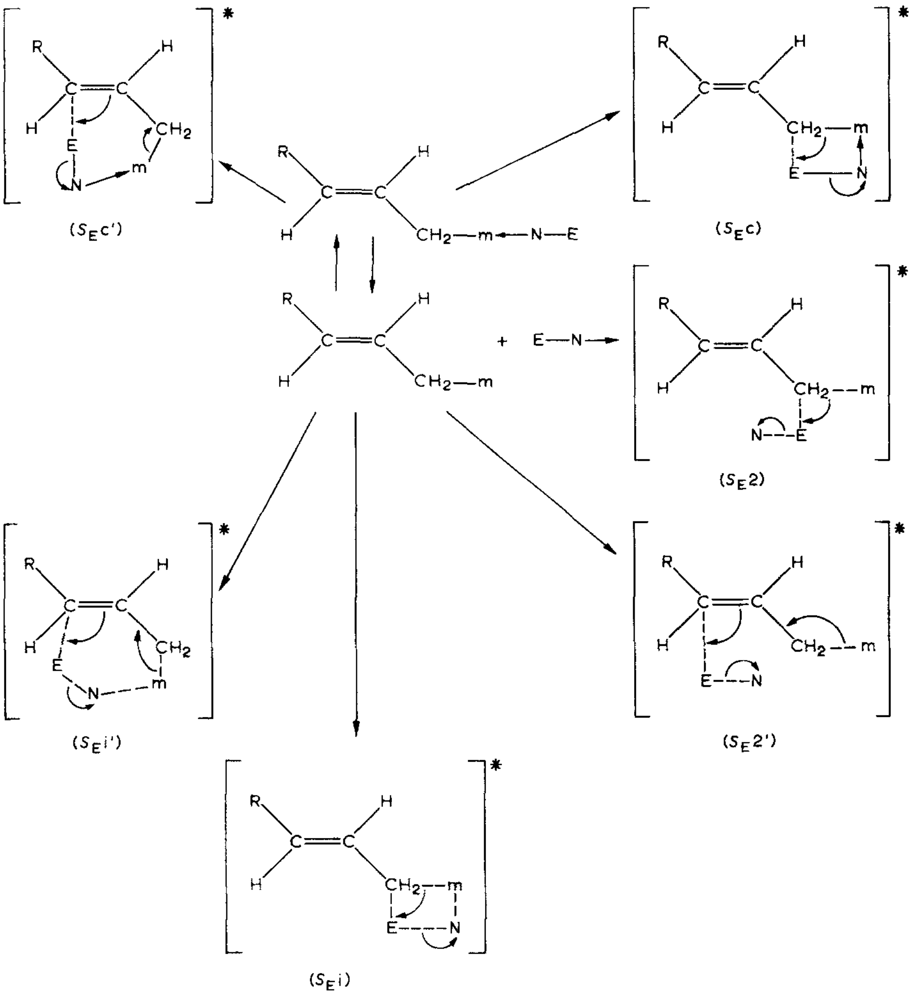
[**] Other workers have referred to the S_F2 process which is essentially identical to the S_Ei mechanism shown in Scheme 1, the name serving mainly to emphasize the four-center nature of the complex[1a].

SCHEME 1



When the metal allyl is "dynamic", as in the case of Grignard reagents in ether solvents[3], the situation is even more complex. Felkin and Frajerman have concluded that substituted allyl Grignard reagents add to carbonyl compounds and to epoxides by a non-cyclic S_E2' rearrangement process[4]. Most significant was their assertion that the primary products, which are formed when steric crowding occurs[5,6], are not due to a direct S_E2 process involving the primary isomer, but arise from the secondary isomer, also via S_E2' rearrangement*. It is important to note, however, that this proposal can apply only if a facile equilibrium exists between the primary and secondary allyl metal forms; that is, the organometallic must be of the "dynamic" allyl type. Since dynamic allyl systems seem to occur most often with electropositive

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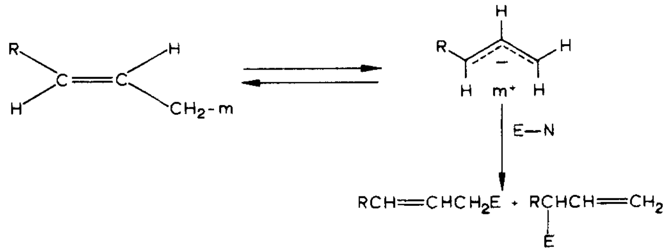
* It has been suggested that the S_E2' transition state is preferred over the "aesthetically more satisfying cyclic S_Ei' transition state"[4] because of orbital symmetry requirements in allylic transition states[1f].

metals in donating solvents or at higher temperatures, it would appear that Felkin's conclusions may not apply to the allyl derivatives of Group IVA and IIB metals, and to those of Group I–IIIA metals under "mild" conditions.

The S_E1 mechanism[1d] has mostly been overlooked in the afore-mentioned papers, although it is clear that an allylic carbanion intermediate would be much more stable than its non-conjugated counterparts. We would expect such a mechanism to be favored especially in very polar solvents and where the ionization step is aided by electropositive metals and electron withdrawing R substituents.



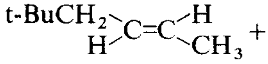
Our interest in this area has rested mainly in the chemistry of allyllithiums. This report summarizes the results of several chemical derivatizations of 3-neopentylallyllithium (NpALi), the 1/1 adduct of tert-butyllithium and 1,3-butadiene, in hydrocarbon media. Proton NMR data on NpALi appear in preceding papers[7].

RESULTS AND DISCUSSION

Protolysis of NpALi in pentane solvent yields three C_8H_{16} olefins [(Ia), (Ib) and (II)] in quantities which are seemingly independent of the nature of the proton donor or the temperature. Most significant is the very low yield of the terminal

$$t\text{-BuCH}_2\text{CH=CHCH}_2\text{Li} + \text{RH} \rightarrow$$

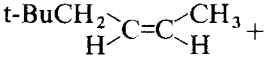
cis/trans ~ 1/3



$$\overset{t\text{-BuCH}_2}{\underset{H}{}}\!\!>\!C\!=\!C\!<\!\overset{H}{\underset{CH_3}{}}$$

(Ia)

+



$$\overset{t\text{-BuCH}_2}{\underset{H}{}}\!\!>\!C\!=\!C\!<\!\overset{CH_3}{\underset{H}{}}$$

(Ib)

$+ t\text{-Bu(CH}_2)_2\text{CH=CH}_2$

(II)

TABLE 1

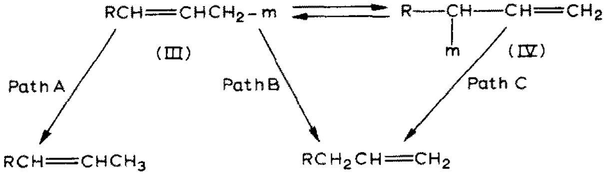
PROTOLYSIS OF NpALi IN n-PENTANE[a]

RH	*Temp. (°C)*	*% (Ia)*	*% (Ib)*	*% (II)*
H_2O	−70; 0	75	23	2
EtOH	−70; 0	74	23	3
t-BuOH	0	79	16	5
$C_3H_7C{\equiv}CH$	−70; 0	78	16	6

[a] Estimated precision of isomer percentages: ±2%. The 11% yield of (II) reported earlier[7b] was found to be in error, primarily as the result of improved GLC analytical methods used here (see Experimental).

olefin (II). These results are in sharp contrast to the results of similar work with alkyl-substituted allylic Grignard reagents[8,9], and with allyl derivatives of mercury[10] and tin[11]. In those cases, the vinyl product [such as (II)] is the major product in an overwhelming number of cases*. For example, 2-butenyltrimethyltin with methanolic HCl gives 98% 1-butene regardless of the *cis/trans* ratio of the starting material[11]. 2-Butenylmercuric derivatives give essentially pure 1-butene when protolyzed with HCl or $HClO_4$ in ethyl acetate and acetic acid solvents respectively[10]. 2-Butenylmagnesium reagents give 70–77% 1-butene in various solvents when reacted with 2*N* H_2SO_4[8], 68% with (sec-butyl)diisopropyl carbinol[9], and 93% with phenylacetylene[9].

Since allyl Grignard reagents are known to be "dynamic" in ether solvents, it is possible that the terminal olefin product may arise from a direct substitution process



at the α-carbon atom of the secondary isomer (path C), or by rearrangement involving the predominant primary isomer (path B)**. Although path B is apparently the route taken by allylmagnesium compounds in their reactions with ketones and epoxides[4], such has not been demonstrated for protolysis reactions. The dependence of olefin distribution on the nature of the proton donor suggests that paths A and C may also be taken[8,9]. Tin and mercury derivatives of this type are generally assumed to be static allyl systems***, *i.e.* contain only structure (III), from which it may be inferred that rearrangement by path B is the sole source of the observed product[10,11].

The protolysis of NpALi in hydrocarbon solvents is distinct from either of the two cases discussed above. PMR and IR data for NpALi[7] and for the 1/1 adduct of isoprene and tert-butyllithium[13] demonstrate that these species are entirely of the primary type (III) in hydrocarbon solvents. The invariance of the olefin yields shown in the previous table suggests that proton transfers to NpALi occur primarily by an S_E2 or S_Ei process without rearrangement. The very low yield of the terminal olefin (II) may be rationalyzed by assuming a small amount of rearrangement (path B) or by a competitive S_E1 process. A choice between these alternatives would be difficult to make at this point.

Reaction with carbon dioxide and ketones is quite another story. As shown in the Table 2, NpALi in pentane often gives substantial amounts of the product corresponding to allylic rearrangement. Table 2 also shows the effect of ketone size on the product distribution. For very hindered ketones, di-tert-butyl ketone and benzophenone, only the "normal" product is observed. A similar result was observed by

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* The exceptions being the reaction of crotylmagnesium bromide with anhydrous ammonium iodide in ether, and with 2 *N* H_2SO_4 in the absence of solvent[9].

** Also possible, and not generally considered, is an S_E1 mechanism involving protonation of a delocalized allylic carbanion.

*** Allyl- and β-methallylmercuric halides show no ^{199}Hg satellites indicating some type of rapid forming and breaking of Hg–C bonds. 2-Butenylmercuric bromide does show satellites, however, and IR spectra also show no evidence of the secondary isomer analogous to (IV)[12].

TABLE 2

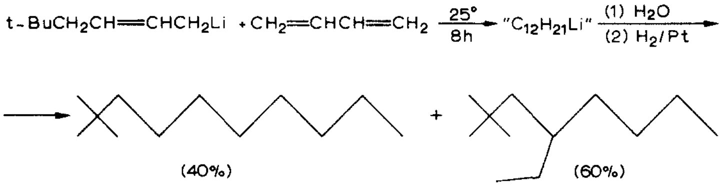
REACTION OF NpALi WITH CARBONYL COMPOUNDS[a]

Reactant	*R*	*Temp.* (°*C*)	*t-BuCH$_2$CH=CHCH$_2$R* trans (%)	cis (%)	*RCH(CH=CH$_2$)CH$_2$-t-Bu* (%)
CO_2	COOH	−75	38	7	55
MeCOEt	(Me)(Et)COH	−75	38	10	52
i-PrCOMe	(i-Pr)(Me)COH	−75	38	11	51
(i-Bu)$_2$CO	(i-Bu)$_2$COH	−75	36		64
(i-Pr)$_2$CO	(i-Pr)$_2$COH	−75	49		51
(t-Bu)$_2$CO	(t-Bu)$_2$COH	−75	100		
(Ph)$_2$CO	Ph$_2$COH	−75	100		

[a] Estimated precision of isomer percentages: ±2% (see Experimental for details).

Young and coworkers[5,6] for di-tert-butyl ketone with 2-butenylmagnesium halides. As we have noted above, however, NpALi is quite a different system from the crotyl Grignard reagent, and one should take care in drawing any analogy between the similar products observed from the two systems. Although Grignard reagents apparently react only by an S_E2' rearrangement process[4], the products in Table 2 must arise from a combination of S_E2' (or S_Ei') and direct S_E2 (or S_Ei) substitution.

Several other reactions of NpALi have been studied in pentane solvent. Reaction with chlorotrimethylsilane gives only the primary products corresponding to structures (Ia) and (Ib), with relative yields of 85% and 15% respectively. Reaction with butadiene has been studied previously by Hsieh and coworkers[14], and we have verified their results. Addition of butadiene results in allylic rearrangement of the neopentylallyl group in NpALi in 60% of the cases (see Experimental for details).



The result is in agreement with the early work of Makowski and coworkers[15] who showed that the amount of terminal vinyl content is very high in the early stages of allyllithium-initiated diene polymerizations. (Normal values of vinyl content in polybutadienes prepared in hydrocarbon solvents are 9–11%)[16]. Whether this effect is due to the changing degree of aggregation of the allyllithium responsible for propagation[7,14], or some other factors, is yet unknown.

Reaction of NpALi with molecular bromine results in a variety of products. Using either normal or inverse addition or the reagents, we find evidence for bromination of the carbon–carbon double bond as well as substitution at the carbon–lithium bond. In any case the reaction is of no synthetic utility. Reaction with 1,2-dibromoethane also is of no use in the preparation of monobromo derivatives. Inverse or normal addition gives only the diolefins (V) and (VI). It is possible that these products

$$\text{t-BuCH}_2\text{CH=CHCH}_2\text{Li} + \text{Br(CH}_2)_2\text{Br} \rightarrow$$

$$\underset{\text{(V)}}{(\text{t-BuCH}_2\text{CH=CHCH}_2)_2} + \underset{\text{(VI)}}{\text{t-BuCH}_2\text{CH(CH=CH}_2)\text{CH}_2\text{CH=CHCH}_2\text{-t-Bu}}$$

result from the coupling of NpALi with the transient NpABr (formed by bromination of NpALi). Hower, we have no evidence to rule out other mechanistic possibilities.

In summary, our results indicate that NpALi in pentane solvent behaves like no other allyl metal compound so far documented. In its reactions with proton donors, NpALi appears to react with retention of geometrical configuration, *i.e.* without significant allylic rearrangement. It seems unlikely that an $S_{\text{E}}1$ process would yield such a low percentage of "rearranged" olefin, although the intermediacy of an allyl carbanion-cation pair may not be ruled out. Reaction with ketones, butadiene and carbon dioxide apparently utilize two mechanistic routes, one involving retention, the other allylic rearrangement. In view of the expected tendency of lithium to coordinate with donor atoms in the absence of a coordinating solvent $S_{\text{E}}c$ and $S_{\text{E}}c'$ routes would probably be preferred. Again, an $S_{\text{E}}1$ mechanism may not be exluded by the available data.

The state of aggregation of the organolithium compound in the transition state is also unknown. Although some kinetic studies indicate that the monomer is the active species for certain reactions in aromatic solvents^{17}, the situation apparently is more complex in aliphatic solvents and more data is needed. If the allylic lithium aggregate remains intact in the transition state, we would expect it to exert a sizeable steric influence on product distributions.

Further work on the reactions of allyllithium compounds in polar and nonpolar solvents which we will report later will pertain to this matter.

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 spectroscopy and IR). Satisfactory carbon and hydrogen analyses were obtained for all compounds prepared.

Preparation of 3-*neopentylallyllithium* (*NpALi*)

Preparation of NpALi for spectroscopic work was described in the previous paper^{7}. For preparation on a larger scale, the following procedure was used. The flask was flushed out with dry nitrogen and cooled to -70°. Liquid butadiene (3.8 ml; 46 mmol) (Phillips Special Purity Grade) was drawn off from a pre-cooled cylinder using a gas-tight syringe and added, through a septum, to the chilled pentane. To this butadiene solution was added tert-butyllithium (40 ml of a 1.24 *M* solution in pentane; 50 mmol) (Foote Mineral Co.). The reaction mixture was allowed to warm to room temperature and the homogenous solution was stirred at this temperature for a further hour.

Protolysis of NpALi

To a solution of the adduct, prepared as described above, was added a slight excess of the appropriate proton donor (See Discussion, Table 1). The contents of the flask were stirred for one hour (although the reactions were apparently instantaneous) and an excess of water added. The hydrocarbon layer was separated, dried ($MgSO_4$) and evaporated to a smaller volume (5 ml). The C_8-olefin fraction (b.p. 99–103°) was isolated in 90–95% yield based on butadiene used to prepare NpALi. A GLC survey of C_8, C_{12} and C_{16} olefins was accomplished using a 100′ × 1/16″ support-coated-open-tubular (SCOT) column, with a squalane liquid phase, at ~ −10°. This was necessary to effect the separation of 5,5-dimethyl-1-hexene and *trans*-5,5-dimethyl-2-hexene.

Carbonation

Carbonation was accomplished by pouring the NpALi solution over a dry ice/pentane slurry. The reaction mixture was acidified and the acids extracted with pentane. The pentane extract was treated with excess base (4 *N* NaOH) and the sodium salts of the acids extracted with water. The aqueous layer was acidified, extracted with diethyl ether and the acids methylated with diazomethane solution. Yield of the esters was 75% based on amount of butadiene used. A 20′ × 1/4″ SE-30 column was used for GLC separation at 170° to yield methyl 2-neopentyl-3-butenoate followed by methyl 6,6-dimethyl-3-heptenoate.

Reaction with chlorotrimethylsilane

Chlorotrimethylsilane (7 ml) was added to the NpALi solution at −70°. A rapid reaction took place and the reaction mixture was allowed to stir overnight. Diethyl ether (30 ml) was added and the mixture distilled until 50 ml of distillate were collected. To the pot-residue was added water (50 ml) and the organic layer extracted with diethyl ether. Evaporation of the ether yielded the crude silanes in 84% yield (based on butadiene) and GLC (20′ × 1/4″ SE-30 column) indicated the presence of only two products which were subsequently identified as *trans*- and *cis*-5,5-dimethyl-1-trimethylsilyl-2-hexene.

Carbonyl addition reactions

These were carried out at room temperature and at −70°. A slight excess of the ketone was added to the NpALi and the reaction mixture stirred for an additional hour after room temperature was attained. The mixture was hydrolyzed with water (50 ml), the organic layer separated and the volatile products removed to leave the crude alcohols (75–85% yield based on butadiene). Preparative GLC on a 10′ × 1/4″ SE-30 column affected separation of the isomers (see Discussion, Table 2).

Reaction with butadiene

Butadiene addition was carried out by adding an equivalent amount of liquid butadiene to the NpALi solution at −75°. The mixture was stirred at room temperature overnight and then quenched with excess ethanol. Work-up of the products followed a procedure similar to that described by Hsieh and coworkers[14]. After ethanolysis and hydrolysis, the organic layer was separated and the aqueous layer was extracted twice with pentane. The organic layers were combined, dried over anhydrous magnesium sulfate and analyzed by GLC. A 10′ × 1/4″ SE-30 column was used with a helium flow rate of 40 ml/min. Initial temperature was 120° for 16 min, followed by a programmed rise at 4°/min to 210° where the temperature was held. Analysis showed olefins in the C_8, C_{12}, C_{16}, C_{20} and C_{24} ranges with relative abundances of 33 %, 43 %, 19 %, 5 % and <1 % respectively. The C_{12} and C_{16} olefins were collected by preparative GLC. PMR showed a 4.7/5.3 ratio of terminal to internal olefin in the 12-carbon compounds and a 4.4/5.6 ratio in the 16-carbon compounds. Hydrogenation of the crude olefin mixture was carried out in cyclohexane solvent with platinum black catalyst at 46 lbf in $^{-2}$ of hydrogen. After 1.75 h, the hydrogenated material was filtered and the mixture separated by GLC. The C_{12} fraction consisted of two compounds which were shown to be 2,2-dimethyldecane (40 %) and 2,2-dimethyl-4-ethyloctane (60 %).

Reaction with 1,2-*dibromoethane*

1,2-Dibromoethane addition was carried out by adding a slight excess of 1,2-dibromoethane to the NpALi at −70°. The reaction mixture was allowed to warm to room temperature and then stirred for a further hour. Water (50 ml) was added and the products extracted with pentane. Preparative GLC on a 10′ × 1/4″ SE-30 column at 130° yielded a 1/1 ratio of 7-ethenyl-2,2,9,9-tetramethyl-4-decene and 2,2,11,11-tetramethyl-4,8-dodecadiene in 68 % yield based on butadiene. Slow inverse addition of the NpALi yielded the same products in a similar ratio.

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