The degree of tritium labeling in uncross-linked polystyrene was determined by dissolving the reacted fluff in benzene and then subjecting the benzene solutions to liquid scintillation counting. Yields expressed as number of tritium atoms incorporated per 100 ev. energy (G) are summarized in Table I. Wilzbach labeling of organic liquids

TABLE I

TRITIUM LABELING OF POLYSTYRENE

T ₁ , pressure, mm.	Additive	Total dose, ^{<i>a</i>} ev. $\times 10^{-13}$	G(Poly- styrene-T
44.2	None	3.0	4.4
23.0	None	2.3	3.7
45.5	NO, 1–45 mm.	3.4	1.5
44.7	Xe, 340 mm.	3.6	14.5
44.5	He, 340 mm.	4.2	9.5

^a The tritium β -radiation dose was calculated from tritium gas in contact with the fluff, assuming complete absorption of energy in the reaction system. Our assumption is based on the low range of tritium β -particles (7 μ in liquid H₂O) and can be substantiated by estimation from findings of Dorfman⁸ on the absorption of tritium β -particles in various gases. Electron density for each fluff capsule is 2 \times 10²¹ electrons per ml., and energy absorption in the gas phase is appreciable only in samples containing xenon or helium as additive.

and solids often suffers from inefficient absorption of radiation energy in the organic matrix. The fact that our observed yields are much higher than even those found for gas phase labeling of similar hydrocarbons⁹ must have resulted from inhibited radical recombination² in the polymer fluff, thereby promoting competitive tritium labeling processes.

The apparently similar effects of Xe and He are not readily explainable. The presence of helium is known to enhance the tritium labeling of nhexane,¹⁰ whereas xenon has been shown to exert a scavenging effect in the isotopic exchange between tritium and methane.¹¹ Our observed enhancement of isotopic exchange due to the presence of xenon may be attributed to gaseous-ions sensitized formation of tritium atoms¹² by reaction (1).

$$X^+ + T_2 \rightarrow XT^+ + T \tag{1}$$

The high efficiency of xenon sensitization for such a reaction has been demonstrated recently by Lampe.¹³ A more critical series of experiments is currently in progress.

A final point of importance is manifested in the relatively high efficiency of tritium labeling observed in our system. A practical method of labeling organic macromolecules by the Wilzbach process is now available with the use of polymer fluffs. Such a technique appears much more promising than the present available methods¹⁴ of tritium labeling of biochemical molecules.

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- J. G. Burr of our Laboratory for stimulating discussion and valuable suggestions. Atomic International J. Y. YANG
- A DIVISION OF NORTH AMERICAN AVIATION, INC. CANOGA PARK, CALIFORNIA Received March 16, 1962

NITROGEN AS LEAVING GROUP IN ELECTROPHILIC SUBSTITUTION AT SATURATED CARBON¹

Sir:

Carbonium ions, radicals and carbenes formed by loss of a molecule of nitrogen from either compounds or ions have in many instances exhibited different behavior than the corresponding species generated through use of other leaving groups. This communication deals with a comparison of the stereochemical capabilities *of carbanions* produced with nitrogen as distinct from other leaving groups such as carbon,^{2a} oxygen^{2b} or hydrogen.^{2c}

The three reactions used for this purpose are formulated.

(1) *R--NHNHTs + B⁻
$$\rightarrow$$

I
(2) *R--NHNH₂ + KIO₄ \rightarrow
II
(3) *R--NNa + NH₂OSO₂⁻ \rightarrow *R--NNH₂ \rightarrow
 \uparrow
Ts IV Ts
[*R--N=N-H] $\xrightarrow{B^-}$ *R⁻ + HB + N₂ \rightarrow *R--H
III
R = C₂H₅ \xrightarrow{C} Ts = SO₂C₆H₄CH₃- p
 \downarrow
C₆H₅

Compound II³ was prepared by a reaction sequence patterned after that reported for the 2-phenyl-2-propylhydrazine.4 preparation of Resolution of II was accomplished by fractional crystallization of its dibenzoyl-d-tartrate salt from water to give (+)-II, $[\alpha]^{25}_{546}$ + 12.8° (l = 1 dm., neat), n^{25} D 1.5354. Hydrogenolysis of this material, $[\alpha]^{25}_{546} + 11.8^{\circ}$ (l = 1 dm., neat), in acetic acid with a platinum catalyst produced (+)-2phenyl-2-butylamine (V), n^{25} D 1.5124, $[\alpha]^{25}_{546}$ +15.8° (l = 1 dm., neat). Application of the Curtius rearrangement to optically pure (+)-2methyl-2-phenylbutyric acid⁵ (VI) gave (-)-2-phenyl-2-butylamine (V), $[\alpha]^{25}_{546}$ -18.2° (l =1 dm. neat). Since the configurations of acid VI and hydrocarbon III are known,^{5b} these reactions established the configurations of amine V and hydrazine II, as well as the rotation of optically pure II ($[\alpha]_{546}^{p} \pm 13.5^{\circ}, l = 1 \text{ dm., neat}$). Sulfon-

(1) This work supported by the National Science Foundation.

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(3) All new compounds involved in this study gave carbon and hydrogen analyses within 0.30% of theoretical.

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			I ABLU I			
Run	Solvent	Base	Concn., N	° ^T ,	Yield,	Net steric course
1	(CH ₂) ₂ COH	(CH ₂) ₂ COK	0.30	100	83	80% Ret.
2	n-C ₄ H ₉ OH	n-C ₄ H ₉ OK	0.30	100	72	68% Ret.
3	C ₂ H ₅ OH	C ₂ H ₆ OK	0.37	100	58	60% Ret.
4	CH₃OH	CH3OK	0.30	100	73	44% Ret.
5	HOCH ₂ CH ₂ OH	HOCH ₂ CH ₂ OK	0.085-1.00	100	21-48	15–37% Ret.
6	H ₂ O	HOK	0.30-1.1-9.7	100	27 - 58	2% Inv10%
						In v .–70% Ret
7	(CH ₃) ₃ COH ^a	(CH ₃) ₃ COK	0.16	53	78	92% Ret.
8	(CH ₃) ₃ COH ^a	$(CH_3)_4N^+OH^-$	0.16	53	59	60% Ret.
9	HOCH ₂ CH ₂ OH ^b	HOCH2CH2OK	0.34	25	52	48% Ret.
10	HOCH₂CH₂OH [♭]	(CH ₃) ₄ N+OH-	0.34	25	50	46% Ret.
11	$(CH_3)_2SO$	HOCH ₂ CH ₂ OK	0.088	53	51	37% Ret.
12	$(CH_3)_2SO$	(CH ₃) ₄ N+OH-	0.11	53	42	34% Ret.

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^a Solutions 0.32 M in water. ^b Solutions 0.68 M in H₂O.

amide (+)-I, m.p. 112-112.2°, $[\alpha]^{25}_{546}$ +32.6° (c 9, dioxane), was prepared from (+)-II, $[\alpha]^{25}_{546}$ +12.8° (l = 1 dm., neat), by the usual method. Repeated recrystallization of grossly optically impure (-)-I from ether-pentane gave optically pure (-)-I, m.p. 112.5-113°, $[\alpha]^{25}_{546}$ -35.4° (c 9, dioxane). These data relate the configurations and maximum rotations of starting materials and products in reactions (1), (2) and (3). Cleavage of sulfonamide (+)-I without base at

Cleavage of sulfonamide (+)-I without base at 100° in water, *t*-butyl alcohol or dimethyl sulfoxide gave completely racemic III. Results obtained in the presence of base are summarized in Table I. Except in ethylene glycol and water, base concentrations were reached where an increase in base did not change stereospecificity. In ethylene glycol, retention increased regularly as base was increased (run 5). In water, as base concentration increased, the reaction occurred first with increasing net inversion and then with increasing net retention (run 6).

Oxidation of II with potassium periodate under conditions of runs 1, 3 and 4 gave results within experimental error of the corresponding cleavages of I. In water, oxidation of II without base at 100° gave 100% racemization, whereas at 0.012to $0.30 \ M$ base, 30-32% inversion was observed (compare with run 6).

Treatment of (-)-2-phenyl-2-butylamine ptoluenesulfonate (95°, 3 M solution of sodium hydroxide in 90% water-10% ethanol) with hydroxylamine-O-sulfonic acid⁶ gave III (10%) with 32% net retention. Cleavage of I under the *average conditions* of the above reaction gave III (83%) with 37% net retention. Oxidation of II under the same average conditions gave III (10%) with 26% net retention. The stereochemical results vary enough with concentrations of hydroxylamine, base and sodium sulfate to make the three results within experimental error of one another.

These data suggest several conclusions: (1) The same intermediate, probably RN_2H , is produced in all three of the reactions employed. (2) This intermediate partitions between a basecatalyzed anionic elimination reaction to give III somewhat stereospecifically, and a homolytic elimination to give racemic III. (3) Generation

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of a proton donor at the front of the carbanion in the base-catalyzed reaction of RN_2H provides for the retention mechanism, whereas a nitrogen molecule as a shield at the front of the carbanion provides for the inversion mechanism.⁷ (4) In relatively non-polar solvents the homolytic cleavage of RN_2H can be eliminated, but not in water or ethylene glycol. (5) In water, different intermediates are involved in the anionic cleavage depending on whether I or II are starting materials.

(7) Compare nitrogen as leaving group with carbon and hydrogen.
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(8) Eastman Kodak Fellow, 1961-1962.

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EVIDENCE FOR PARALLEL CONTROL OF REACTION RATE AND STEREOCHEMISTRY via THE ELECTROSTATIC INFLUENCE OF REMOTE SUBSTITUENT DIPOLES

Sir:

LOS ANGELES,

We wish to report evidence we have obtained in studies of sodium borohydride reduction of 4substituted cyclohexanones indicating that, in systems where rate variations are strongly governed by remote substituent effects, parallel control of product stereochemistry also is exercised. Furthermore, the existence of a field effect of this nature appears to be unexpected in view of assumptions to the contrary applied in various interpretations of rate and stereochemical effects.¹⁻⁶

The rates of reduction obtained by use of the kinetic method devised by Brown and co-workers⁷ are presented in the accompanying data table. The existence of a linear free energy relationship

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