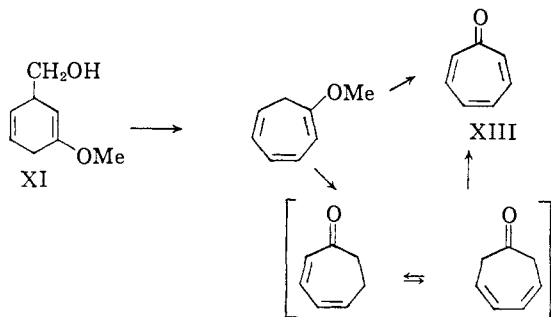
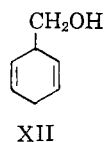


Lithium aluminum hydride reduction of the crude dihydroacid obtained by Birch reduction of 3-methoxybenzoic acid (X) gives 3-methoxy-1,4-

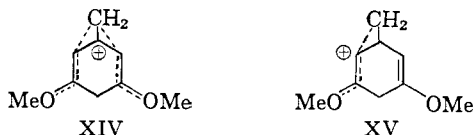


dihydrobenzyl alcohol (XI; b.p. 93–96° (0.2 mm.); C, 68.71; H, 8.83) in modest yield.⁶ The n.m.r. spectrum of the alcohol XI shows a two proton peak at 4.41 p.p.m. and a one proton peak at 5.48 p.p.m.⁸ For comparison the olefinic protons of 1,4-dihydrobenzyl alcohol (XII) appear as a four proton peak at 4.33 p.p.m., and the olefinic protons of 3,5-dimethoxy-1,4-dihydrobenzyl alcohol (IV) appear as a two proton peak at 5.50 p.p.m. Tosylation of XI and solvolysis in refluxing pyridine gives a



mixture of methoxycycloheptatrienes (b.p. 67–70° (20 mm.); $\lambda_{\text{max}}^{\text{EtOH}}$ 289 μ). Bromine oxidation of the methoxycycloheptatrienes gives in low yield tropone (XIII, λ_{max} 223, 227, 231, 235, 238, 307 μ). Acid hydrolysis of the mixture of methoxycycloheptatrienes gives a mixture of 2,4- and 3,5-cycloheptadienones⁹ (5.90, 6.02, 6.16, and 6.31 μ) which air oxidizes to tropone in somewhat better yield.¹⁰

The solvolytic ring expansion of the tosylates of IV, VII and XI is of considerable interest. Contemplation of the possibilities for anchimerically assisted ionization of V suggests either a doubly assisted ionization leading to an ion such as XIV (not necessarily symmetric) or a singly assisted ionization to an ion such as XV.



This mechanistic dichotomy is somewhat analogous to that encountered in the ionization of pentamethyl

(6) A by-product which may be derived from the tetrahydroacid reported^{6,7} to be the product of Birch reduction of 3-methoxybenzoic acid is also obtained. The formation of XI requires the formation of 3-methoxy-1,4-dihydrobenzoic acid in the Birch reduction of X. The mechanistic significance of this observation will be discussed in the complete report of this investigation.

(7) A. J. Birch, P. Hextall and S. Sternhell, *Aust. J. Chem.*, **7**, 256 (1954).

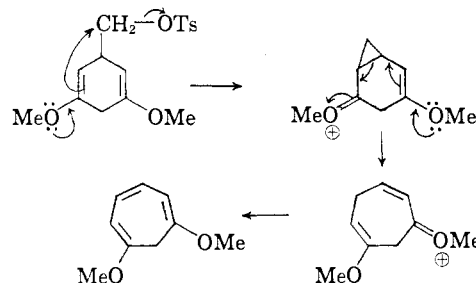
(8) Tau values relative to internal tetramethylsilane in carbon tetrachloride (G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958)).

(9) J. Meinwald, S. L. Emerman, N. C. Yang and G. Büchl, *J. Am. Chem. Soc.*, **77**, 4401 (1955).

(10) E. E. van Tamelen and G. T. Hildahl, *ibid.*, **78**, 4405 (1956).

cyclopentadienylcarbinyl brosylate¹¹ and tosylate.¹² Comparison of the behavior of 3,5-dimethoxy-1,4-dihydrobenzyl tosylate (V) and 1,4-dihydrobenzyl tosylate in refluxing pyridine strongly suggests the incursion of an assisted ionization which favors ring expansion in the case of V. In refluxing pyridine the tosylate V (0.62 molar) is completely destroyed in 30 seconds. In contrast 1,4-dihydrobenzyl tosylate (0.76 molar) is not completely destroyed after one hour in refluxing pyridine, and no cycloheptatriene is obtained in the work up.¹³ The principal reaction in this case appears to be alkylation of the pyridine. Attempts to obtain satisfactory solvolysis rates for the tosylates of IV, VII, XI and XII using collidine as solvent are in progress.

It is interesting to note that the ring expansion of V can be considered the mechanistic analog of the peracid oxidation of benzal ketones to enol esters.¹⁴



Acknowledgment.—This research was supported by grant CY-4253 from the Cancer Division, National Institutes of Health, Public Health Service.

(11) L. De Vries, *ibid.*, **82**, 5242 (1960).

(12) S. Winstein and M. Battiste, *ibid.*, **82**, 5244 (1960).

(13) Acetolysis (ca. 36 hours at 90°) of 1,4-dihydrobenzyl tosylate gives cycloheptatriene in good yield.⁵

(14) E. Wenkert and M. Rubin, *Nature*, **170**, 708 (1952).

(15) Recipient of a travel grant from the Wellcome Trust.

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RECEIVED DECEMBER 23, 1960

DIRECT RADIATION-INDUCED SYNTHESIS OF IODOBENZENE-¹³¹I FOLLOWING FISSION PRODUCT RECOIL INTO BENZENE SOLUTION¹

Sir:

In the last several years, the excited chemical species created during the dissipation of nuclear energy frequently have been utilized for the direct synthesis of various radioisotopically-labeled molecules.² Processes accompanying fission recoil—kinetic energy of recoil, radiation damage to the surroundings, and later the beta decay of the primary fission fragments—furnish abundant opportunity for the formation of excited chemical species which may then react with the incorporation of fission product radioactivity into particular chemical compounds.³ We have experimentally caused

(1) This research has been supported by A.E.C. Contract No. AT-(11-1)-407.

(2) See the review by A. P. Wolf in *Ann. Rev. Nuclear Sci.*, **10**, 259 (1960).

(3) Some of the chemical effects of fission fragments have been reviewed by G. N. Walton in *Progress in Nuclear Physics*, **6**, 193 (1957). The reactions of fission fragments recoiling into solid ferrocene and

direct recoil of fission fragments into organic solutions through neutron irradiation of 1-2 ml. samples in quartz tubes internally coated with 1.67 mg. of U_3O_8 , and have observed organically bound fission product radioactivity afterward.

After irradiation for 12-24 hours in a neutron flux of $1-2 \times 10^{12}$ n./cm.²/sec., more than 50% of the mass 131 atoms recoiling into a benzene solution can be isolated readily as iodobenzene- I^{131} . Molecular iodine and iodobenzene carriers and additional benzene were added to each irradiated sample, and the inorganic iodine was extracted into aqueous sulfite solution. The organic phase, with added naphthalene, was distilled at atmospheric pressure using a 12" column packed with glass rings. From one such iodobenzene fraction, one aliquot was counted directly and two others were used to form appropriate derivatives, which were then recrystallized to constant radioactivity, as shown in Table 1. The half-life and gamma ray spectrum of each aliquot showed no radioactivities other than I^{131} .⁴ The constant specific activity per iodobenzene equivalent shown in the last column of Table I demonstrates that the I^{131} is actually chemically bound as iodobenzene.

TABLE I

 I^{131} RADIOACTIVITY IN IODOBENZENE AND IN TWO DERIVATIVES^a

	Weight, g.	C.p.m.	C.p.m./g. iodobenzene equivalent
Iodobenzene	8.86	1910 ± 20	216 ± 2
1-Bromo-4-iodobenzene	4.17	662 ± 7	220 ± 3
4,4'-Diiododiphenyl sulfone	1.36	272 ± 5	227 ± 4

^a Total iodobenzene carrier = 36.6 g.

The yields of inorganic I^{131} and of alkyl iodide- I^{131} also have been determined. Carrier ethyl iodide was added to the b.p. 185° distillation fraction and then converted to silver iodide with ethanolic silver nitrate solution. The inorganic iodine was also measured as silver iodide. The relative yields of each from two separate experiments are shown in Table II.

TABLE II

OBSERVED YIELDS OF DIFFERENT I^{131} -LABELED SPECIES FROM FISSION RECOIL INTO BENZENE SOLUTION^a

Flux, n./cm. ² /sec.	1.0×10^{12}	2.0×10^{12}
Hours of irradiation	24	12
Calculated yield of I^{131} recoiling into solution (d.p.m.)	1.2×10^6	1.2×10^6
Yields (d.p.m.)		
Iodobenzene	8.0×10^5	6.0×10^5
Inorganic iodine	2.4×10^5	4.3×10^5
Alkyl iodides, b.p. less than 185°	0.6×10^5

^a All activities have been corrected for chemical yield and for decay since the end of irradiation.

chromium hexacarbonyl recently have been investigated by F. Baumgartner and P. Reichold, in a paper presented to the I.A.E.A. Symposium on Chemical Effects of Nuclear Transformations, Prague, October, 1960.

(4) The experiments to date have always involved search for antimony isotopes of shorter half-life, as well as iodine, in organic combination. As a result, the iodobenzene fraction has not been isolated until after the other iodine radioactivities have already decayed away.

Since I^{131} is formed in the primary fission process in negligibly small yields, the original mass 131 atom recoiling into the benzene solution will be Sn^{131} , Sb^{131} , or Te^{131} , and the I^{131} will subsequently be formed in the solution through the beta plus gamma decay of Te^{131} and Te^{131m} in whatever chemical forms tellurium isotopes exist in this solution. Most of the decay chains will reach I^{131} while the sample is still undergoing irradiation, and the possible mechanisms for formation of the labeled iodobenzene will include reactions not only with the stable radiation damage molecules, but with the steady state concentrations of more reactive chemical entities.

Similar experiments with other solvents have always shown volatile, organically bound I^{131} activity; as yet, their chemical identity and percentage yields of radioactivity have not been determined. Evidence also has been obtained for partial organic incorporation of antimony and tellurium fission isotopes, but without substantial radioactivity in any identified compound.

Further experiments are also in progress involving the carrier-free separation of iodobenzene- I^{131} , and an estimate of the limits on specific and total radioactivity obtainable by this method of synthesis.

These experiments reported here suggest that convenient radiation-induced syntheses of many I^{131} -labeled molecules can be obtained through proper choice of the organic solvent used in the irradiation tubes. Further work will be necessary to show whether any of the other fission isotopes can be similarly incorporated in useful amounts. The experiments also suggest that the direct utilization of fission recoil energy for radiation synthesis of unlabeled molecules will normally be accompanied by the formation of highly-radioactive organic molecules, with both the advantages and disadvantages that this will bring.

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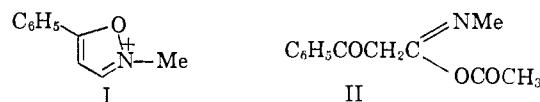
DONALD ORMOND
F. S. ROWLAND

RECEIVED DECEMBER 30, 1960

THE REACTION OF ISOXAZOLIUM SALTS WITH BASES

Sir:

In 1902, Mumm¹ made the striking observation that the N-methyl-5-phenylisoxazolium cation (I) reacts with extraordinary facility with acetate ion.



When the reaction was carried out in aqueous solution at room temperature, a crystalline substance precipitated in a few minutes. The product was formulated as the iminoanhydride (II). Subsequent studies revealed that isoxazolium salts react with similar great ease with a wide variety of carboxylates, and other nucleophiles.² It has been as-

(1) O. Mumm, "Dissertation," Kiel, 1902.

(2) K. Meyer, "Dissertation," Kiel, 1903; G. Münchmeyer, "Dissertation," Kiel, 1910; C. Bergell, "Dissertation," Kiel, 1912; A. Wirth, "Dissertation," Kiel, 1914; W. Stülcken, "Dissertation,"