Metal Catalysis in Organic Reactions. Part II.[1] Products and Stereochemical Aspects of the Isomerization of Heptenes by the Tri-isobutyl-aluminium–Bis-N-methylsalicylideneaminenickel System

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The isomerization of some C_7 olefins in the presence of tri-isobutylaluminium–bis-N-methylsalicylideneaminenickel has been studied. The susceptibility to isomerization of the substrates was found to be related to their structure: in particular 1-olefins were rapidly converted mainly into (E)-2-olefins. Moreover, whereas linear internal olefins were isomerized, branched chain internal olefins were unreactive under the conditions adopted. The isomerization of (S)-4-methylhex-1-ene to (S)-(E)-4-methylhex-2-ene occurred without racemization. The nature of the active species is discussed and reaction paths are suggested.

SOLUBLE catalytic systems formed by interaction of organoaluminium compounds with N-alkylsalicylidene-aminenickel(II) complexes have been observed to be active in several reactions involving trialkylaluminium compounds and unsaturated substrates, such as alkenes,[2–4] terminal alkynes,[5] and nitriles.[1] In our investigations on metal-catalysed displacement reactions between tri-isobutylaluminium and 1-olefins,[4] the occurrence of double bond isomerization under certain conditions has been observed. We have now investigated the dynamics and the stereochemistry of the double bond migration.

The results of the isomerization of some C_7 olefins by the catalytic tri-isobutylaluminium–bis-N-methylsalicyl-ideneaminenickel system, together with stereochemical data concerning the isomerization of (S)-4-methylhex-1-ene, are reported here.

Products of the Isomerization.—The experiments were carried out in the absence of solvent by treating the nickel complex at 0 °C with weighed amounts of tri-isobutylaluminium and adding the olefinic substrate at the same temperature. The reaction mixtures were kept at 25 °C for the required time, then the products recovered at 0.1 mmHg in a liquid-air trap. The isomer

distributions were determined by g.l.c. analysis, and all the components were identified by comparison of their retention times with those of authentical samples. In order to avoid low isomerization conversions due to the competitive displacement reactions,[2] a 10 : 1 molar ratio of alkene to tri-isobutylaluminium was used. The reactivity of the olefins was found to depend on the molar ratio of aluminium to nickel derivatives: the isomerization rate was very low at values ≥100 : 1,[2–4] but appreciable isomerization was observed at ratios in the range 100—10 : 1. At very low values (<10) some dimerization took place.

Results of the isomerization of heptenes, at Al : Ni values of 50 : 1 (Tables 1 and 2) show that the susceptibility to isomerization depends on the structure of the olefin. Terminal alkenes are isomerized generally faster than their internal isomers, and linear olefins faster than branched chain isomers. In particular, hept-1-ene and 4-methylhex-1-ene react rapidly, whereas branched chain internal olefins are only slowly isomerized. The behaviour of 3-methylhex-1-ene is anomalous: this olefin isomerizes more slowly than 2-ethylpent-1-ene.†

In the isomerizations of linear heptenes (E)-hept-2-ene

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† Preliminary results have shown that 3-methylpent-1-ene and 3,7-dimethyloct-1-ene, whose structures resemble that of 3-methylhex-1-ene, are isomerized very fast under the conditions adopted.

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[5] L. Lardicci, A. M. Caporusso, and G. P. Giacomelli, *Chimica e Industria*, 1974, **56**, 230.

is always the predominant isomer, and the isomer distribution does not change appreciably after 3 and up to 5 h, with the exception of the isomerization of (E)-hept-2-ene. In no case does the isomer distribution correspond to that evaluated from thermodynamic equilibrium data,[6] and depends on the substrate employed, except in the case of (E)- and (Z)-hept-3-ene, which afford the same product distribution after 5 h (Table 1). In the isomerization of 4-methylhex-1-ene, the predominant isomer is (E)-4-methylhex-2-ene, formed together with (Z)-4-methylhex-2-ene (E : Z ratio ca. 6 : 1) and minor amounts of 3-methylhex-2-enes. 3-Methylhex-3-enes, from a double bond migration to the γ-position of the carbon chain, were not detected.

In order to evaluate the extent of any racemization during isomerization accurately, it was necessary to confirm the reported maximum rotatory power of (S)-(E)-4-methylhex-2-ene,[7] since a parallel investigation of the stereochemistry of β-elimination reactions had indicated the possibility that the reported value was wrong.[7] In fact, pyrolysis of (4S)-2-dimethylamino-4-methylhexane N-oxide yielded (S)-4-methylhex-1-ene, $[\alpha]_D^{25}$ −2.82° (neat), optical purity (o.p.) 93.1%,[8] and (S)(E)-4-methylhex-2-ene, $[\alpha]_D^{25}$ +39.28°, o.p. 86.0%.[7] Because of this discrepancy in optical purities a sample of the olefin was converted into (S)-3-methylhexane[8] by a reaction sequence not affecting the chiral carbon atom (Scheme 1).[9] On the basis of these results, it was

TABLE 1

Isomerization of linear heptenes by tri-isobutylaluminium–bis-N-methylsalicylideneaminenickel at 25 °C [a]

Substrate	Reaction time (h)	Isomerization (%)	Relative isomer percentages (mole%) [b]				
			Hept-1-ene	(E)-Hept-2-ene	(Z)-Hept-2-ene	(E)-Hept-3-ene	(Z)-Hept-3-ene
Hept-1-ene [c]	3	99	1	79	16	3	1
	5	99	1	79	16	3	1
(E)-Hept-2-ene [c]	3	28	1	72	15	10	2
	5	44	1	56	14	25	4
(Z)-Hept-2-ene [c]	3	77	1	63	23	11	2
	5	80		67	20	11	2
(E)-Hept-3-ene [c]	3	67		51	9	33	7
	5	70		54	9	30	7
(Z)-Hept-3-ene [c]	3	93		54	10	29	7
	5	92		52	9	31	8

[a] Molar ratios: Al : Ni 50 : 1, C=C : Al 10 : 1. [b] Determined by g.l.c. analyses of the recovered products. [c] By hydrolysis of the residual mixture, heptane was also recovered.

TABLE 2

Isomerization of 4-methylhex-1-ene and its isomers by tri-isobutylaluminium–bis-N-methylsalicylideneaminenickel at 25 °C [a]

Substrate	Reaction time (h)	Isomerization (%)	Relative isomer percentages (mole %) [b]							
			4-Methyl-hex-1-ene	4-Methyl-hex-2-ene (E)	4-Methyl-hex-2-ene (Z)	3-Methyl-hex-3-ene (E)	3-Methyl-hex-3-ene (Z)	3-Methyl-hex-2-ene (E)	3-Methyl-hex-2-ene (Z)	3-Methyl-hex-1-ene	2-Ethyl-pent-1-ene
4-Methyl-hex-1-ene [c]	3	99	1	77	13			5	4		
	5	99	1	77	13			5	4		
(E)-4-Methyl-hex-2-ene	5	6		94	4			2			
	24	9		91	7			2			
(E)-3-Methyl-hex-3-ene	5	≃1	ca. 1			ca. 99	Trace				
(E)-3-Methyl-hex-2-ene	5	0						100			
(Z)-3-Methyl-hex-2-ene	5	≃1	Trace			Trace		ca. 99			
3-Methylhex-1-ene [c]	5	8						5	3	92	
	24	43		Trace				27	16	57	
2-Ethylpent-1-ene [c]	5	20		1	Trace	5		9	5		80

[a] Molar ratios: Al : Ni 50 : 1, C=C : Al 10 : 1. [b] Determined by g.l.c. analysis of the recovered products. [c] By hydrolysis of the residual mixtures, 3-methylhexane was also recovered.

By hydrolysis of the residual reaction mixtures from linear heptenes and terminal branched chain heptenes, the corresponding alkane was recovered.*

Isomerization of (S)-4-*Methylhex-1-ene*.—To elucidate mechanistic aspects of the reaction, we have investigated the stereochemistry of the isomerization of (S)-4-methylhex-1-ene to (S)-(E)-4-methylhex-2-ene.

* Since internal olefins are not susceptible to the displacement reaction,[2] the heptane must arise in these cases from isomerization to hept-1-ene followed by a displacement reaction with tri-isobutylaluminium.

possible to attribute to the olefin sample the same optical purity (93%) as the recovered (S)-3-methylhexane; thus the rotatory power $[\alpha]_D^{25}$ +42.1° for optically pure (S)-(E)-4-methylhex-2-ene was evaluated.
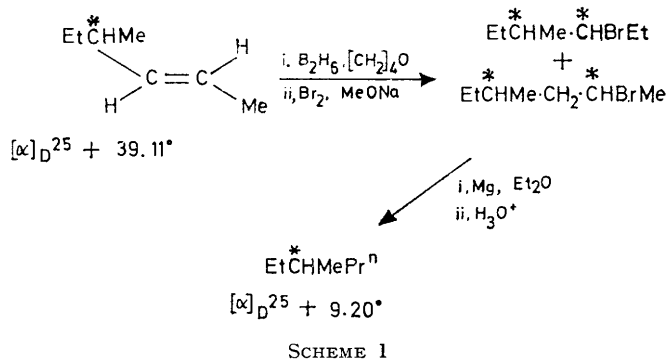
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Under the experimental conditions adopted for the isomerization reactions, (S)-4-methylhex-1-ene, $[\alpha]_D^{25}$ —2.84° (neat),[8] affords after 5 h 77% of (S)-(E)-4-methylhex-2-ene,[7] $[\alpha]_D^{25}$ +39.34° (neat) and 13% of (S)-(Z)-4-methylhex-2-ene,[7] $[\alpha]_D^{25}$ +29.00° (neat). In a

EtĊHMe
$\diagdown$
  C = C
$\diagup$ $\diagdown$
H   Me H

$[\alpha]_D^{25}$ + 39.11°

i. B₂H₆.[CH₂]₄O
ii. Br₂, MeONa →

EtĊHMe·ĊHBrEt
+
EtĊHMe·CH₂·ĊHBrMe

i, Mg, Et₂O
ii, H₃O⁺ ↙

EtĊHMePr^n

$[\alpha]_D^{25}$ + 9.20°

SCHEME 1

second run (reaction time 1 h), unchanged (S)-4-methylhex-1-ene, having the same optical purity as the starting olefin, was also recovered. Therefore the isomerization of (S)-4-methylhex-1-ene to (S)-(E)-4-methylhex-2-ene was deduced to occur stereospecifically,* at least under the experimental conditions adopted.

DISCUSSION

The main feature of the isomerization of the heptenes is that terminal olefins are converted mainly into mixtures of (E)- and (Z)-2-olefins (Tables 1 and 2), as observed in the isomerization of terminal olefins by some rhodium,[10] iridium,[11] alkylchromium,[12] titanium,[13] and other nickel complexes.[14]

In the present system, olefin reactivity generally decreases as the number of substituents at the unsaturated carbon atoms increases and the E to Z interconversion is not appreciably catalysed (Tables 1 and 2). We expected the double bond to move reversibly along the chain of 4-methylhex-1-ene: the complete stereospecificity of the isomerization of (S)-4-methylhex-1-ene to (S)-4-methylhex-2-ene does not, however, fit this hypothesis. It therefore appears that steric factors may play an important role in this isomerization.

The present results and other evidence [1,5] give reason to believe that the actual catalyst is an alkylnickel compound, which presumably also contains the nickel ligand originally present. By analogy with previous proposals,[14,15] such a species could produce a complex hydride nickel system $(L_n NiH)$.[15,†]

In the absence of isolable intermediates, any mechan-

ism must remain speculative; however the olefin isomerization may be interpreted in terms of a hydride addition–elimination mechanism (Scheme 2).[12,16] On this basis the predominant formation of (E)- rather than (Z)-2-olefins can be reasonably related to steric factors which determine the preferred conformations in the alkylnickel compounds (2) and hence cause stereoselective elimination of the hydridonickel species.[12,14]

The proposed mechanism accounts for the finding that internal olefins are only slowly isomerized. The addition of the hydridonickel species to such olefins would be hindered or even prevented by steric interactions among the alkyl groups bonded to the unsaturated carbon atoms and the catalytic system. Thus the lack of racemization during the isomerization of (S)-4-methylhex-1-ene is also explained.

Steric factors, related to differences in structure of the alkyl group bound to the γ-carbon atom may also be responsible for the different susceptibilities towards isomerization of the series of 1-olefins, 3-methylpent-1-ene, 3-methylhex-1-ene, and 3,7-dimethyloct-1-ene.

$L_n NiH + CH_2=CH\cdot CH_2\cdot CH\diagdown_{R'}^{R} \rightleftharpoons L_n Ni-CH_2CH_2\cdot CH_2\cdot CH\diagdown_{R'}^{R}$
(1)
$\updownarrow$
$L_n Ni-CH\diagdown_{Me}^{CH_2\cdot CH\diagdown_{R'}^{R}} \rightleftharpoons L_n NiH + MeCH=CH\cdot CH\diagdown_{R'}^{R}$
(2)

SCHEME 2

However, the mechanism of Scheme 2 does not explain why 4-methylhex-1-ene and its isomers are isomerized directly to 3-methylhex-2-ene, without the formation of the intermediate 3-methylhex-3-ene (Table 2). In principle this result might be explained in accord with other suggestions [10,13,17,18] that rearrangement occurs within the complexed species without requiring the formation of the intermediate olefins.

The synthesis of (S)-(E)-4-methylhex-2-ene from (S)-1-chloro-2-methylbutane may be better achieved, with comparable optical yields, through preparation and isomerization of (S)-4-methylhex-1-ene (38% yield) than
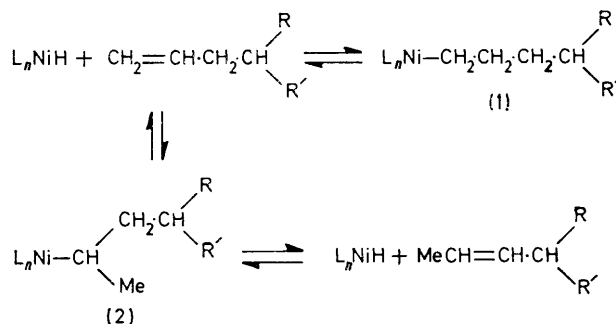
* On the hypothesis that the isomerization process is stereospecific even for the formation of (S)-(Z)-4-methylhex-2-ene, this olefin is to be attributed the maximum rotatory power $[\alpha]_D^{25}$ +31.0°, 10% lower than that previously reported.[7] Recently, $[\alpha]_D^{25}$ values of 39.4 and +29.9° were found, respectively, for (S)-(E)- and (S)-(Z)-4-methylhex-2-ene (S. Bertozzi, R. Lazzaroni, and P. Salvadori, Chimica e Industria, 1975, 57, 494).

† This hypothesis seems consistent with preliminary n.m.r. investigations on C_6D_6 solutions of bis-N-methylsalicylideneaminenickel and tri-isobutylaluminium (Al : Ni 20 : 60). The spectra show the presence of isobutene, which could arise from an alkylnickel precursor via a nickel hydride β-elimination.

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via Boord synthesis (7%) [7] or Cope elimination (7%; present work). Thus, such an isomerization procedure appears to be a convenient route to such optically active olefins.

EXPERIMENTAL

(*E*)- and (*Z*)-3-Methylhex-2-ene, 3-methylhex-1-ene, and all the n-heptenes were commercial products which were carefully purified by distillation over sodium wire. (*R*)(*S*)-4-Methylhex-1-ene [19] and (*E*)-3-methylhex-3-ene [20] were prepared according to established procedures. 2-Ethyl-pent-1-ene was prepared (52%) from hexan-3-one according to Cainelli's procedure.[21] (*S*)-4-Methylhex-1-ene, $[\alpha]_D^{25}$ $-2.84°$ (neat),[8] was obtained (49%) from (*S*)-1-chloro-2-methylbutane, $[\alpha]_D^{25}$ $+1.59°$ (neat),[8] *via* (+)-(*4S*)-1-bromo-2-ethoxy-4-methylhexane.[19] Tri-isobutylaluminium was obtained from Texas Alkyl Inc., Houston. Distillation, handling of the organometallic compound, and all the isomerization reactions were carried out under dry, purified nitrogen. Bis-*N*-methylsalicylideneamine-nickel was prepared and purified as reported elsewhere.[22] G.l.c. analyses were performed on a Perkin-Elmer F11 or F30 instrument (flame ionization detectors). For linear heptenes, a 100 m Squalane capillary column at 50 °C and a nitrogen flow rate of 12 ml min⁻¹ were used; for 4-methylhex-1-ene and its isomers, 200 × 0.30 cm columns packed with 30% silver nitrate–diethylene glycol on 60—80 mesh Chromosorb P at 40 °C and a nitrogen flow rate of 6 ml min⁻¹ were employed. Preparative g.l.c. was carried out on a Perkin-Elmer F21 instrument equipped with a 300 × 0.8 cm column filled with 20% silver nitrate–ethylene glycol on 60—80 mesh Chromosorb A at 25 °C and a nitrogen flow rate of 180 ml min⁻¹. Optical rotations were measured with a Schmidt–Haensch or Perkin-Elmer 142 polarimeter.

Preparation of (S)-(E)-4-*Methylhex-2-ene*.—Phosphorus tri-bromide (62.2 g, 0.23 mol) was added slowly at 0 °C to (+)-(*4S*)-4-methylhexan-2-ol (72.1 g, 0.62 mol), b.p. 103° at 115 mmHg, $[\alpha]_D^{25}$ $+11.01°$ (neat) [23] [prepared (85%) from (S)-1-chloro-2-methylbutane, $[\alpha]_D^{25}$ $+1.59°$ (neat)] to afford (56%) (*4S*)-2-bromo-4-methylhexane, b.p. 87—88° at 60 mmHg, α_D^{25} $+30.73°$ (neat) ($l = 1$).

A 500 ml stainless steel rocking autoclave was charged with the bromide (50.8 g, 0.28 mol) and dimethylamine (94.7 g, 2.1 mol); the mixture was heated at 50° (1 h), 80° (4 h), and 100 °C (4 h). The organic product, purified by way of the corresponding hydrochloride, yielded (57%) pure (*4S*)-2-*dimethylamino-4-methylhexane*, b.p. 51° at 15 mmHg, n_D^{25} 1.4197, α_D^{25} $+11.85°$ (neat) ($l = 1$) (Found:

C, 75.3; H, 14.45; N, 9.5. $C_9H_{21}N$ requires C, 75.45; H, 14.75; N, 9.75%).

The corresponding *N*-oxide (0.156 mol) was pyrolysed [24] within 1 h at 100 °C and at 1.5 mmHg to yield (75%) a mixture containing 4-methylhex-1-ene (57%), (*E*)-4-methyl-hex-2-ene (36%), and (*Z*)-4-methylhex-2-ene (7%) (by g.l.c.). By preparative g.l.c., pure (*S*)-4-methylhex-1-ene $[\alpha]_D^{25}$ $-2.82°$ (neat),[8] and (*S*)-(*E*)-4-methylhex-2-ene, $[\alpha]_D^{25}$ $+39.28°$ (neat), were recovered.

(S)-3-*Methylhexane from* (S)-(E)-4-*Methylhex-2-ene*.—A 0.68M-solution of borane in tetrahydrofuran (30 ml) was added dropwise at -10 °C to a well stirred solution of (S)-(*E*)-4-methylhex-2-ene (5.0 g, 51 mmol), $[\alpha]_D^{25}$ $+38.11°$ (neat), in tetrahydrofuran (10 ml). The mixture was kept at room temperature for 2 h and then bromine (8.2 g, 51.3 mmol) and sodium methoxide (4.6 g, 85 mmol) in methanol (25 ml) were added simultaneously at such a rate that the mixture was always slightly yellow and a reaction temperature of 20—25 °C was maintained.[25] The organic products were recovered and distilled to give (60%) a mixture of (*4S*)-2-bromo- and (*4S*)-3-bromo-4-methyl-hexane, b.p. 78° at 50 mmHg. The bromides were treated with magnesium (0.73 g, 30 mg atom); hydrolysis then yielded (20%) crude (*S*)-3-methylhexane, which, after purification, showed $[\alpha]_D^{25}$ $+9.20°$ (neat).[8]

Olefin Isomerization Procedure.—Reaction vessels equipped with a Versilic silicone cap, a glass stopcock, and a magnetic stirrer were used. At least two runs were performed for each substrate. In a typical run, tri-iso-butylaluminium (1.00 g, 5.04 mmol) was transferred from a sealed glass vial to the reaction vessel containing the nickel complex (0.0329 g, 0.10 mmol), cooled at 0 °C; the olefin (4.94 g, 50.4 mmol) was injected by hypodermic syringe through the cap and then the flask was placed in a thermostatted (25 ± 0.3 °C) water-bath. After the required time the isomerization products were recovered during 1 h in a liquid-air trap at 16 mmHg. G.l.c. analyses were performed directly on the mixture.

Isomerization of (S)-4-*Methylhex-1-ene*.—The above procedure was used. (S)-4-Methylhex-1-ene (6.55 g, 66.7 mmol), $[\alpha]_D^{25}$ $-2.84°$ (neat), was stirred for 5 h in the presence of tri-isobutylaluminium (1.32 g, 6.67 mmol) and the nickel complex (0.044 g, 0.13 mmol). The product mixture was separated by preparative g.l.c. to yield pure (S)-(*E*)-4-methylhex-2-ene, $[\alpha]_D^{25}$ $+39.34°$ (neat),[7] and (S)-(*Z*)-4-methylhex-2-ene, $[\alpha]_D^{25}$ $+29.00°$ (neat).[7] In a repeat run (reaction time 1 h), preparative g.l.c. gave pure (S)-4-methylhex-1-ene, $[\alpha]_D^{25}$ $-2.87°$ (neat),[8] and (S)-(*E*)-4-methylhex-2-ene, $[\alpha]_D^{25}$ $+39.40°$ (neat).[7]

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