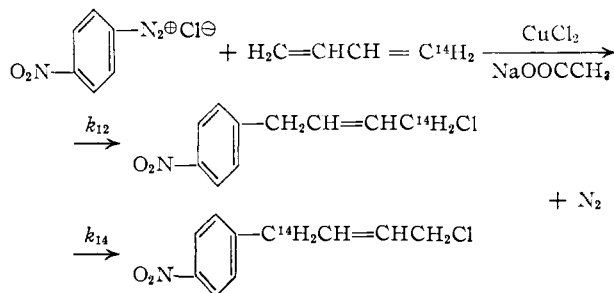## Examination of a Meerwein Reaction for an Intramolecular Isotope Effect with Carbon-14[1]

By Gus A. Ropp and Vernon F. Raaen

Because of an interest in the occurrence of carbon-14 isotope effects in addition reactions, a Meerwein[2] reaction of carbon-14 labeled butadiene was examined for an isotope effect

Use of the unsymmetrically-labeled symmetrical molecule, butadiene-1-C^{14}, provides a simple method of measurement of the ratio, k_{14}/k_{12}, of the rate constant of the reaction of the diazonium compound with a labeled end-carbon atom of butadiene to the rate constant of the reaction with an unlabeled end-carbon atom. Thus in the event $k_{14} \neq k_{12}$, the ratio of these rate constants could be evaluated as the ratio of the specific activities of the carbon-14 in the α-carbon atom of the side-chain of the product, 1-chloro-4-(p-nitrophenyl)-butene-2, to the specific activity of the δ-carbon atom of the side chain

$$k_{14}/k_{12} = S_\alpha/S\Delta$$

The specific activity of the α-carbon atom, S_α, would be given by the specific activity of the p-nitrobenzoic acid obtained from vigorous oxidation of the Meerwein reaction product
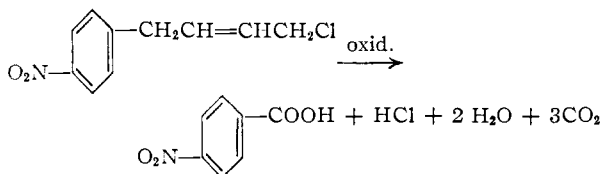
Since this reaction is nearly quantitative it could be assumed that there is no isotope fractionation in the oxidation and that the specific activity of the p-nitrobenzoic acid truly represents the specific activity of the α-carbon atom. In practice, isolation of the δ-carbon atom would be more difficult, and it would be much simpler to obtain the total specific activity of the 1-chloro-4-(p-nitrophenyl)-butene-2 and to calculate the isotope effect as

$$k_{14}/(k_{12} + k_{14}) = S_\alpha/(S_\alpha + S_\delta) = S_\alpha/S_{total}$$

From $k_{14}/(k_{12} + k_{14})$, k_{14}/k_{12} could be easily calculated. The value, S_{total}, would be measured more readily for the easily purified solid 1-(p-nitrophenyl)-1,3-butadiene, obtained by the dehydrohalogenation[2]
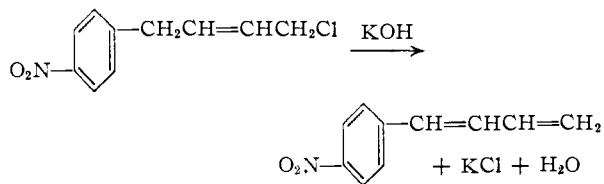
than for the liquid 1-chloro-4-(p-nitrophenyl)-butene-2. This dehydrohalogenation also is essentially quantitative, and it could, therefore, be assumed that the specific activity of the diene would truly represent the specific activity of the chloride and give S_{total}. This method should be applicable generally to the evaluation of isotope effects in addition reaction of unsymmetrically labeled symmetrical compounds.

After the above reactions were carried out, the specific activity of the purified p-nitrobenzoic acid was found to equal one-half the specific activity of the purified 1-(p-nitrophenyl)-1,3-butadiene within experimental error, thus indicating no preference on the part of the diazonium compound for reaction with a labeled or unlabeled end-carbon atom in butadiene. This result is understandable if one assumes that the reaction proceeds through an initial rate-controlling[3] break-up of the diazonium compound to yield an extremely active fragment such as the p-nitrophenyl radical. If every such fragment immediately reacts with a butadiene molecule as rapidly as it is formed, the distribution between the labeled and unlabeled end-carbon atoms of a labeled butadiene molecule should be statistical. This result is also in accord with recent results reported by Urry[4] who demonstrated that the most active of a series of free radicals appeared to give least isotope selectivity in abstracting hydrogen from deutero-organic compounds.

The synthesis of 1,3-butadiene-1-C^{14} from methyl-C^{14} iodide via methyl-C^{14}-vinylcarbinol which was dehydrated at 300° over phosphorus pentoxide involved only conventional procedures. The Meerwein reaction and dehydrohalogenation of the 1-chloro-4-(p-nitrophenyl)-butene-2 have been described elsewhere.[2] The specific activity of the labeled diene was shown by Van Slyke combustion[5] and radioassay[5] of the resulting carbon dioxide to be 2.66 μc. per mmole. A 2-g. sample of the labeled 1-chloro-4-(p-nitrophenyl)-butene-2 was boiled three hours with 15 g. of sodium dichromate, 50 ml. of water and 15 ml. of C.P. sulfuric acid. The resulting purified p-nitrobenzoic acid obtained had a specific activity of 1.35 μc. per mmole. Although the specific activity of the acid appeared to be about 1.5% greater than one-half the specific activity of the diene, this difference was too small to indicate definitely isotope selectivity in view of the limited accuracy of the assay method used.

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(2) G. A. Ropp and E. C. Coyner, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1951, Volume 31, p. 80.

(3) Cf. D. H. Hey and W. A. Waters, Chem. Revs., 21, 169 (1937); C. C. Price, "Reaction at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., p. 52.

(4) W. H. Urry, Reports of the Organic Division of the American Chemical Society, Symposium, Denver, Colo., June, 1951, p. 30.

(5) O. K. Neville, This Journal, 70, 3501 (1948).