

stant as long as sufficient complex was present to absorb all of the incident light. The several mechanistic pathways consonant with these findings cannot be distinguished without detailed quantum yield studies. Work to these ends is now underway.

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Synthesis of *meso*-, *rac*-, and (-)-(4*R*, 6*R*)-2,4,6,8-Tetramethylnonane, the Simplest Low Molecular Weight Model Compounds of Isotactic and Syndiotactic Polypropylene

Sir:

No low molecular weight models of the two known^{1,2} crystalline diastereoisomeric polypropylenes have been prepared up to now. We wish to report the preparation, the separation, and the identification of the two diaster-

The paraffin has been shown by v.p.c. (90-m. squalane capillary column)⁵ to be a mixture of two components only, that having the larger retention time predominating (54%). The two components, separated by accurate rectification, controlling the composition of the 34 fractions by v.p.c., were in fact the two possible diastereoisomers of 2,4,6,8-tetramethylnonane as shown by identical elemental composition, molecular weight, and MRD by different boiling and melting points (Table I), by infrared spectra that were practically identical in the C-H stretching region but remarkably different in the region between 1400 and 700 cm.⁻¹ (Figure 1), and by n.m.r.⁶ spectra (Figure 2) which were different.

In order to establish which of the two diastereoisomers was the *meso* (isotactic, a) and which was the racemic (syndiotactic, b), the optically active mixture was prepared by the same method, starting with (+)(*R*)-2,6,8-trimethylnonan-4-one (II).

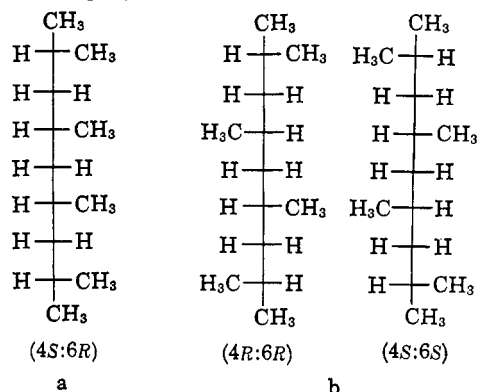
Compound II was prepared starting with 2,4-dimethylpentanoic acid which had been resolved as re-

Table I

Compound	B.p., °C. (mm.)	M.p., °C.	Analysis, %		Mol. wt., ^b Found	<i>n</i> _D ²⁵	<i>d</i> ₄ ²⁵	MRD, ^c found
			C	H				
a ^d	82.5 (20)	-58 to -56	84.71	15.27	188	1.4192	0.7469	62.35
b ^e	85 (22)	-60 to -58	84.74	15.12	188	1.4187	0.7460	62.36

^a Calcd. for C₁₃H₂₈: C, 84.69; H, 15.31. ^b Calcd. for C₁₃H₂₈: 184.36. ^c Calcd.: 62.40. ^d Steric purity ~95%. ^e Steric purity >98%.

eoisomers of 2,4,6,8-tetramethylnonane, which is the simplest paraffin of the type CH₃(CH(CH₃)CH₂)_nCH(CH₃)₂ existing in two diastereoisomeric forms (shown in the Fischer projections a and b).



By allowing 2,6,8-trimethylnonan-4-one^{3,4} to react with methylmagnesium bromide, 2,4,6,8-tetramethylnonan-4-ol (I), b.p. 110° (17 mm.), *n*_D²⁰ 1.4393 (*Anal.* Found: C, 77.88; H, 13.88), has been obtained.

The alcohol on dehydration by rapid distillation in the presence of iodine gave a mixture of isomeric olefins which by hydrogenation (H₂) in the presence of Raney nickel at 120° yielded 2,4,6,8-tetramethylnonane. *Anal.* Found: C, 84.05; H, 15.15; mol. wt. (cryoscopic in benzene), 187.

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ported by Levene and Bass.⁷ From a sample of acid having [α]_D²⁰ -8.42° (neat) (optical purity 40%), by reduction with LiAlH₄ and reaction with PBr₃ (+)(*R*)-1-bromo-2,4-dimethylpentane⁸ (III) was obtained; [α]_D²⁰ +2.91° (neat).

The Grignard compound prepared starting with III was treated with 3-methylbutanal, yielding (-)(6*R*)-2,6,8-trimethylnonan-4-ol, [α]_D²⁰ -1.14° (neat), which by chromic acid oxidation yielded II, [α]_D²⁰ +2.62° (neat).

The mixture of paraffins α¹⁷_D (*l* = 1) -1.92 ± 0.025° (neat, 1-dm.) which contained 46 ± 2% of the isomer with lower retention time yielded, by rectification, optically active fractions the composition of which was determined by v.p.c. (Perkin-Elmer Model F 11 vapor fractometer, 2-m. column of Apiezon L on Chromosorb P, flame ionization detector, 105°).

A plot of the rotation of the fractions measured in a microtube (accuracy of ±0.025°) against their composition is linear and extrapolates to α¹⁷_D +0.04 ± 0.05° (neat, 1 dm.)⁹ for the lower boiling isomer, indicating that this isomer is the *meso* (isotactic) diastereoisomer (a) while the higher boiling diastereoisomer, which has α¹⁷_D (*l* = 1) -3.75 ± 0.05° (1 dm.)⁹ and [M]¹⁷_D (extrapolated to 100% optical purity) -23.0 ± 0.3°, in good agreement with the value calculated according to Brewster (-24°), is the *R*:*R* (syndiotactic) diastereoisomer (b).

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(6) We thank Dr. Iavarone of the Institute of Organic Chemistry of the University of Rome for the determination of some n.m.r. spectra.

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

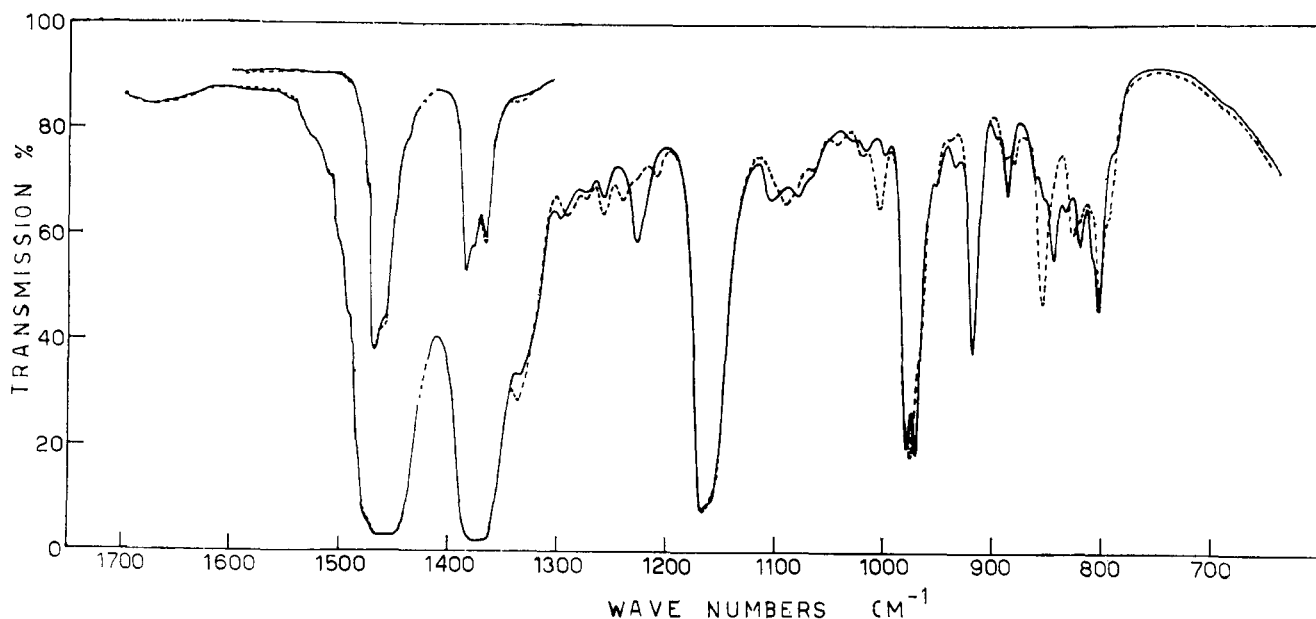


Figure 1. Infrared spectra of — higher boiling paraffin, and ----- lower boiling paraffin, between 1700 and 650 cm^{-1} .

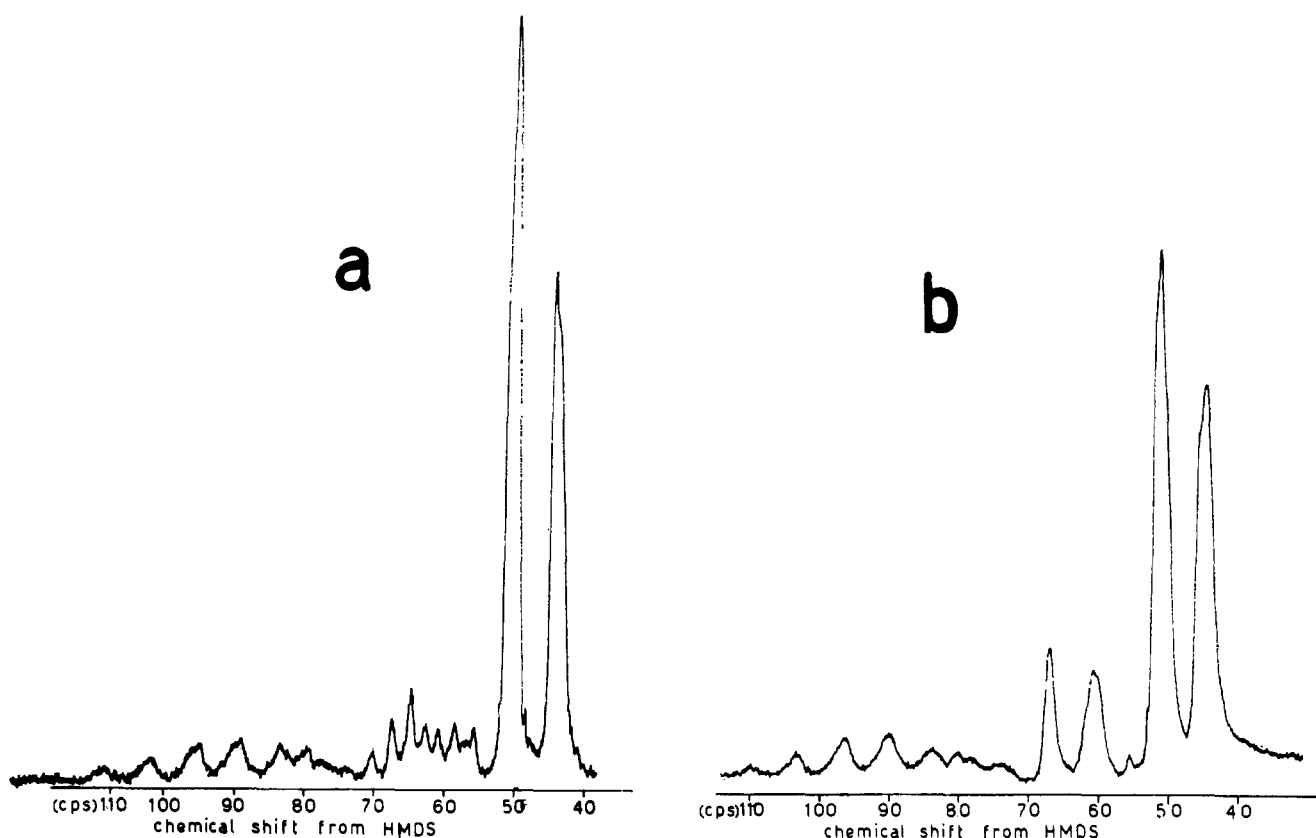


Figure 2. N.m.r. spectra (60 Mc.p.s.) of (a) lower boiling paraffin and (b) higher boiling paraffin in 15% *o*-dichlorobenzene solution (160°).

The peculiar similarity of the infrared and n.m.r. spectra of the diastereoisomers a and b with the corresponding spectra, respectively, of isotactic and syndiotactic polypropylene¹⁰⁻¹⁶ confirms the structure origi-

nally proposed^{1,2} for the two crystalline polymers of propylene.

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