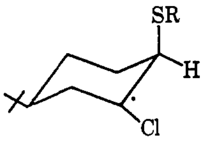
accumulation of products from the more stable[9] intermediate **7**. On the other hand, low temperature and high thiol concentration promote rapid displacement from the kinetically favored **6**. Radical-chain additions of HX species to 4-*t*-butylcyclohexenes, examined under similar reaction conditions, lead to decreasing amounts of products with axial-X groups in the following order: HBr > RSH > ArSH > AcSH > HSH. Reversibility is less important for the former three addenda, as a consequence of the lower stability of alkanethiyl radicals and the high transfer rate with ArSH, and especially with HBr.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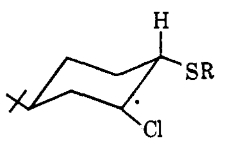
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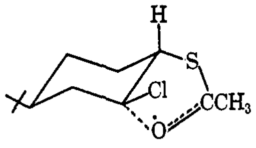
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The displacement reactions with intermediates **6** and **7** lead to over-all *trans* stereoselectivity, but that from **6** is considerably higher and is enhanced at low temperatures and high thiol concentrations. One tempting explanation for preferential *trans*-diaxial addition (to produce **2**) involves an *unsymmetrically* bridged thiyl radical as previously utilized.[3] However, if a bridged intermediate is dominant in promoting the high **2**/**3** adduct ratio, a significant variation in the magnitude of this ratio would be anticipated as the thiol addendum is altered. Although additional accurate data are required, it appears that the proportions of adducts **2** to adducts **3** are very similar for most thiols under identical conditions. Furthermore, even *symmetrically* bridged sulfur radicals, if such are intermediates, cannot maintain configurational integrity in additions to acyclic olefins.[1]

On the other hand, preferential axial chain transfer has been established for the 4-*t*-butyl-[10] and 1-thiolacetylmethyl-4-*t*-butylcyclohexyl[4] radicals. The vicinal, axial 1-thiyl substituent of **6** should direct displacement at C-2 even more toward the axial position, and a bridged thiyl radical is not required.

A surprising observation is that the ratio **4**/**5** is relatively insensitive to reaction conditions. The "open-chain" intermediate **7** appears to control product formation; however, it is intriguing to note that *trans* addition is favored over *cis* addition (**4**/**5** $\sim$ 1.8–2.6). Investigations of additions of other thiols to 1- or 2-halo-4-*t*-butylcyclohexenes have indicated that thiolacetic acid seems to be unique in providing a **4**/**5** ratio > 1.[2,3] A possible rationale for this reversal could involve the five-membered, bridged intermediate **8** in equilibrium with **7**, since this pathway is unavailable to alkyl- and arylthiols. However, a dipolar factor may be contributory, particularly in light of the results reported for 1-methyl-4-*t*-butylcyclohexene and thiolacetic acid.[4]

In the present case, the observed concentration effect does not involve chair–chair interconversions,[7] but rather comes mainly from reversibility of the addition step complemented by a secondary effect of variable chain-transfer preference with the axial thiyl radical **6**.

In the full article we shall elaborate a general scheme to accommodate all available data on the stereochemistry of radical additions of thiols to cyclohexenes. The present report serves to clarify certain existing ambiguities and also emphasizes the need for complete product identification.

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Received February 6, 1967

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[9] It has been suggested that intermediates of type **7** arise by rapid and irreversible conformational reorganization of an initial twist-boat radical.[4,5]

[10] F. D. Greene, C. Chu, and J. Walia, *J. Am. Chem. Soc.*, **84**, 2463 (1962); *J. Org. Chem.*, **29**, 1285 (1964).

Coordination-Catalyzed Skeletal Rearrangement of 1,4-Dienes

Sir:

Our forthcoming publication[1] describes the addition of α-olefins to conjugated dienes, to produce high yields of 1,4-dienes. A homogeneous catalyst, prepared *in situ* from the reaction of a bis(tertiary phosphine)nickel(II) salt and an alkylaluminum compound, is employed. In an extension of this work we have investigated the behavior of the 1,4-diene products in the presence of the catalyst species.

3-Methyl-1,4-pentadiene (I, 0.012 mole), bis(tri-*n*-butylphosphine)nickel dichloride (0.001 mole), and diisobutylaluminum chloride (0.004 mole) were mixed in 100 ml of dry deoxygenated toluene. During 90 min at 24°, *ca.* 53% of I was converted to a mixture of products which included components with vpc retention times corresponding to a 35% yield of 1,4-hexadiene (*trans*:*cis* ratio = 11), a 4% yield of *trans*-2-methyl-1,-3-pentadiene, 8% *cis*-3-methyl-1,3-pentadiene, a 15% combined yield of *trans*-3-methyl-1,3-pentadiene and *trans,trans*-2,4-hexadiene, and 3% *trans,cis*-2,4-hexadiene. Two components, *ca.* 9 and 7%, have not been resolved and identified. The remainder was nonvolatile material, presumably oligomers of conjugated C-6 products.

It is apparent that the 3-methyl-1,3-pentadienes are derived from the double bond positional isomerization of I. However, the remaining products arise from skeletal rearrangements. A strong indication that the remaining C-6 conjugated products are derived from 1,4-hexadiene, as the primary rearrangement product, was found when *trans*-[2] and *cis*-1,4-hexadienes[3] were treated separately with the catalyst under the above conditions. During 120 min, 34% of the *trans* isomer was converted to *trans,trans*- and *trans,cis*-2,4-hexadiene (*trans,trans*:*trans,cis* ratio = 2.7) in 87% yield.

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[1] R. G. Miller, T. J. Kealy, and A. L. Barney, submitted for publication.

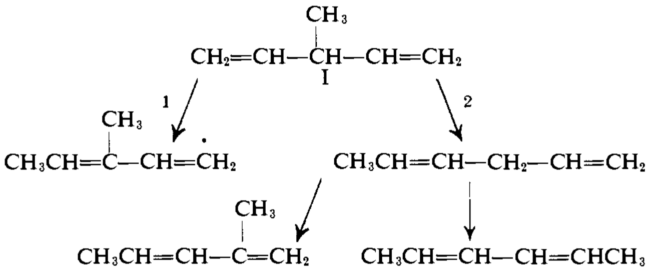
[2] T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **87**, 5638 (1965).

[3] G. Hata, *ibid.*, **86**, 3903 (1964).

The major product from the *cis*-1,4-hexadiene was derived from a skeletal rearrangement. In addition to the *trans,cis*- and *cis,cis*-2,4-hexadienes (*trans,cis*:*cis,cis* ratio = 4.0) afforded in 22% yield, a 75% yield of *trans*-2-methyl-1,3-pentadiene was obtained, the conversion of the 1,4-hexadiene to products being *ca.* 70%.[4]

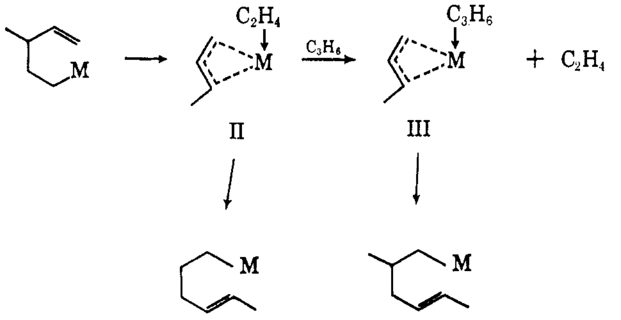
The products from all of these reactions were isolated and characterized in experiments in which the concentration of diene precursor was increased by a factor of 9–10 over those described above in order to provide sufficient material with which to work. In general, this led to lower yields of rearranged products. The compounds, after isolation by preparative vpc, were identified by their nmr and/or infrared spectra and by comparison of vpc retention times with those of authentic samples.[5] Proof that the reactions were indeed catalyzed by a species derived from the interaction of diisobutylaluminum chloride with bis(tri-*n*-butylphosphine)nickel dichloride in the presence of the dienes was obtained from a series of experiments in which I and the 1,4-hexadienes were mixed independently with the aluminum and the nickel catalyst precursors. In all cases, the 1,4-diene was recovered unchanged.

It appears that all of the characterized C-6 products from the interaction of I with the catalyst arise from two primary reaction paths: (1) the double bond positional isomerization of I, and (2) a skeletal rearrangement of I to afford the 1,4-hexadienes.

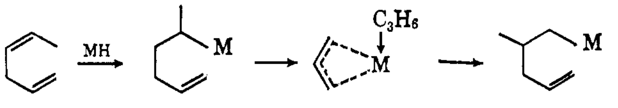


Information suggesting the nature of path 2 was obtained from experiments in which I was mixed with the catalyst in the presence of an excess of propylene. Admixture of 41 g (0.52 mole) of I with 81 g (1.9 moles) of propylene and the catalyst precursors (Al:Ni = 6:1, mmoles) in 400 ml of toluene for 19 min in the 86–90° range (same conditions as utilized for the codimerization of propylene and butadiene to give 2-methyl-1,4-hexadiene[1]) afforded a 9% yield of *trans*-2-methyl-1,4-hexadiene. Other products included 1,4-hexadiene (*trans*:*cis* ratio = 4) in 4.5% yield, *cis*-3-methyl-1,3-pentadiene in 5% yield, and *trans*-3-methyl-1,3-pentadiene in 5% yield based on 52% recovery of I. These compounds accounted for *ca.* 98% of the products in the 64–94° boiling point range.

The isolation of appreciable quantities of 2-methyl-1,4-hexadiene in these experiments suggests that interaction of the catalyst with I can lead to a species which possesses a C-4 fragment and ethylene bonded to nickel, such as II. Displacement of the ethylene by propylene could lead to a species like III from which 2-methyl-1,4-hexadiene results. The double bond positional isomerization of the 1,4-dienes and the rearrangement of I to 1,4-hexadiene could arise through the two possible modes of addition of a nickel hydride to a terminal double bond.[6] A 2,1 addition of NiH affords products that, on NiH elimination, could give either the 1,4-diene precursor or its conjugated isomers. However, the 1,2-addition products, possessing terminal C–Ni bonds, could give the 1,4-diene precursor or possibly generate ethylene and a C-4 fragment *via* a Ni–C *β* elimination.[7] The latter mode of reaction appears, at present, to offer the best rationalization of the formation of a C-7 diene from a C-6 precursor in these experiments. The possible participation of "fragmentation" products such as II or isomeric *σ*-methylallyl species is being investigated.



Although the rearrangement of I to 1,4-hexadiene can be explained by the intervention of elimination products such as II, other pathways cannot be excluded. The rearrangements of 1-methyl-1-pent-4-enyl derivatives of sodium, lithium, and magnesium[8] provide a close analogy to the gross rearrangement of I. The formation of 2-methyl-1,3-pentadiene from *cis*-1,4-hexadiene can be rationalized by a C–M elimination–addition route analogous to that suggested above. However, the expected diene product here is 2-methyl-1,4-pentadiene.



Our observation that the rate of rearrangement of *cis*-1,4-hexadiene exceeds the rate of double bond isomerization of 2-methyl-1,4-pentadiene and our failure to detect the latter diene in the rearrangement product mixtures indicate that if this process is operating here, the primary 1,4-diene product is isomerized before it becomes free of the metal.[9] Other

[4] No evidence was found that 2-methyl-1,3-pentadiene was produced from *trans*-1,4-hexadiene. The combined amount of *cis*-1,4-hexadiene and 2-methyl-1,3-pentadiene in the product mixture from the *trans* isomer was slightly less than the level of *cis*-1,4-hexadiene (3%) present in the starting material. This also eliminated the possibility that appreciable isomerization of *trans*- to *cis*-1,4-hexadiene took place under these conditions.

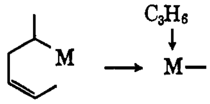
[5] Standard mixtures of most products described herein were analyzed by vpc to determine the relationship between mole ratio and relative signal intensity. Product ratios of 2-methyl-1,3-pentadiene were based on signal intensity alone.

[6] We have no evidence that would demonstrate the participation of an actual nickel hydride complex in these reactions. The results described here and elsewhere[1] are consistent with the capability of the catalyst to effect a gross addition of a nickel hydride to an olefinic bond.

[7] An accurate determination of the amount of ethylene present in product mixtures from the reaction of I, propylene, and the catalyst was not achieved. Vpc analyses of the recovered propylene indicated the presence of a component with the retention time of ethylene in amounts *ca.* 20–30 times that present in the propylene reagent. Butadiene was not detected in the reagents or in the product mixtures.

[8] (a) E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963); (b) E. A. Hill and J. A. Davidson, *J. Am. Chem. Soc.*, **86**, 4663 (1964).

[9] An alternative elimination–addition route involving a propenylnickel intermediate could give the conjugated diene directly.



pathways seem equally plausible, particularly one involving the participation of a cyclopropylcarbinylnickel derivative.[10]

Carbon–metal β-elimination products have been reported in the pyrolyses of neopentyl derivatives of sodium,[11] potassium,[12] and aluminum,[13] systems in which a β elimination of M–H is precluded. The rearrangements of cyclobutylcarbinyl[8b] and cyclopropylcarbinyl[10] Grignard reagents can be pictured as formally involving intramolecular C–M eliminations.

Further study of the 1,4-diene rearrangements and the extention of the investigation to other transition metal systems are in progress.

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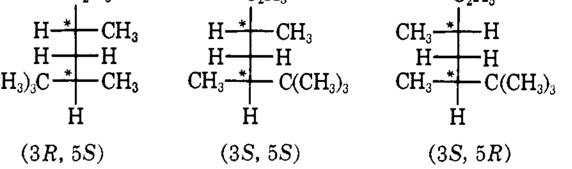
Conformational Rigidity[1,2] in Aliphatic Paraffins. Synthesis and Determination of Absolute Configuration of (3*S*,5*S*)- and (3*R*,5*S*)-2,2,3,5-Tetramethylheptane

Sir:

The high optical activity in solution of some stereoregular polymers obtained from optically active α olefins[3] has been attributed[2,4] substantially to the fact that few conformations having high optical rotation of the same sign are allowed for the monomeric unit of such polymers in solution.

As no low molecular weight paraffins were known having [*M*] of the same order of magnitude of the one found for the monomeric unit of these polymers, we have synthesized (3*R*,5*S*)- and (3*S*,5*S*)-2,2,3,5-tetramethylheptane (I and II, respectively); for I the existence of two conformations having [*M*] +180 and +60°, and for II the existence of one conformation having [*M*] −180° can be foreseen by the Brewster method[5] (Chart I).

Chart I



(3*R*, 5*S*) I (3*S*, 5*S*) II (3*S*, 5*R*) IX

A mixture of the two diastereoisomers I and II has been prepared starting with (−)(*S*)-3-methylpentanal, bp 120–121° (760 mm), $n^{25}\mathrm{D}$ 1.4002, $[\alpha]^{25}\mathrm{D}$ −7, 10°, having an optical purity of 97%,[6] and allowing it to react with *t*-butylmagnesium chloride.

The (−)(5*S*)-2,2,5-trimethylheptan-3-ol (III) thus obtained, bp 85° (20 mm), $n^{25}\mathrm{D}$ 1.4350, $d^{25}{}_4$ 0.8305, $[\alpha]^{25}\mathrm{D}$ −2.17° (neat) (*Anal.* Calcd for $C_{10}H_{22}O$: C, 75.88; H, 14.01. Found: C, 75.91; H, 13.80), was oxidized according to Brown[7] to (+)(*S*)-2,2,5-trimethylheptan-3-one (IV), bp 75° (22 mm), $n^{25}\mathrm{D}$ 1.4193, $d^{25}{}_4$ 0.8183, $[\alpha]^{25}\mathrm{D}$ +19.16° (neat) (*Anal.* Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.64; H, 12.96), which was allowed to react with methylmagnesium bromide, yielding (+)(5*S*)-2,2,3,5-tetramethylheptan-3-ol (V), bp 90° (20 mm), $n^{25}\mathrm{D}$ 1.4390, $d^{25}{}_4$ 0.8387, $[\alpha]^{25}\mathrm{D}$ +10.13° (neat) (*Anal.* Calcd for $C_{11}H_{24}O$: C, 76.67; H, 14.04. Found: C, 76.21; H, 14.06).

V was dehydrated by distillation in the presence of I_2 and the mixture of olefins thus obtained was finally hydrogenated at 120° by H_2 in the presence of Raney nickel, yielding a mixture of I and II, bp 61–62° (18 mm), $n^{25}\mathrm{D}$ 1.4202, $d^{25}{}_4$ 0.7465, $[\alpha]^{25}\mathrm{D}$ −0.69° (neat), $[\alpha]^{25}\mathrm{D}$ −0.83° (*c* 15, *n*-pentane). *Anal.* Calcd for $C_{11}H_{24}$: C, 84.52; H, 15.48. Found: C, 84.73; H, 15.59.

The mixture was analyzed by vpc (50-m squalane capillary column); only two components were present, the one with the higher retention time prevailing (60 ± 3%).

By fractional crystallization from propane at −80°, mixtures of I and II having different compositions have been obtained; a sample having a diastereoisomeric purity of 95% showed bp 54–55° (14 mm), $n^{25}\mathrm{D}$ 1.4208, $[M]^{25}\mathrm{D}$ −87.47 ± 0.1° (neat), $[M]^{25}\mathrm{D}$ −87.52 ± 1° (*c* 20.47, *n*-pentane). *Anal.* Calcd for $C_{11}H_{24}$: C, 84.52; H, 15.48. Found: C, 84.81; H, 15.22.

By plotting the composition of such mixtures *vs.* their optical rotation and extrapolating at 100% of diastereoisomeric purity, the optical rotation has been calculated for both diastereoisomers.

Taking in account the optical purity of the starting material we have assigned $[M]^{25}\mathrm{D}$ +137.8 ± 3° (*c* 20.47, *n*-pentane)[8] to the lower retention time diastereoisomer, $[M]^{25}\mathrm{D}$ −97.5 ± 4° to the higher retention time diastereoisomer.

In order to establish the relationship between the sign of the optical rotatory power and the absolute configuration of the two asymmetric carbon atoms of the diastereoisomers we have prepared a mixture of (3*S*,5*S*)- and (3*S*,5*R*)-2,2,3,5-tetramethylheptane (II and IX, respectively), starting with (−)(*R*)-2,3,3-trimethylbutan-1-ol, $[\alpha]^{25}\mathrm{D}$ −15.5° (*c* 3.41, ethanol), optical purity 37.4%.[9] (−)(*R*)-1-chloro-2,3,3-trimethylbutane (VI), bp 89–91° (158 mm), $n^{20}\mathrm{D}$ 1.4313, $d^{25}{}_4$ 0.8872, $[\alpha]^{25}\mathrm{D}$ −19.93° (neat) (*Anal.* Calcd for $C_7H_{15}Cl$: C, 62.44; H, 11.23; Cl, 26.33. Found: C, 62.39; H, 11.15; Cl, 26.44), was obtained from the alcohol by reaction with $SOCl_2$ in pyridine, and its Grignard reagent was allowed to react with propanal.

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(8) Standard deviation calculated by the least-squares method.

(9) The optical purity has been calculated on the basis of the pure (−)(*R*)-2,3,3-trimethylbutan-1-ol, $[\alpha]^{25}\mathrm{D}$ −41.4°: M. Farina and E. M. Peronaci, *Chim. Ind.* (Milan), **48**, 602 (1966); *Chem. Abstr.*, **65**, 12091*a* (1966).