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 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 hydrocarbons[9] must have resulted from inhibited radical recombination[2] in the polymer fluff, thereby promoting competitive tritium labeling processes.

TABLE I

TRITIUM LABELING OF POLYSTYRENE

T_2, pressure, mm.	Additive	Total dose,[a] ev. × 10^{-18}	G(Polystyrene-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 H_2O) and can be substantiated by estimation from findings of Dorfman[8] on the absorption of tritium β-particles in various gases. Electron density for each fluff capsule is 2 × 10^{21} electrons per ml., and energy absorption in the gas phase is appreciable only in samples containing xenon or helium as additive.

The apparently similar effects of Xe and He are not readily explainable. The presence of helium is known to enhance the tritium labeling of *n*-hexane,[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 atoms[12] by reaction (1).

$$X^+ + T_2 \rightarrow XT^+ + T \qquad (1)$$

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 methods[14] of tritium labeling of biochemical molecules.

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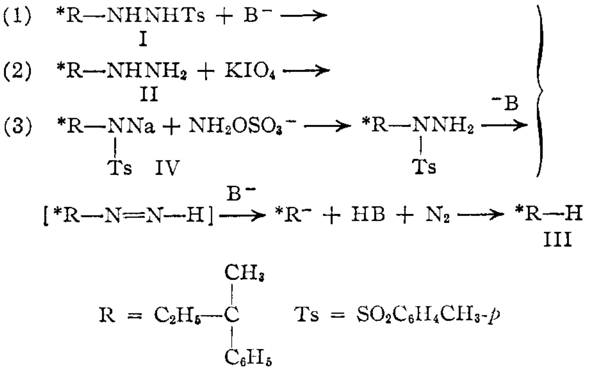
NITROGEN AS LEAVING GROUP IN ELECTROPHILIC SUBSTITUTION AT SATURATED CARBON[1]

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.



Compound II[3] was prepared by a reaction sequence patterned after that reported for the preparation of 2-phenyl-2-propylhydrazine.[4] 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° (l = 1 dm., neat), in acetic acid with a platinum catalyst produced (+)-2-phenyl-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 (+)-2-methyl-2-phenylbutyric acid[5] (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 ($[\alpha]^{D}_{546}$ ±13.5°, l = 1 dm., neat). Sulfon-

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

(2) (a) D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen and J. Allinger, *J. Am. Chem. Soc.*, **81**, 5774 (1959); (b) D. J. Cram, C. A. Kingsbury and A. Langemann, *ibid.*, **81**, 5785 (1959); (c) D. J. Cram, C. A. Kingsbury and B. Rickborn, *ibid.*, **81**, 3688 (1961).

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TABLE I

Run No.	Solvent	Base		T, °C.	Yield, %	Net steric course
		Nature	Concn., N			
1	$(CH_3)_3COH$	$(CH_3)_3COK$	0.30	100	83	80% Ret.
2	n-C_4H_9OH	n-C_4H_9OK	0.30	100	72	68% Ret.
3	C_2H_5OH	C_2H_5OK	0.37	100	58	60% Ret.
4	CH_3OH	CH_3OK	0.30	100	73	44% Ret.
5	$HOCH_2CH_2OH$	$HOCH_2CH_2OK$	0.085–1.00	100	21–48	15–37% Ret.
6	H_2O	HOK	0.30–1.1–9.7	100	27–58	2% Inv.–10% Inv.–70% Ret.
7	$(CH_3)_3COH$[a]	$(CH_3)_3COK$	0.16	53	78	92% Ret.
8	$(CH_3)_3COH$[a]	$(CH_3)_4N^+OH^-$	0.16	53	59	60% Ret.
9	$HOCH_2CH_2OH$[b]	$HOCH_2CH_2OK$	0.34	25	52	48% Ret.
10	$HOCH_2CH_2OH$[b]	$(CH_3)_4N^+OH^-$	0.34	25	50	46% Ret.
11	$(CH_3)_2SO$	$HOCH_2CH_2OK$	0.088	53	51	37% Ret.
12	$(CH_3)_2SO$	$(CH_3)_4N^+OH^-$	0.11	53	42	34% Ret.

[a] Solutions 0.32 M in water. [b] Solutions 0.68 M in H_2O.

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 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 0.012 to 0.30 M base, 30–32% inversion was observed (compare with run 6).

Treatment of (−)-2-phenyl-2-butylamine p-toluenesulfonate (95°, 3 M solution of sodium hydroxide in 90% water–10% ethanol) with hydroxylamine-O-sulfonic acid[6] 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 base-catalyzed anionic elimination reaction to give III somewhat stereospecifically, and a homolytic elimination to give racemic III. (3) Generation 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.

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

Sir:

We wish to report evidence we have obtained in studies of sodium borohydride reduction of 4-substituted 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-workers[7] are presented in the accompanying data table. The existence of a linear free energy relationship

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