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REACTION OF AMINE–BORANES AND AMINE–MONOCHLOROBORANES WITH TRIALKYLETHYLENES

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SUMMARY

At suitably elevated temperatures (usually between 80° and 180°) 2-methyl-2-pentene is hydroborated quantitatively by amine–boranes and amine–monochloroboranes to yield trialkylboranes and dialkylchloroboranes respectively. Substantial migration of the boron atom from its original point of attachment often occurs subsequent to the addition at such temperatures. An amine–monochloroborane reacts less rapidly than the corresponding amine–borane and boron migration in the resulting organochloroborane occurs at a substantially slower rate. These conclusions are drawn from the ratios of the alcohols obtained by alkaline hydrogen peroxide oxidation of the organoboranes.

Cis–trans-isomerization is observed in the excess of olefin in the reaction of *trans*-3-methyl-2-pentene with triethylamine–borane. The extent of this isomerization is more dependent on reaction temperature than time. In the equivalent reaction with triethylamine–monochloroborane the amount of *cis–trans*-isomerization is found to be considerably reduced.

INTRODUCTION

Ashby[1] has reported the reaction of trialkylamine–boranes with various terminal olefins and dialkylethylenes at 200°:

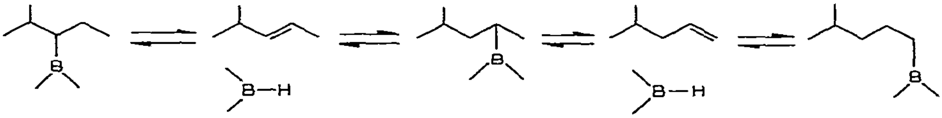
$$R_3N{\cdot}BH_3 + 3\,R'CH{=}CH_2 \xrightarrow{200^\circ} (R'CH_2CH_2)_3B + R_3N \qquad (1)$$

No information is available on the reaction of trialkylethylenes with amine–boranes, nor of any type of olefin with amine–monochloroboranes. Possible *cis–trans*-isomerization of excess of olefin in such high temperature hydroboration reactions has also so far eluded study.

Hydroboration is a potential novel method of crosslinking Natural Rubber (*cis*-1,4-polyisoprene) provided that the reaction can be controlled and rendered technologically acceptable. The high reactivity and gaseous nature of both diborane and monochloroborane obviously eliminates their direct application as crosslinking agents. However in complexed form with trialkylamines, they are stable liquids or solids which dissociate at an elevated temperature dependent on the amine moiety.

It was necessary to establish whether hydroboration of trialkylethylenes could be achieved by thermal reaction with these complexes. Sterically, this would be unfavourable if the mechanism involved only a partial dissociation of the boron–nitrogen bond prior to boron–hydrogen addition, as proposed by Ashby. In order to crosslink rubber the borane must add to at least two olefin molecules. This therefore necessitates complete reaction in the case of monochloroborane.

The extent of migration of the boron atom under the conditions of this hydroboration was also an important factor for study owing to the implications that might follow in the rubber system. Such migration is reported[2] to proceed by a succession of elimination and addition reactions for example:



(2)

If this were to occur sufficiently rapidly in the hydroborated rubber at high temperature, the crosslink would be thermolabile and result in a "thermoplastic rubber".

Finally, compared to normal hydroboration reactions a large excess of double bonds will be present in the rubber system. Since as little as 5% *cis–trans*-isomerization of these bonds can cause a serious drop in the tensile strength of the crosslinked polymer, it was necessary to study the extent of this type of isomerization in a suitably chosen trialkylethylene.

RESULTS AND DISCUSSION

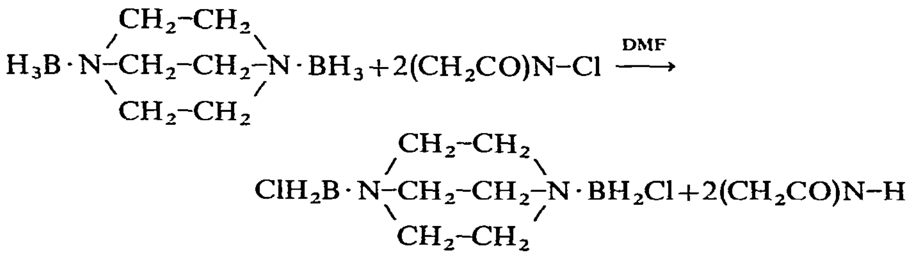
Trialkylamine–boranes were conveniently prepared[3] by the action of carbon dioxide on potassium borohydride at 0–10° in the presence of the appropriate amine

$$2\,KBH_4+CO_2+2R_3N+H_2O \rightarrow 2\,R_3N\cdot BH_3+K_2CO_3+2\,H_2 \tag{3}$$

$$R_3N\cdot BH_3+(CH_2CO)_2N\text{–}Cl \rightarrow R_3N\cdot BH_2Cl+(CH_2CO)_2N\text{–}H \tag{4}$$

[eqn. (3)], and the respective monochloroborane complex was then obtained by reaction of the amine–borane with one equivalent of *N*-chlorosuccinimide in benzene[4] [eqn. (4)]. The complexes of borane and monochloroborane with trimethylamine and triethylamine (R = Me, Et) prepared in this manner had physical properties in agreement with those already published[3–5].

Triethylenediamine–bisborane prepared by a method previously used for phosphite complexes[6] had an IR spectrum consistent with that reported by Gatti and Wartik[7], and was chlorinated in *N,N*-dimethylformamide solution to yield triethylenediamine–bis(monochloroborane) [eqn. (5)].



$$H_3B\cdot \underset{\diagdown\;CH_2-CH_2\;\diagup}{\overset{\diagup\;CH_2-CH_2\;\diagdown}{N-CH_2-CH_2-N}}\cdot BH_3+2(CH_2CO)N\text{–}Cl \xrightarrow{DMF}$$

$$ClH_2B\cdot \underset{\diagdown\;CH_2-CH_2\;\diagup}{\overset{\diagup\;CH_2-CH_2\;\diagdown}{N-CH_2-CH_2-N}}\cdot BH_2Cl+2(CH_2CO)N\text{–}H \tag{5}$$

In most experiments the olefin has been used in 100% excess based on available B–H in order to ensure complete reaction to the trialkyl- or dialkylchloroborane and to stimulate in part the large excess of unsaturation that would prevail in rubber. The total extent of reaction was determined from the yield of alcohols obtained after oxidation of the resulting organoborane with alkaline hydrogen peroxide[8] and not by the loss of olefin (as exercised by Zweifel[9]).

To establish the conditions under which amine–boranes might be expected to crosslink Natural Rubber, triethylamine–borane was caused to react with 2-methyl-2-pentene at various temperatures from 80–165°. The yields of alcohols found on oxidation of the resulting organoboranes are shown in Fig. 1 and Table 1 (expts. 1–14). The percentage ratio of alcohols was determined by GLC and is accurate to ±1%. Below 100° the reaction is slow compared to the hydroboration of a trialkylethylene with uncomplexed diborane, whilst at 140° and above the reaction is extremely rapid. The extent of isomerization of the organoborane is indicated by the distribution of the methylpentanols obtained on alkaline hydrogen peroxide oxidation[8]. At 100° and below boron migration does not proceed as far as the terminal positions; at 165° this occurs readily (expt. 13). Fig. 1 shows an initial rapid migration of boron from its original point of attachment at carbon 3 (anti-Markovnikov addition) to carbon 4 whilst hydroboration is actually occurring, and then only a slow migration after completion of the addition. This is consistent with the belief of Brown and Zweifel[10] that B–H species catalyse the migration. Thus, during hydroboration (up to 2 h) B–H species are available for this catalysis, but on completion of the addition and hence in the absence of B–H, only a slow isomerization occurs.

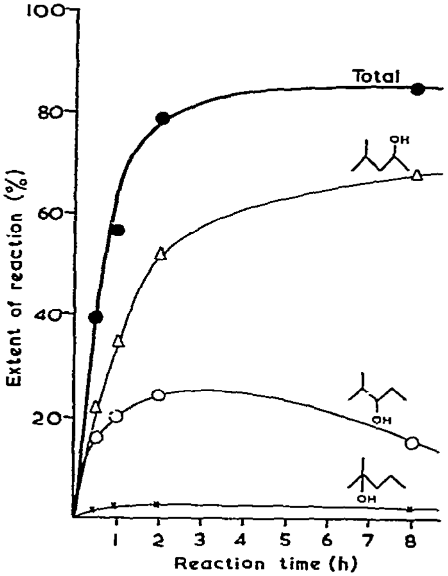
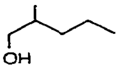
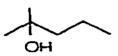
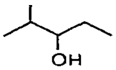
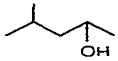
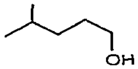


Fig. 1. Course of reaction of triethylamine–borane with 2-methyl-2-pentene (100% excess) at 100° as determined by alkaline hydrogen peroxide oxidation.

In comparison, the results of hydroboration of 2-methyl-2-pentene with tri-

TABLE 1

REACTION OF BORANE AND MONOCHLOROBORANE COMPLEXES WITH 2-METHYL-2-PENTENE

Expt.	Mol. ratio complex/ olefin	Time (h)	Temp. (°C)	Percentage alcohol after oxidation					Total yield (%)
									
TEB[a]									
1	1/6	1	80	0	6	64	30	0	15
2	1/6	2	80	0	5	53	42	0	24
3	1/6	4	80	0	6		45	0	37
4	1/6	1	90	0	6	54	40	0	28
5	1/6	2	90	0	5	46	49	0	45
6	1/6	1	120	1	1	14	81	3	81
7	1/6	0.17	140	2	1	15	78	4	87
8	1/6	0.25	140	2	1	7	81	9	70
9[b]	1/3	0.25	140	11	2	4	40	43	61
10	1/6	0.5	140	2	1	12	79	6	79
11	1/6	1	140	2	1	6	82	9	88
12[b]	1/3	1	140	8	1	3	39	49	51
13	1/6	4	165	5	1	5	18	71	87
14[b]	1/3	4	165	22	0	2	5	71	89
TECB[a]									
15	1/4	0.17	140	0	5	78	17	0	64
16	1/4	0.5	140	0	6	66	28	0	78
17	1/4	1	140	0	7	54	39	0	80
18	1/4	32	140	1	3	11	61	24	69[c]
19	1/4	64	140	3	2	8	33	54	79[d]
20	1/4	128	140	1	1	4	19	75	74[e]
TMB[a]									
21	1/6	6	160	4	1	4	16	75	84
TMCB[a]									
22	1/4	3	140	0	5	50	45	0	24
23	1/4	6	140	0	3	23	74	0	39
24	1/4	1	160	0	4	17	76	3	35
25	1/4	3	160	1	2	9	69	19	47
26	1/4	6	160	4	2	6	38	50	51
27	1/4	16	160	4	1	2	5	88	74

[a] TEB = triethylamine–borane; TECB = triethylamine–monochloroborane; TMB = trimethylamine–borane; TMCB = trimethylamine–monochloroborane. [b] Equivalent of olefin. [c] 32% $Et_3N \cdot HCl$ isolated. [d] 54% $Et_3N \cdot HCl$ isolated. [e] 41% $Et_3N \cdot HCl$ isolated.

ethylamine–monochloroborane are shown in Fig. 2 and Table 1 (expts. 15–17). Figs. 1 and 2 contrast directly the addition of the two complexes at 100°, and it is clear that not only is the reaction with the monochloroborane complex considerably less rapid, but also that boron migration in the resulting organochloroborane is virtually absent at that temperature. A similar difference in behaviour is also shown at 140°. Comparison of experiments 7 and 15 shows that when the addition occurs with triethylamine–borane, 78% of the boron attachments are isomerized to carbon 4 in

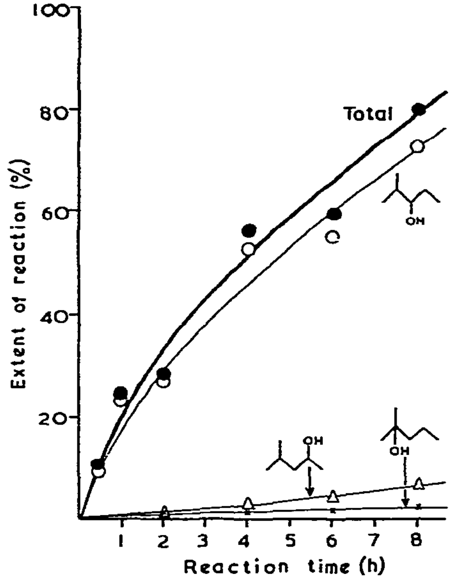
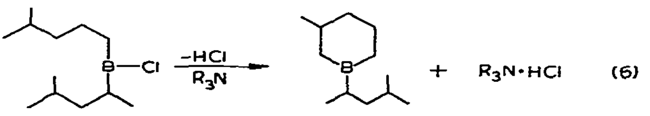


Fig. 2. Course of reaction of triethylamine–monochloroborane with 2-methyl-2-pentene (100% excess) at 100° as determined by alkaline hydrogen peroxide oxidation.

10 min, whereas with triethylamine–monochloroborane 78% remains at its original point of addition. Even after 1 h at 140°, over 50% of boron is still attached at carbon 3 in the monochloroborane reaction compared to only 6% with the borane (expts. 11 and 17). No migration of the boron atom to a terminal position was observed in any of the dialkylchloroboranes prepared from triethylamine–monochloroborane under the conditions of reaction so far described. Under more severe reaction conditions—heating for 32, 64 and 128 h at 140° (expts. 18–20)—isomerization to the terminal positions did occur, increasing to 75% after 128 h, and was accompanied by an unexpected formation of the amine hydrochloride. The mechanism for the formation of this hydrochloride is not presently understood since boron heterocycle formation[11] [eqn. (6)] would have resulted in the formation of diol on oxidation



with a proportionate loss in yield of 4-methyl-1-pentanol, whilst involvement of a further molecule of 2-methyl-2-pentene would have resulted in the additional formation of methylpentenols. Neither of these features was observed.

The reaction of 2-methyl-2-pentene with trimethylamine–borane and with trimethylamine–monochloroborane complexes follows a similar pattern to that described above. However, trimethylamine forms stronger complexes which require higher temperatures for reaction with the olefin. This, in turn, facilitates isomerization and renders the effect of the chlorine atom in the borane less discernible. A slower particularly expt. 14)]. It is difficult to envisage a mechanism by which additional olefin molecules could influence the direction of addition *per se*. However, if these molecules intercept B–H groups eliminated from primary adducts, anti-Markovnikov addition would appear to be favoured over Markovnikov [even if the restrictions (*i*) and (*ii*) mentioned above apply, provided that elimination occurs predominantly with double-bond shift].

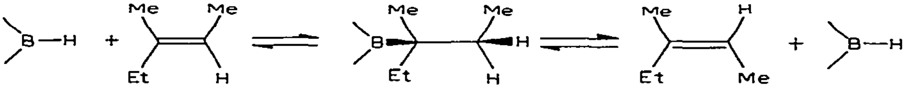
TABLE 2

REACTION OF BORANE AND MONOCHLOROBORANE COMPLEXES WITH 3-METHYL-2-PENTENE: *cis–trans*-ISOMERIZATION IN EXCESS OF OLEFIN

Expt.	Mol. ratio complex/olefin	Time (h)	Temp. (°C)	% *cis*
Initial olefin		0	0	3.3
Controls olefin only		3	140	3.1
		1.5	180	2.9
TEB[a]				
28	1/6	1.5	100	5.3
29	1/6	6	100	6.8
30	1/6	1.5	120	8.6
31	1/6	1.5	140	12.4
32	1/6	3	140	13.0
33	1/6	6	140	14.5
34	1/6	1.5	160	17.2
35	1/6	1.5	180	19.9
TECB[a]				
36	1/4	1.5	140	2.9
37	1/4	1.5	180	6.8

[a] TEB = triethylamine–borane; TECB = triethylamine–monochloroborane.

The same concept serves to explain the *cis–trans*-isomerization which occurs in the excess of olefin during reaction of *trans*-3-methyl-2-pentene with triethylamine–borane (Table 2). Since the mechanism of boron migration is believed[10] to involve both *cis*-addition and *cis*-elimination of B–H, geometrical isomerization of this olefin can occur if, and only if, addition occurs in the Markovnikov sense to C-3; subsequent elimination may then afford either the *cis* or the *trans* olefin [eqn. (7)].



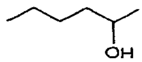
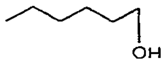
(7)

Cis–trans-isomerization is thus linked to Markovnikov addition. Hence, increase in reaction time has a relatively small effect on the extent of isomerization (reversibility is catalyzed by B–H species which are in low concentration once initial addition is complete), whereas a higher reaction temperature enables the steric resistance to Markovnikov addition to be more easily overcome and increases the rate of elimination and hence leads to a greater rate of isomerization (Table 2) (Compare the greater extent of Markovnikov addition to 2-methyl-2-pentene at 165°; expts. 12 and 14 of Table 1).

Monochloroborane complexes appear to exhibit greater anti-Markovnikov selectivity in their addition to olefins than do borane complexes. This is exemplified (Table 3) by the 97–98% selectivity shown in the reaction of several amine–monochloroborane complexes with 1-hexene compared with the 91% selectivity shown by triethylamine–borane (and the 93% observed by Brown and Zweifel[10] for equilibration of the corresponding organoborane for 1 h at the higher temperature of 160°). Monochloroborane complexes should therefore cause less *cis–trans*-isomerization of *trans*-3-methyl-2-pentene than do borane complexes if the above explanation is correct. This is confirmed by comparison of expts. 36 and 37 with 31 and 35 (Table 2), respectively. Alkaline hydrogen peroxide oxidation of the organoborane formed in expt. 36 further demonstrates the preference (99%) for anti-Markovnikov addition with monochloroborane complexes (expt. 43 of Table 4). However, after 1.5 h at 180° (expt. 45), although *cis–trans*-isomerization is still considerably reduced compared to the borane complex (expt. 37 *cf.* to 35), a substantial percentage (22%) of Markovnikov addition has occurred (presumably owing to the higher temperature overcoming steric hindrance). This is explicable if the elimination from the chloroborane adducts [*cf.* eqn. (7)] is more difficult than elimination from the borane adducts,

TABLE 3

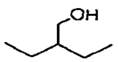
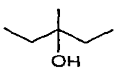
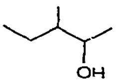
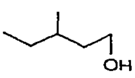
REACTION OF BORANE AND MONOCHLOROBORANE COMPLEXES WITH 1-HEXENE

Expt.	Complex[a]	Mol. ratio complex/ olefin	Time (h)	Temp. (°C)	Percentage alcohol after oxidation		Total yield (%)
							
38	TEB	1/3	0.25	140	9	91	71
39	TECB	1/4	1	140	2	98	93
40	TEDCB	1/8	1	150	2	98	91
41	TMCB	1/4	1	140	3	97	60
42	TMCB	1/8	1	140	3	97	85

[a] TEB = triethylamine–borane; TECB = triethylamine-monochloroborane; TEDCB = triethylenediamine–bis(monochloroborane); TMCB = trimethylamine-monochloroborane.

TABLE 4

REACTION OF BORANE AND MONOCHLOROBORANE WITH 3-METHYL-2-PENTENE

Expt.	Complex[a]	Mol. ratio complex/ olefin	Time (h)	Temp. (°C)	Percentage alcohol after oxidation				Total yield (%)
									
43	TECB	1/4	1.5	140	0	1	97	2	96
44	TEB	1/6	1.5	160	4	1	9	86	
45	TECB	1/4	1.5	180	7	15	61	17	80

[a] TEB = triethylamine–borane; TECB = triethylamine–monochloroborane.

a feature which is supported by the observation of less boron migration both here (expt. 45 *cf.* to 43, the latter also at a lower temperature) and also in the 2-methyl-2-pentene reactions.

In conclusion therefore monochlorination of amine–boranes results in a more strongly complexed borane species requiring a higher temperature for addition to olefins. There is less high temperature migration of boron in the organochloroborane and, in the presence of excess of double bonds, less *cis–trans*-isomerization occurs when the monochlorinated amine–borane is the hydroborating agent. The use of these complexes to crosslink Natural Rubber, the prime cause for this investigation into their reaction with trialkylethylenes, is the subject of another publication[14].

EXPERIMENTAL

The 2-methyl-2-pentene was fractionated to 99% purity on a high efficiency 5 ft. dixon gauze ring column. Trimethylamine– and triethylamine–boranes were prepared according to the method of Farbenfabriken Bayer Aktiengesellschaft[3]. Trimethylamine–monochloroborane was obtained by chlorination of the amine–borane with *N*-chlorosuccinimide in benzene[4].

Preparation of triethylamine–monochloroborane

N-Chlorosuccinimide (13.3 g, 0.1 mole) in *N,N*-dimethylformamide (DMF) (50 ml) was added dropwise with stirring to a solution of triethylamine–borane (11.5 g, 0.1 mole) in DMF (50 ml) at 25–30°. Stirring was continued for a further 1 h and the reaction mixture left overnight. After removal of the DMF on a rotary evaporator under vacuum (40°/0.2 mm), ether (100 ml) was added to dissolve the chloroborane followed by water (100 ml) to dissolve the succinimide. The ether layer was separated and the aqueous layer washed with ether (3 x 50 ml). The combined ethereal layers were dried ($MgSO_4$). Removal of the ether yielded triethylamine–monochloroborane (12.7 g, 85%) with IR spectrum and m.p. corresponding to those quoted in the literature[5].

Preparation of triethylenediamine–bis(monochloroborane)

Triethylenediamine–bisborane was obtained by a method previously used for phosphite complexes[6]. Sodium borohydride (56.7 g, 1.5 moles) and triethylenediamine (56 g, 0.5 mole) were added to DMF (1 l) and carbon dioxide passed in with stirring for *ca.* 6 h with the temperature maintained at 25–30°. The sodium formate precipitated was filtered off and the DMF removed on a rotary evaporator under vacuum (40°/0.2 mm) to yield triethylenediamine–bisborane (65 g, 93%) with IR spectrum consistent with that published[7]. *N*-Chlorosuccinimide (101 g, 0.76 mole) in DMF (450 ml) was added with stirring to a solution of triethylenediamine–bisborane (53 g, 0.38 mole) in DMF (700 ml) at 20°. The DMF was removed on a rotary evaporator under vacuum (40°/0.2 mm) to leave a mixture of the monochloroborane and succinimide. The latter was removed by washing with water (3 x 250 ml) to yield, after drying, triethylenediamine–bis(monochloroborane) as a white powder (66.4 g, 84%). (Found: C, 34.3; H, 7.8; B, 10.4; N, 13.4. $C_6H_{16}B_2Cl_2N_2$ calcd.: C, 34.5; H, 7.7; B, 10.4; N, 13.4%.)

Reaction of 2-methyl-2-pentene with amine–boranes

2-Methyl-2-pentene (2.52 g, 0.03 mole) was added by bulb-to-bulb distillation to the amine–borane (0.005 mole) and the mixture sealed under vacuum. After reaction under the required conditions, the mixture was transferred with diglyme (15 ml) into a flask containing 3 *N* sodium hydroxide (2.8 ml) and treated dropwise with an excess of 100 volume hydrogen peroxide. The resulting alcohols, accompanied by diglyme, were extracted with ether and the combined ethereal solution dried ($MgSO_4$). The ether was carefully removed using a Fenske column and the yield and ratios of methylpentanols determined by GLC after addition of a known weight of n-pentanol as internal standard.

Reaction of 2-methyl-2-pentene with amine–monochloroboranes

2-Methyl-2-pentene (1.68 g, 0.02 mole) was added by bulb-to-bulb distillation to the amine–monochloroborane (0.005 mole) and the mixture sealed under vacuum. After reaction under the required conditions, the mixture was transferred with diglyme (15 ml) into a flask containing 3 *N* sodium hydroxide (4.0 ml) and treated dropwise with an excess of 100 volume hydrogen peroxide. The resulting alcohols were isolated and estimated as above.

Reaction of 3-methyl-2-pentene with triethylamine–borane and triethylamine–monochloroborane

trans-3-Methyl-2-pentene (1.25 g, 0.015 mole) was added by bulb-to-bulb distillation to triethylamine–borane (0.29 g, 0.0025 mole) or triethylamine–monochloroborane (0.56 g, 0.0037 mole) and the mixture sealed under vacuum. After reaction under the required conditions the excess of olefin was isolated from the mixture by bulb-to-bulb distillation and washing free of liberated triethylamine with water (6 x 2 ml). The change in *cis*/*trans* ratio of the olefin was estimated by GLC.

For analysis of the boron attachments in the organoborane products after removal of volatile matter, the procedure was as described above for 2-methyl-2-pentene except that tetrahydrofuran was substituted for diglyme as solvent since the latter tended to obscure part of the 3-methylpentanol region of the chromatogram.

ACKNOWLEDGEMENT

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