as a transition state for an intramolecular isomerization may be prohibitive. Finally, in further support of an intermolecular process is the observation that the stable isomer, PdNCS, reacts (eq 3) slower than does the less stable form.

Preliminary observations show that in the solid state at room temperature there is complete isomerization of [(Et$_4$dien)PdSCN]SCN in 3 days, but under the same conditions there is no isomerization of [(Et$_4$dien)PdSCN]PF$_6$. Also the rate of isomerization of [(Et$_4$dien)PdSCN]$^+$ in nonpolar solvents such as benzene is slower than it is in water solution. These and other observations on systems of this type will be reported in detail later.

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The Isotopic and Phase Effects in Neutron-Irradiated Ethyl Bromide[1]

Sir:

The differences in the isotopic yields and the effects of phase on the relative yields of radiobromine produced by a nuclear process in organic bromides were repeatedly investigated and were the subject of many contradictory reports.[2] In a recent publication[3] Shaw and co-workers have shown that although the total organic yields of ^{80m}Br and ^{82}Br in neutron-irradiated ethyl bromide are quite similar, the repartition of their activity between the products is different. Current work in our laboratory seems to indicate that this isotopic effect could be correlated to the changes in the yields of different fractions upon irradiation in liquid and solid phase.

Carefully purified ethyl bromide[4] a containing 10^{-3} *M* fraction of bromine scavenger was irradiated for 1 to 3 sec in the pneumatic channels of EL 3 (CEA, Saclay), with a neutron flux about 10^{12} neutrons/cm^2/sec. The solid-state irradiations were performed with polycrystalline material at approximately $-196°$. Samples were kept in liquid nitrogen before and after irradiation; since the irradiation time was very short, the samples were not cooled while exposed to the neutron flux.[5] Liquid-state irradiations were done at room temperature and the samples kept at 0° until extracted. Fifty minutes after irradiation the samples were extracted with a reducing wash. After the addition of carriers, the separation was made by gas chromatography.[4] The fractions were collected at the end of the column and counted three times: (1) 4 hr after extraction, (2) 20 hr later, and (3) 48 hr after extraction, when the remaining activity is due practically to ^{82}Br (35-hr half-life) only. This last measurement was used as a control. In this manner the yield of both bromine isotopes was determined from the same sample.

The results presented in Table I represent the mean ratios for at least three experiments; the mean deviations of the percentage yields did not exceed ±5 to 7% for the main fractions (about twice the value of the statistical counting error).

Table I. Isotope and Phase Effects in Neutron-Irradiated Ethyl Bromide

Products	Isotope effect[a] Liquid	Isotope effect[a] Solid	Phase effect[b] ^{80m}Br	Phase effect[b] ^{82}Br
Bromomethane	2.5	2.8	1.5	1.4
Dibromomethane	1.8	1.7	1.1	1.2
Tribromomethane	1.3	1.0	1.2	1.3
Ethyl bromide	1.0[c]	1.0[c]	2.2	2.4
Dibromoethane	0.8	0.6	12.5	16.0
Tribromoethane	0.7	0.7	4.7	4.0

[a] Yield for ^{80m}Br/yield for ^{82}Br. [b] Yield in solid phase/yield in liquid phase. [c] The ratio becomes >1 for heavily scavenged systems.[3]

The results obtained for the liquid-phase irradiations are in very good agreement with those of Shaw, although the neutron flux and irradiation times were completely different.[3,6] This was considered a confirmation of the purity of the material used, the separation method, and the absence of any parasite phenomenon.[7]

The complete analysis of the irradiation products in ethyl bromide shows that the activity is distributed between twelve separable products. In this communication we will only comment upon a few relevant features concerning the main fractions; work is currently done in our laboratory to obtain a more detailed understanding of this and similar systems.

An important point arising from Table I is the obviously "nonrandom" behavior of the two bromine isotopes; the isotopic yield ratio for a given product is remarkably constant when passing from the liquid to the solid phase despite the fact that the individual yields change by factors varying by as much as 1 to 16. The results in Table I also indicate that the products resulting from H-atom substitution show an isotope effect favoring ^{82}Br (yield for ^{80m}Br/yield for ^{82}Br < 1) and a very important phase effect, whereas those resulting from the scission of a C–C bond as well as the substitution of a Br atom (once diffusive reactions are eliminated at high scavenger concentrations[3]) present an isotope effect favoring ^{80m}Br (yield for ^{80m}Br/yield for ^{82}Br > 1), and show little or no difference in yield in the two phases.

The recent discovery[8a,b] that most ^{82}Br is produced through an isomeric transition from ^{82m}Br (6.2-min

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[1] This work was done under a research contract with the Commissariat á l'Energie Atomique.

[2] (a) For a recent review of the subject, see J. E. Willard, "Chemical Effects of Nuclear Transformations," Vol. 1, IAEA, Vienna, 1965, p 221; (b) R. M. A. Hahne and J. E. Willard, *J. Phys. Chem.*, **68**, 2582 (1964); (c) N. Nesmeyanov and E. S. Filatov, *Radiokhimiya*, **3**, 501 (1961); (d) J. E. Willard, ref 2a, 1961, p 215; (e) A. E. Richardson and A. F. Voigt, *J. Chem. Phys.*, **28**, 854 (1958); (f) M. Milman, *J. Am. Chem. Soc.*, **80**, 5592 (1958).

[3] T. E. Gilroy, G. Miller, and P. F. D. Shaw, *ibid.*, **86**, 5033 (1964).

[4] A detailed account of the experimental techniques will be published elsewhere; the chromatographic analysis and the calculation of the organic yields follow the same principles as those described in ref 3.

[5] The approximately estimated time the samples were out of liquid nitrogen is about 30–60 sec.

[6] P. F. D. Shaw, private communication.

[7] J. A. Merrigan and E. P. Rack, *J. Phys. Chem.*, **69**, 2795 (1965).

[8] (a) J. F. Emery, *J. Inorg. Nucl. Chem.*, **27**, 903 (1965); (b) O. U. Anders, *Phys. Rev.*, **138**, B1 (1965).

half-life) suggests that formation of activated products arises mainly from the consequences of internal conversion and subsequent Auger electron emission (*i.e.*, ion–molecule reactions or radical–radical recombinations). If it is assumed that recoil energy is the main factor in determining the chemical fate of ^{80m}Br, it could be expected that this different nuclear origin and chemical activation would be reflected in differences in the isotopic yield.[3]

It is still unclear in what way the change from the liquid to the solid state affects the chemical consequences of a nuclear event.[2a] One of the possible interpretations would be that a truly "hot" process (that is, the result of a direct impact of an energetic atom on a molecule, or one which is followed by an extremely rapid recombination of the fragments formed) should not be greatly affected by a structural change of the surrounding "cage." Conversely, the organic yield of other processes could increase if the solidified cage were able to keep together thermalized organic fragments (that would have diffused apart in the liquid) and would only have allowed H atoms to diffuse away.

In the light of these assumptions and since the phase and isotope effect appear to be correlated, it can be tentatively concluded (thus confirming the hypothesis proposed in ref 3) that the breaking of a C–C and C–Br bond may be primarily caused by atoms having recoil energy, while H-atom substitution is caused mainly by isomeric transition activation.

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Photochemistry of Phenyloxiranes. II. New Precursor for Phenylcarbene[1]

Sir:

In an earlier communication[2] we reported our preliminary data on the photofragmentation of a variety of aryl-substituted epoxides to phenylcarbenes (or behaviorly related species) and ketones or aldehydes. The scope and synthetic utility of this reaction for the preparation of phenylcyclopropanes and -propenes as well as the stereochemical features of the observed addition processes have now been investigated. In view of the breadth of scope of this reaction and the novel stereochemical features, we now wish to supplement our previous report with further experimental details and results.

Representative compounds accessible from stilbene oxide (I) are tabulated below (Table I). Unquestionably I represents the most convenient precursor for phenylcarbene which in turn will add stereospecifically to olefins and also reacts with acetylenes and benzenes. Furthermore, the yields of phenylcyclopropanes reported herein invariably exceed those previously attainable by alternate routes using other phenylcarbene or carbenoid precursors.[3]

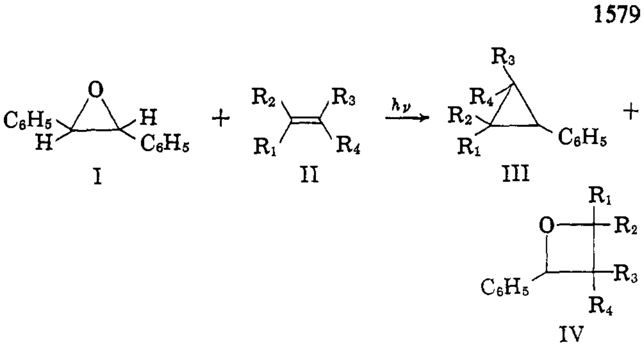

Table I

	Olefin II	R_i, II, III, and IV	Yield of III,[a] %
(a)	Isobutene	$R_1 = R_2 = H$ $R_3 = R_4 = CH_3$	60
(b)	*cis*-2-Butene	$R_1 = R_4 = H$ $R_2 = R_3 = CH_3$	65
(c)	*trans*-2-Butene	$R_1 = R_3 = H$ $R_2 = R_4 = CH_3$	65
(d)	2-Methyl-2-butene	$R_1 = H$ $R_2 = R_3 = R_4 = CH_3$	75
(e)	2-Methyl-1-butene	$R_1 = R_2 = H$ $R_3 = CH_3$; $R_4 = C_2H_5$	70
(f)	2,3-Dimethyl-2-butene	$R_1 = R_2 = R_3 = R_4 = CH_3$	60

[a] No attempt was made to maximize the yield which is based upon the initial epoxide concentration. In all irradiations (50 hr) 20–30% of the epoxide was recovered.

The simplicity of the transformation I + II → III + IV leaves little to be desired. Best results are obtained when the initial epoxide concentration is approximately 0.2–0.3 *M*. Irradiations are conducted conveniently in serum-capped quartz test tubes employing the neat olefin or acetylene as a solvent, and stirring was found advantageous.[4] In those cases where olefin or acetylene volatility precludes irradiation under these conditions a thick-walled quartz tube equipped with a commercially available pressure fitting was employed.[5] The period of irradiation was generally 50 hr. It is necessary, however, that photolysis be terminated prior to complete disappearance of epoxide; otherwise the cyclopropanes, which are unstable under these conditions, begin to absorb light and isomerize to olefins.[6] Complete separation of the cyclopropanes from the oxetanes, which also are formed, may be achieved easily by a single short-path distillation under reduced pressure. Aside from these easily separable oxetanes only trace amounts of other nonpolymeric side products were obtained. Insertion products appeared to be formed only in the case of IId (<5%).

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(1) We wish to thank the Army Research Office (Durham) for financial support of this program, and the National Science Foundation for an nmr equipment grant (NSF-GP-3674).

(2) H. Kristinsson and G. W. Griffin, *Angew. Chem.*, 77, 859 (1965).

(3) G. L. Closs and K. A. Moss, *J. Am. Chem. Soc.*, 86, 4042 (1964).

(4) An air-cooled Rayonet Chamber Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 8-w germicidal lamps (2537 A) was used as a light source.

(5) The quartz tubes were easily adapted to fit a Fisher-Porter Co. (Lab Crest Scientific Division, Warminster, Pa.) aerosol compatibility coupling equipped with a needle valve.

(6) H. Kristinsson and G. W. Griffin, unpublished results.