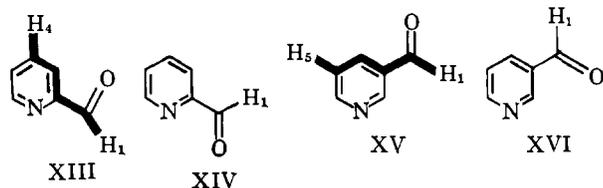


(5) H_1 of pyridine-4-carboxaldehyde is a triplet with $J = 0.35$ c.p.s. J_{H_1, H_4} of pyridine-2-carboxaldehyde is 0.60 c.p.s. in dimethyl sulfoxide and 0.50 c.p.s. in carbon tetrachloride. J_{H_1, H_6} of pyridine-3-carboxaldehyde is 0.44 c.p.s. in carbon tetrachloride⁸; we find it to be 0.50 c.p.s. in dimethyl sulfoxide. If these aldehydes are planar, then pyridine-2-carboxaldehyde exists 70–85% as XIII and 15–30% as XIV. Similarly, pyridine-3-



carboxaldehyde exists approximately 70% as XV and 30% as XVI.

The preference of certain conformations over others can be readily explained in terms of competitive hydrogen bonding and dipole, electrostatic, and resonance interactions.

Acknowledgment.—We thank the United States Atomic Energy Commission for financial support, Grant AT(11-1)-1189.

(8) V. J. Kowalewski and D. G. de Kowalewski, *J. Chem. Phys.*, **36**, 266 (1962).

(9) Fellow of the Alfred P. Sloan Foundation.

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RECEIVED SEPTEMBER 16, 1963

Preparation of Solutions of Pure Nitrous Acid

Sir:

The existence of solutions of pure nitrous acid has not been previously reported in the literature and the following technique for their production has been developed. Solutions of sodium nitrite in mixtures of water and ethylene glycol dimethyl ether (glyme) are ion exchanged at -30° to produce effluent solutions of relatively pure nitrous acid.

The process was originally used for the preparation of pure polyamine nitrites by direct neutralization, but can also be used to prepare the nitrites of other cations or for nitrosation and diazotization reactions.

Following is a typical example of the generation of nitrous acid solutions: A 1×16 -cm. column of acid form Dowex 50W-X4 was equilibrated at -30° with a 66% solution of glyme in water. Through this column at -30° was passed 0.284 g. (4.12 mequiv.) of NaNO_2 as a 3% solution in 66% glyme-water. Flow rate was 12 ml./min. which gave a column residence time of about 24 sec. The nitrite solution was followed by 30 ml. of glyme-water.

Column effluent was collected in water containing 5.57 mequiv. of KOH, and back titration of the effluent solution showed a recovery of 97% of theoretical acidity.

Recovery of NO_2^- was determined by the following methods. The neutralized effluent was purged with N_2 through a gas diffusion tube to eliminate the possible presence of dissolved nitrogen oxide gases. A sample of neutralized and purged effluent was then titrated with ceric sulfate which showed a recovery of 94% of the NO_2^- . Evaporation of a portion of the neutralized effluent gave a weight balance which also corresponded to a 94% recovery of HNO_2 . Less than 4 p.p.m. of sodium was found in the effluent solution (about 0.01 mequiv.). These results indicate that the production of nitrous acid is nearly quantitative, allowing for a

small amount of column holdup and analytical inaccuracies. If the difference between 97% acidity recovery and 94% nitrite recovery is real, then this may represent decomposition of HNO_2 to HNO_3 and NO . However, the solids recovered are entirely accountable for as KNO_2 , which refutes the decomposition. The fate of about 3% of the HNO_2 therefore remained uncertain.

Yost and Russell¹ report the rate of decomposition of nitrous acid as being proportional to the fourth power of nitrous acid concentration, and very temperature dependent. This extreme dependence of rate on concentration and temperature showed the importance of operating at low temperatures and concentrations in order to prepare pure HNO_2 .

The effect of concentration is illustrated by the 98% recovery of nitrous acid at as high a temperature as 0° when the NaNO_2 concentration was reduced to 1.17%.

The applicability of this technique is limited mainly by the need for a nonreactive solvent system which will hold usable amounts of nitrite salts at low temperature. In this work, the glyme-water system was found most useful, although three-component freezing-point diagrams were also explored for NaNO_2 -water with dimethyl ether, dimethyl sulfoxide, acetone, and methanol. It is quite possible that the reactivities of the last three toward HNO_2 would limit their usefulness. Temperatures of phase separation for the NaNO_2 -glyme-water system are shown in Table I.

NaNO ₂	Composition, % Glyme	Water	Temperature of phase separation, °C.
7	45	48	-35
8	60	32	-5
8.68	41.3	50	-34
10	50	40	-26
10	40	50	-29
14	30	56	-20

For those interested in extremely low temperatures, the following may be useful: A -44° freezing point is achieved with 12% NaNO_2 , 40% dimethyl sulfoxide, and 48% water. A -50° freezing point is achieved with 12% NaNO_2 , 38% methanol, and 50% water.

(1) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, New York, N. Y., 1946, pp. 58-61.

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CLYDE S. SCANLEY

RECEIVED SEPTEMBER 14, 1963

Optically Active Vinyl Polymers. X. Synthesis of Optically Active Poly- α -olefins from Racemic Monomers by Asymmetric Catalysts

Sir:

Although the resolution of the polymers of some racemic α -olefins in fractions having optical activity of opposite sign¹ seems to indicate that the polymerization rate of the two antipodes on a single catalytic center is remarkably different, no asymmetric catalyst which electively polymerizes one of the two antipodes of racemic α -olefins has been described.²

The polymerization of racemic 3,7-dimethyl-1-octene and 3-methyl-1-pentene has been investigated now using catalysts prepared from TiCl_4 and bis[(S)-2-methylbutyl]zinc having $[\alpha]^{25D} +9.93^\circ$ (optical purity 96%).³

(1) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Natta, *J. Am. Chem. Soc.*, **84**, 1487 (1962).

(2) P. Pino, F. Ciardelli, and G. P. Lorenzi, paper presented at the International Symposium of Macromolecular Chemistry, Paris, July 1-6, 1963.

TABLE I
POLYMERIZATION OF RACEMIC 3-METHYL-1-PENTENE AND 3,7-DIMETHYL-1-OCTENE IN THE PRESENCE OF (+)-BIS[(S)-2-METHYL-BUTYL]-ZINC/TiCl₄ CATALYST

Monomer	Run	Polymerization conditions				Recovered monomer		
		ZnR ₂ moles ^a TiCl ₄ moles	Olefin moles ZnR ₂ moles ^a	T, °C.	Duration, hr.	α ²⁵ D, deg.	[α] ²⁵ D, deg.	Optical purity, %
3-Methyl-1-pentene	A	2.1	4.7	20-25	236	-0.07 ^{b,c}	-0.75 ^e	2.0 ^g
3,7-Dimethyl-1-octene	B	2.8	5.0	20-25	111	-0.20 ^d	-0.28 ^f	1.7 ^h
				50	20			
3,7-Dimethyl-1-octene	C	2.8	5.1	20-25	279	-0.36 ^d	-0.52 ^f	3.2 ^h

^a R = (S)-2-methylbutyl. ^b After purification by Br₂ addition and regeneration of the olefin by Zn in methanol. ^c *l* = 2 dm.; *c* = 4.7 g./dl., methanol. ^d After purification by distillation on Na; *l* = 1 dm. ^e In methanol solution. ^f Homogeneous. ^g Taking for the optically pure 3-methyl-1-pentene [α]²⁵D 36.0° (*c* 4.65 g./dl., methanol solution). ^h Taking for the optically pure 3,7-dimethyl-1-octene [α]²⁵D 16.3° (homogeneous).

TABLE II
RELATIVE POLYMERIZATION RATE^a OF (S) AND (R) ANTIPODES IN THE PRESENCE OF (+)-BIS[(S)-2-METHYL-BUTYL]ZINC/TiCl₄ CATALYST

Run	Initial monomer, g.	Total polymer, g.	Conversion, ^b %	Recovered monomer		Polymerized monomer		Optical purity, %	Relative polymerization rate ^a
				(S)antipode, ^c moles × 100	(R)antipode, ^c moles × 100	(S)antipode, ^d moles × 100	(R)antipode, ^d moles × 100		
A	2.9	0.21	7.2	1.57	1.63	0.15	0.10	20.0	1.50
B	3.5	0.51	14.6	1.04	1.08	0.20	0.16	11.1	1.25
C	5.4	1.17	21.7	1.46	1.55	0.46	0.37	10.8	1.24

^a Moles of polymerized (S) monomer/moles of polymerized (R) monomer. ^b Weight of the total unfractionated polymer after precipitation with methanol/weight of the initial monomer. ^c Calculated from the optical purity and the weight of recovered monomer. The weight was evaluated subtracting the weight of the polymer from the weight of the initial monomer. ^d Evaluated as the difference between moles of initial monomer/2 and moles of recovered antipode of the same absolute structure.

TABLE III
PHYSICAL PROPERTIES OF DIFFERENT FRACTIONS OF POLY-3,7-DIMETHYL-1-OCTENE OBTAINED BY POLYMERIZATION OF THE RACEMIC MONOMER WITH (+)-BIS[(S)-2-METHYL-BUTYL]ZINC/TiCl₄ CATALYST (RUN B)

Fraction ^a	%	α ^D (<i>l</i> = 1), deg.	[α] _D , deg.	[η] _D ^b , dl./g.	M.p., °C ^c
Acetone sol.	49.2	+0.46 ^d	+7.8 ^d	n.d.	...
Acetone insol., ethyl acetate sol.	14.6	+0.28 ^d	+12.6 ^d	0.22	147-150
Ethyl acetate insol., diethyl ether sol.	8.0	+0.10 ^e	+12.1 ^e	0.28	n.d.
Diethyl ether insol., diisopropyl ether sol.	9.2	+0.13 ^f	+17.5 ^f	n.d.	198-202
Diisopropyl ether insol., cyclohexane sol.	19.0	+0.11 ^f	+18.0 ^f	0.91	242-248

^a Obtained by exhaustive extraction of the polymer with boiling solvents in a Kumagawa apparatus. ^b Determined in tetralin at 120°. ^c Determined by X-ray method. ^d At 25° in benzene. ^e At 50° in benzene. ^f At 25° in cyclohexane.

By polymerizing from 7 to 22% of the monomer, the recovered nonpolymerized α-olefin, after accurate purification, showed a measurable optical activity (Table I). The sign of the rotatory power of the recovered monomer indicates that, in both cases, the monomeric antipode preferentially polymerized is the one having the same absolute structure⁴ of the optically active 2-methylbutyl groups present in the catalytic mixture.

From the optical activity of the recovered monomers and from the extent of conversion of the monomers to polymer it appears that, in the range of conversions and in the experimental conditions we have adopted, the ratio between the over-all polymerization rate of the two antipodes is between 1.2 and 1.5 (Table II).

The optical activity of the polymer fractions does not decrease at the increase of the viscosity average molecular weight (\bar{M}_v) and stereoregularity as observed in the polymers in which the optical activity is mainly due to the influence of the optically active terminal groups.^{2,5,6} In fact, in the case of the poly-3,7-dimethyl-1-octene, the optical activity increases at the increase of the \bar{M}_v and the melting point, that is the stereoregularity, of the fraction (Table III).

The optical purity of the low molecular weight fractions soluble, respectively, in acetone, ethyl acetate, and ethyl ether cannot be evaluated, owing to the relatively

large contribution to the optical rotation by the (S)-2-methylbutyl terminal groups.⁷ For the last fraction, which is a stereoregular high molecular weight fraction, the optical purity can be estimated on the basis of the optical activity of the corresponding fraction obtained in the polymerization of (R)-3,7-dimethyl-1-octene, having optical purity of 75%⁸; the optical purity thus calculated is about 12% and therefore is not very different from the optical purity of the polymerized monomer (Table II).

In the case of the poly-3-methyl-1-pentene, the increase of the optical activity of the fractions at the increase of their stereoregularity is smaller; in fact, the acetone insoluble, ethyl acetate soluble fraction has [α]²⁵D +13.1° (benzene, *c* 0.534 g./dl.), and the diethyl ether insoluble, benzene soluble fraction has [α]⁶⁰D +14.5° (benzene, *c* 1.029 g./dl.).

The above results show that by treating TiCl₄ with bis[(S)-2-methylbutyl]zinc, an asymmetric catalyst for the polymerization of α-olefins is obtained which is able to polymerize preferentially the (S) antipode of a racemic α-olefin having an asymmetric carbon atom in the α position with respect to the double bond.

However, at the present it is not possible to establish if the (S)-2-methylbutyl group, originally bound to the zinc, which initiates most⁷ of the polymer chains, is responsible for the preferential polymerization of one enantiomer of the racemic monomer, or if the particular stereoselectivity of the process is connected with the presence of one or more asymmetric alkyl groups, di-

(3) L. Lucarini, Thesis, Univ. of Pisa, 1963. We thank Drs. L. Lardicci and L. Lucarini for a sample of (+)-bis[(S)-2-methylbutyl]zinc.

(4) (S)-3-Methyl-1-pentene is dextrorotatory [P. Pino, L. Lardicci, and L. Centoni, *J. Org. Chem.*, **24**, 1399 (1959)]; (R)-3,7-dimethyl-1-octene is levorotatory [J. von Braun and W. Teuffert, *Ber.*, **62**, 235 (1929)].

(5) D. Braun and W. Kern, paper presented at the International Symposium of Macromolecular Chemistry, Paris, July 1-6, 1963.

(6) H. L. Frisch, C. Schuerch, and M. Szwarc, *J. Polymer Sci.*, **11**, 559 (1953).

(7) G. Natta, I. Pasquon, and L. Giuffrè, *Chim. Ind. (Milan)*, **43**, 871 (1961).

(8) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Montagnoli, *Makromol. Chem.*, **61**, 207 (1963).

rectly bound to the catalytic center, which cause the preferential absorption of one antipode at the transition metal.

Further work is in progress to establish the possible influence of different metal alkyls and transition metals on the stereoelectivity of the process and to obtain more information on the structure of the optically active polymers we have synthesized.

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RECEIVED OCTOBER 9, 1963

Stereochemical Consequences of Ion-Pair Formation Involving Carbanions

Sir:

Earlier work¹ demonstrated that base-catalyzed hydrogen isotope exchange between hydroxylic solvent and the benzyl position of 2-phenylbutane (I) could be made to occur with high retention, total racemization, or net inversion, depending on the solvent used. The

With ammonia as base, k_e and k_a increased by an estimated 10^5 to 10^7 in passing from *tert*-butyl alcohol to tetrahydrofuran to methanol to dimethyl sulfoxide (runs 3, 1, 10, and 9). This fact points to formation of a highly charged transition state from noncharged starting materials. With propylamine as base in tetrahydrofuran, addition of either lithium bromide or propylammonium acetate (0.5 *N*) increased the rates by 10^2 to 10^3 (runs 2, 5, and 7). A similar salt effect has been observed in carbonium ion formation from uncharged starting materials in nonpolar solvents.³ These striking medium effects point to carbanion formation in the isotopic exchange reactions.

The values of k_e/k_a varied from about 148 (exchange with high retention) to 1 (complete racemization) to 0.69 (high inversion), depending on the base-solvent system. In tetrahydrofuran with ammonia as base, $k_e/k_a \sim 148$ (run 1). The formulas provide an interpretation of this result.^{1b}

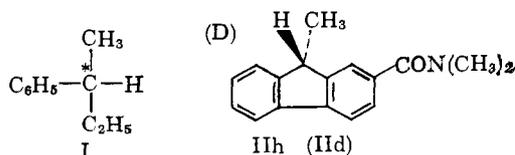
These data provide strong evidence for formation of an ammonium carbanide ion pair, which dissociates in tetrahydrofuran much slower than the ammonium ion rotates and collapses (k_{-1} and $k_3 \gg k_2$). Isotope effect evidence for $k_{-1} > k_2$ was obtained in other

TABLE I
STEREOCHEMICAL COURSE OF BASE-CATALYZED HYDROGEN-DEUTERIUM EXCHANGE AT THE 9-POSITION OF 2-[N,N-DIMETHYL-CARBOXAMIDO]-9-METHYLFLUORENE (IIh) OR 9-DEUTERATED MATERIAL (IId)^a

Run no.	Start. matl. Type	Concn., <i>M</i>	Base Type	Concn., <i>M</i>	Solvent	Temp., C°	Time, hr.	% ^c Rac.	% ^c Exch.	k_e/k_a^d	Steric course
1	II d	0.020	NH ₃	0.2	THF ^e	145	5	2	95	148	High ret.
2	II d	0.022	PrNH ₂	0.5	THF ^e	145	1	7	100	>56	High ret.
3	II d	0.028	NH ₃	0.8	<i>t</i> -BuOH	200	3	8	100	>50	High ret.
4	II d	0.020	C ₆ H ₅ OK	<0.1	C ₆ H ₅ -C ₆ H ₅ OH ^f	75	<2	1.2	20	18	High ret.
5	II d	0.022	PrNH ₂	0.5	THF-LiBr ^g	75	1	40	94	5.6	Ret.
6	II d	0.023	Pr ₃ N	1	C ₆ H ₅ -C ₆ H ₅ OH ^f	145	4.3	6	25	5	Ret.
7	II d	0.042	PrNH ₂	0.5	THF-PrNH ₃ OAc ^g	75	2	60	93	3	Ret.
8	II h	0.06	KHCO ₃	0.06	DOCH ₂ CH ₂ OD ^h	50	4.7	46	48	1	Rac.
9	II d	0.017	NH ₃	0.2	(CH ₃) ₂ SO	25	1.5	9	8	1	Rac.
10	II d	0.032	NH ₃	0.8	CH ₃ OH	75	4	31	31	1	Rac.
11	II h	0.16	C ₆ H ₅ OK ⁱ	0.024	(CH ₃) ₃ COD ^j	25	7	54	50	0.9	Rac.
12	II d	0.12	Pr ₃ N	0.7	CH ₃ OH	75	13	59	46	0.69	High inv.
13	II d	0.14	Et ₃ N	0.5	THF-LiBr ^g	145	42	72	25	0.23	...

^a 0.97-0.99 atom of deuterium per molecule. ^b $\alpha_{\text{obs}} > 0.6^\circ$. ^c Deuterium analyses performed through infrared measurements at 1150 cm.⁻¹ using standards of known isotopic composition. ^d Calculated assuming $k_{\alpha^H}/k_{\alpha^D} = 1$. ^e THF = tetrahydrofuran. ^f 10% phenol by weight. ^g 0.5 *M* in salt. ^h 1.98 atoms of deuterium per molecule. ⁱ Solution was 0.024 *M* in phenol. ^j 0.96 atom of deuterium per molecule.

relatively low acidity of 2-phenylbutane coupled with steric constraints to planarity of the derived carbanion placed both experimental and theoretical limitations on the system.

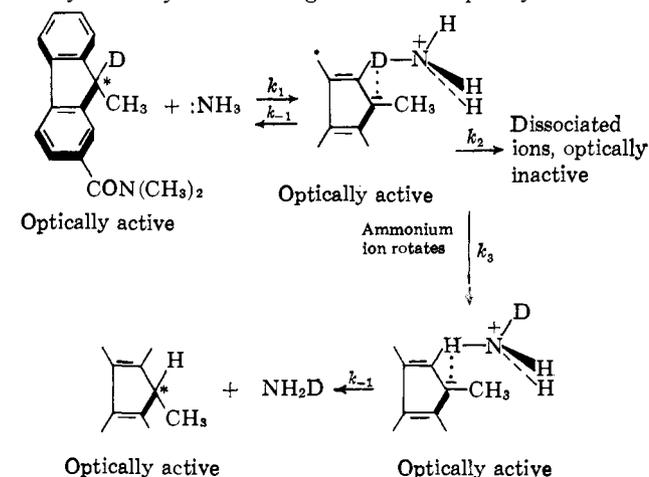


System II, with an estimated pK_a of 23 (I is probably around 50), gives an anion which tends to be planar, since it is isoelectronic with and has the shape of anthracene. Optically pure II, deuterated and nondeuterated in the 9-position, was prepared by conventional means.² The relative rates (one point) of racemization (k_a) and isotopic exchange (k_e) have been roughly determined in a variety of solvent-base systems. The experimental conditions and results are tabulated in Table I.

(1) (a) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961); (b) D. J. Cram, *Chem. Eng. News*, **41**, No. 33, 92 (1963).

(2) All new compounds gave carbon-hydrogen analyses within 0.3% of theory.

systems.⁴ The intramolecular character of the base-catalyzed allylic rearrangement of 3-phenyl-1-butene



(3) S. Winstein, S. Smith, and D. Darwish, *J. Am. Chem. Soc.*, **81**, 5511 (1959).

(4) D. J. Cram, D. A. Scott, and W. D. Nielsen, *ibid.*, **83**, 3696 (1961).