

amino acids.² A maximum of 50% hydrolysis of the racemate was achieved in a few hours, which was not altered by addition of fresh enzyme and further incubation. The liberated L-amino acid was separated from the digest as usual, and recrystallized as glistening prisms from 50% alcohol; N calcd. 11.8, found 11.7; $[\alpha]^{25D} + 10.0^\circ$ (4.00% in H₂O); yield 80% on the chloroacetyl derivative. The chloroacetyl-D-allothreonine in the mother liquor was extracted, hydrolyzed with 2 N HCl, and isolated in 62% yield after neutralization and recrystallization from 50% alcohol; N found 11.7; $[\alpha]^{25D} - 9.8^\circ$ (4.00% in H₂O).

The optical rotation values of the allothreonine isomers are in agreement with those given by West and Carter⁶ and by Elliott,⁷ and the assignment of their configuration is in accord with that recently reported by Elliott⁷ on the basis of organic chemical procedures.

We thank Dr. H. E. Carter for a gift of DL-allothreonine.

(6) West and Carter, *J. Biol. Chem.*, **122**, 611 (1938).

(7) Elliott, *J. Chem. Soc.*, 62 (1950).

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OBSERVATIONS OF THE MANNICH REACTION WITH OPTICALLY ACTIVE SUBSTITUTED MANDLIC ACIDS

Sir:

We have found that the Mannich reaction involving *d*-o-nitromandelic acid ($[\alpha]^{20D} + 346^\circ$ in ethanol), formaldehyde and piperidine, yielded the expected Mannich base α -piperidinomethyl-o-nitromandelic acid in an optically active form ($[\alpha]^{20D} + 439^\circ$ in ethanol). The *l*-acid gave a product whose rotation was $[\alpha]^{20D} - 449^\circ$ in ethanol. The lack of racemization appears to render inadmissible the enolization step postulated by Alexander and Underhill¹ for all compounds that undergo the Mannich reaction which have a methynyl group on a carboxyl group. Their investigation concerned the Mannich reaction with ethylmalonic acid, formaldehyde and dimethylamine.

The possibility of oxygen alkylation rather than carbon alkylation required by the Mannich reaction was eliminated by means of Zerewitinoff tests performed on the Mannich base.

A series of reactions with *d*-o-nitromandelic acid at various pH values and temperatures indicated that the condensation occurred too rapidly to permit a satisfactory study of its kinetics. The results obtained at 20° and 0° were virtually identical. Reaction occurred without apparent change in rate at pH values of 7.2, 8.5 and 9.3, while at pH 3.1 (piperidine hydrochloride), it failed to occur.

(1) E. Alexander and E. Underhill, *THIS JOURNAL*, **71**, 4014 (1949).

The investigation of this reaction and other similar reactions is continuing and will be reported in the near future.

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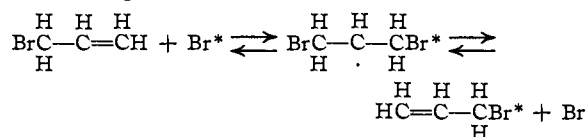
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RAYMOND I. BASHFORD, JR.

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ISOTOPIC EXCHANGE OF ATOMIC BROMINE WITH ALLYLIC VINYLIC HALIDES^{1,2}

Sir:

Recent work^{3,4} indicates that most bromine atoms produced by slow neutron capture attain thermal energy before exchanging with gaseous hydrogen bromide. An efficient organic reagent for radioactive atoms is very desirable and it occurred to us that vinylic and allylic halides might serve this purpose by the following type of exchange



Such reagents should be quite efficient since the exchange velocity depends primarily upon addition at the double bond, with a small or zero energy of activation.

We have found that neutron bombardment of gaseous mixtures consisting of 1-25 mm. of bromoolefin and 180 mm. of hydrogen bromide yields 80% organic activity. This high efficiency, which is practically independent of bromoolefin concentration over the range studied, has been interpreted elsewhere.⁴

Other experiments have demonstrated the efficiency of these olefins as reagents for Br* in the liquid state. Liquid ethyl bromide containing approximately one volume per cent. of a bromoolefin was subjected to thermal neutron bombardment. Additional bromoolefin and its addition product (*e.g.*, allyl bromide and 1,2-dibromopropane) were added after bombardment and separated by distillation. The addition product was invariably inactive, and the bromoolefin contained 25-50% of the total activity. This efficiency for the nascent Br* is maintained down to concentrations as low as 0.01 volume per cent. α , β -Dibromoethylene, 2-bromopropene and allyl chloride have been equally effective.

We have previously reported² the temperature coefficient of competitive exchange of nascent Br* with α , β -dibromoethylene and allyl bromide when both are present during neutron bombardment. We have recently found that the significance of this result has been obscured by a

(1) Work supported in part by A.E.C. Contract No. At(11-1)38.

(2) Presented at the 116th Meeting of the A.C.S., Atlantic City, September, 1949.

(3) W. H. Hamill and R. R. Williams, Jr., *J. Chem. Phys.*, **16**, 1171 (1948).

(4) R. R. Williams, Jr., and W. H. Hamill, *ibid.*, in press.