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COUPLING OF OPTICALLY ACTIVE ORGANOBORANES: ALKANES CONTAINING TWO CHIRAL CENTRES

Summary — Optically active hydrocarbons containing two chiral centres are prepared by reaction of trialkylboron compounds with alkaline silver nitrate in methanol solution. The stereospecificity of the process is evaluated on the basis of the optical rotations of the same alkanes obtained through independent sequences. At last the maximum rotations so established are compared with those calculated by a semiempirical method.

Riassunto — *Boro alchili otticamente attivi: sintesi di alcani con due centri chirali.* Viene descritta la preparazione di alcune paraffine otticamente attive, aventi due centri chirali, mediante dimerizzazione di boro alchili con nitrato di argento ed alcali in metanolo. Vengono valutati i poteri rotatori massimi delle paraffine preparate e confrontati con i valori ottenuti mediante calcoli semiempirici.

Treatment of an alkaline solution of organoboranes with silver nitrate is an useful method for the synthesis of symmetrical and unsymmetrical alkanes, since the reaction proceeds very mildly and with excellent yields. (H. C. BROWN and C. H. SNYDER, 1961; S. W. BREUER and F. A. BROSTER, 1972; R. MURPHY and R. H. PRAGER, 1976). However to date no optically active organoborane has been used, and the stereospecificity of the coupling reaction is still unknown. In the course of synthetic works concerning the preparation of alkanes and dienes having two chiral centres A. M. CAPO-RUSSO et al., 1976; G. P. GIACOMELLI et al., 1978 a), it had appeared useful to known the maximum rotatory power of the correspond-

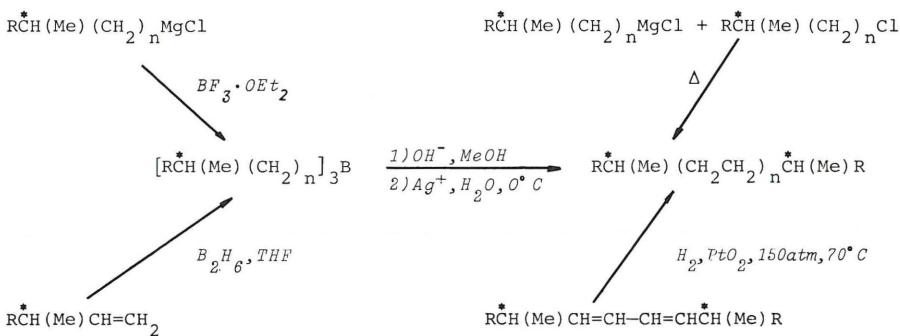
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ing optically active paraffins, to which the unsaturated compounds could be easily correlated. The availability of optically active alkylboranes of suitable structures had therefore prompted us to undertake the synthesis and the determination of the relationship optical activity-optical purity of some chiral alkanes of general formula.

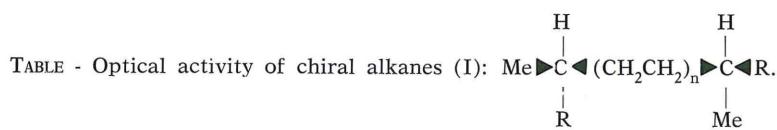


The preparation of (**I**) was generally achieved by reaction of the appropriate trialkylboron compound $[\overset{*}{\text{RCH}}(\text{Me})(\text{CH}_2)_n]_3\text{B}$ (**II**) with potassium hydroxide in methanol solution, followed by dropwise addition of silver nitrate in aqueous solution at 0°C: in all cases the yields were nearly quantitative. Compounds (**II**) ($n = 1$) were prepared directly from the corresponding alkyl chloride, while compounds (**II**) ($n = 2$) were obtained through hydroboration of the suitable chiral α -olefin (Scheme).

Scheme



Since the stereospecific conversion of the alkanes (**I**) into convenient substrates was not possible, the extent of racemization was indirectly evaluated by comparison of the rotatory powers of (**I**) with those of the same alkanes prepared through independent sequences (Scheme), such as Wurtz-like reactions and hydrogenation of the appropriate optically active diene compound. The data obtained (Table) have shown that all methods afforded (**I**) with comparable optical rotations.



R	n	$[\text{M}]_D^{25}$			Number of allowed conformations ^c
		Maximum experimental value ^a	Method ^b	Calculated value ^c	
Et	1	+ 28.3 ^d	A	+ 30	14
		+ 23.8	A ^e		
		+ 29.0	B		
Et	2	+ 30.5 ^f	A	+ 27	77
		+ 27.8	A ^e		
		+ 30.5	C		
Pr ⁱ	1	+ 56.5	A	+ 60	27
		+ 56.5	B		
Pr ⁱ	2	+ 64.1	A	+ 71	138
		+ 63.9	B		
Bu ^t	1	+149.4	A	+150	2
		+149.2	B		
Bu ^t	2	+159.2	A	+193	9
		+159.0	C		

^a Based on the optical purity of the starting intermediate. ^b Methods: A - silver ion induced coupling. B - Wurtz-like reaction. C - hydrogenation of the diene. ^c According to Brewster. ^d R. L. LETSINGER (1948), P. PINO *et al.* (1962), L. LARDICCI and L. LUCARINI (1964). ^e In diglyme. ^f L. LARDICCI and P. PINO (1961), P. PINO *et al.* (1963), L. LARDICCI and L. LUCARINI (1964).

Moreover, taking into account the good results obtained by Brewster's empirical method (J. H. BREWSTER, 1974) in the calculation of the rotatory power at the D line of optically active low

molecular weight alkanes, we have evaluated the optical rotations of (**I**) by using the Brewster's rules. As shown in the Table, the sign and the magnitude of the experimental molar rotations of the synthesized alkanes correspond, within the accuracy limits applied, to that predicted by the Brewster's method, with the exception of (**I**) ($R = Bu^t$, $n = 2$), the calculated rotation being in this case larger than 15% with respect to the experimental value.

Therefore all data obtained indicate that the coupling process is to be considered nearly stereospecific at least in the cases investigated providing that dimerization of the radical intermediate is faster than racemization. It is however noteworthy that, when the coupling reaction is carried out in diglyme, a certain degree of racemization is observed even when the chiral centre is in the γ -position with respect to the metal atom (Table).

EXPERIMENTAL

(*3S, 6S*)-3,6-dimethyloctane - A) A 2M solution of potassium hydroxide in methanol (25 ml) was added at 0°C, over 0.5 h, with efficient stirring to a solution of tris [(R)-2-methylbutyl] boron (**II**), $[\alpha]^{25}_D + 49.50$, (P. PINO et al, 1962) (28.4 mmol), followed by the dropwise addition of a 5M aqueous solution of silver nitrate (22 ml). The mixture was stirred at 25°C (2h), then the paraffin separated by steam distillation. The organic phase was washed with water, extracted with pentane and dried. The solvent was then removed by distillation and the alkane isolated in 97% yield; b.p. 159°C, $n^{25}_D 1.4113$, $[\alpha]^{25}_D + 19.07$. By analogous procedure, carried out in diglyme instead of methanol, (**I**) ($R = Et$, $n = 1$), $[\alpha]^{25}_D + 16.01$, was obtained (76% yield). B) An ether solution of (*S*)-1-chloro-2-methylbutane, $[\alpha]^{25}_D + 1.60$ (L. LARDICCI, 1961), (14 mmol) was added slowly to magnesium turnings (7 mgatoms), and the mixture refluxed for 4 h. After hydrolysis, the organic phase, separated and dried, afforded by preparative g.l.c., (**I**) ($R = Et$, $n = 1$), $[\alpha]^{25}_D + 20.01$.

(*3S, 6S*)-2,3,6,7-tetramethyloctane - A) From tris[(*S*)-2,3-dimethylbutyl]boron, $[\alpha]^{25}_D - 34.20$ (toluene) (G. P. GIACOMELLI et al., 1978 b) (**I**) ($R = Pr^i$, $n = 1$) was recovered in 95% yield; b.p. 97°C (38 mm), $d^{25}_D 0.7632$, $[\alpha]^{25}_D - 24.04$ (Found C, 84.6; H, 15.3. $C_{12}H_{26}$ requires C, 84.6; H, 15.4%). B) From (*R*)-1-chloro-2,3-dimethylbut-

ane, $[\alpha]^{25}_D = 7.19$ (A. M. CAPORUSSO et al., 1973) (**I**) ($R = \text{Pr}^i$, $n = 1$), $[\alpha]^{25}_D = 24.04$ was recovered by preparative g.l.c.

(*3S, 6S*)-2,2,3,6,7,7-hexamethyloctane - a) From tris[(*S*)-2,3,3,-trimethylbutyl]boron, $[\alpha]^{25}_D = 43.67$ (toluene), (G. P. GIACOMELLI et al., 1978 b) (**I**) ($R = \text{Bu}^t$, $n = 1$) was obtained in 98% yield; b.p. 103°C (18 mm), n^{25}_D 1.4328, d_4^{25} 0.7791, $[\alpha]^{25}_D = 61.17$ (Found C, 84.6; H, 15.0. $C_{14}H_{30}$ requires C, 84.8; H, 15.2%). b) From (*R*)-1-chloro-2,3,3-trimethylbutane, $[\alpha]^{25}_D = 44.21$ (A. M. CAPORUSSO et al., 1973), (**I**) ($R = \text{Bu}^t$, $n = 1$), $[\alpha]^{25}_D = 65.13$ was recovered.

(*3S, 8S*)-3,8-dimethyldecane - a) From tris[(*S*)-3-methylpentyl]-boron, $[\alpha]^{25}_D + 15.63$, (P. PINO et al., 1962), (**I**) ($R = \text{Et}$, $n = 2$) was recovered in 95% yield; b.p. 80°C (15 mm), n^{25}_D 1.4218, d_4^{25} 0.7514, $[\alpha]^{25}_D + 17.29$. The reaction, when carried out in diglyme, afforded (**I**) ($R = \text{Et}$, $n = 2$), $[\alpha]^{25}_D + 15.73$. c) A solution of (*E, Z*) (*3S, 8S*)-3,8-dimethyldeca-4,6-diene, $[\alpha]^{25}_D + 54.14$ (heptane) (G. P. GIACOMELLI et al., 1978 a) (1g) in methanol (2 ml) was hydrogenated over PtO_2 (20 mg) at 150 atm and 70°C (1 h). After removal of the catalyst, (**I**) ($R = \text{Et}$, $n = 2$), $[\alpha]^{25}_D + 15.52$, was recovered in 55% yield.

(*3R, 8R*)-2,3,8,9-tetramethyldecane - a) From (*S*)-2,3-dimethylpent-1-ene, $[\alpha]^{25}_D + 26.91$ (A. M. CAPORUSSO et al., 1973) through hydroboration procedure in THF, followed by silver ion induced coupling, (**I**) ($R = \text{Pr}^i$, $n = 2$) was obtained in 99% yield; b.p. 115°C (20 mm), d_4^{25} 0.7698, $[\alpha]^{25}_D + 19.56$ (Found C, 84.7; H, 15.1. $C_{14}H_{30}$ requires C, 84.8; H, 15.2%). b) From (*S*)-1-chloro-3,4-dimethylpentane, $[\alpha]^{25}_D = 24.70$, (A. M. CAPORUSSO et al., 1973), (**I**) ($R = \text{Pr}^i$, $n = 2$), $[\alpha]^{25}_D = 23.37$ was recovered by preparative g.l.c..

(*3R, 8R*)-2,2,3,8,9,9-hexamethyldecane - a) From (*R*)-3,4,4-trimethylpent-1-ene, $[\alpha]^{25}_D + 27.62$ (A. M. CAPORUSSO et al., 1973) (**I**) ($R = \text{Bu}^t$, $n = 2$) was obtained in 93% yield; b.p. 83°C (0.7 mm), n^{25}_D 1.4391, d_4^{25} 0.7869, $[\alpha]^{25}_D + 46.28$ (Found C, 84.7; H, 14.9. $C_{16}H_{34}$ requires C, 84.9; H, 15.1%). c) From (*E, E*) (*3S, 8S*)-2,2,3,8,9,9-hexamethyldeca-4,6-diene, $[\alpha]^{25}_D = 88.02$ (heptane), (G. P. GIACOMELLI et al., 1978 a) (**I**) ($R = \text{Bu}^t$, $n = 2$), $[\alpha]^{25}_D = 56.80$, was recovered in 73% yield through hydrogenation.

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