block polymer is established. Many other block polymers were prepared by this technique.

The naphthalene–sodium initiator gives block polymers of the type A·B·A, or A·B·C·B·A.[6] The presence of two living ends was proved by experiments which will be reported later. However, the same method can be applied to conventional initiators of anionic polymerization yielding block polymers of the type A·B· or A·B·C.

(6) In these and in the following formulas letter A, B and C stand for blocks of monomers, *i.e.*, A....A, B....B, or C....C.

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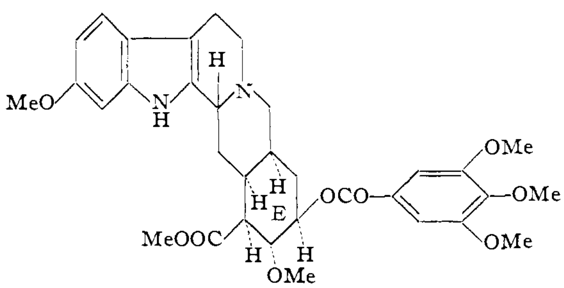
RECEIVED MARCH 29, 1956

A SIMPLIFIED ROUTE TO A KEY INTERMEDIATE IN THE TOTAL SYNTHESIS OF RESERPINE

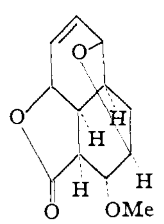
Sir:

Recently we recorded[1] the total synthesis of reserpine (I), through a route involving the meth-

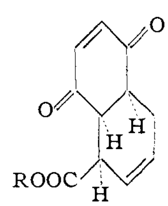


I

oxy-ether (II), which was prepared from the *p*-benzoquinone–vinylacrylic acid adduct (III, R = H) by a five-stage process. We now wish to report



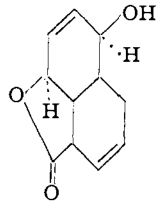
II



III

that the key intermediate (II), *which contains all five of the asymmetric carbon atoms of Ring E of reserpine, properly oriented*, is readily preparable from the *p*-benzoquinone–methyl vinylacrylate adduct (III, R = Me) in two simple operations.

The adduct (III, R = Me) (m.p. 103–104°, found: C, 65.07; H, 5.57), from *p*-benzoquinone



IV

(1) R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey and R. W. Kierstead, THIS JOURNAL, **78**, 2023 (1956).

and methyl vinylacrylate in benzene, was smoothly converted by aluminum isopropoxide in hot isopropyl alcohol to the hydroxylactone (IV) (m.p. 122–123°, found: C, 68.79; H, 6.50), which with bromine in methanol, followed by sodium methoxide, gave the methoxylactone (II).

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RECEIVED APRIL 19, 1956

INVESTIGATION OF SYNTHESIS *VERSUS* REËNTRY IN TWO ORGANIC NITROGEN CONTAINING SYSTEMS UNDER NEUTRON IRRADIATION[1]

Sir:

Previous work by the authors[2] has shown that both anthracene-C^{14} and acridine-C^{14} are produced by the neutron irradiation of acridine. These products are formed by *reëntry*[3] of the recoiling carbon-14 which travels a considerable distance after being "born."[4]

It became increasingly evident from our work on this and other systems that the inordinate difficulty in bringing the products to radiochemical purity was possibly due to *synthesis*[5] products which were difficult to remove because of their presence in the parent compound. In most cases it would be reasonable to expect their chemical behavior to be similar to that of the parent compound. Trace degradation products may also be important.

We have irradiated benzene in 2-methylpyrazine, and acetamide, in the Brookhaven Reactor. The presence of two possible *synthesis* products, toluene and propionamide, were then investigated by carrier methods.

In the case of acetamide, both propionamide and propionic acid were added as carriers on the assumption that the synthesized, excited three carbon fragment might in some cases collapse to give propionic acid. The hydrolysis was carried out both in acid and base to investigate possible differences in the state of the irradiated material. Degradations were carried out by the method of Phares.[6] The results are given in Tables I and II.

While it is clear from these results that *synthesis* does take place, *it becomes evident that the reaction to give toluene or propionamide involves processes other than a simple displacement* by a "hot" methyl radical.[7] The activity in the methylene, carboxyl, and ring carbons of the carrier materials studied cannot be credited to an inversion[8] reaction, al-

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) A. P. Wolf and R. C. Anderson, THIS JOURNAL, **77**, 1608 (1955).

(3) We prefer *reëntry* to retention in describing this process in order to avoid the implication, in the case of anthracene, that the molecule containing the N^{14} undergoing nuclear transformation is the same molecule which then contains the C^{14} in its ring.

(4) W. F. Libby, THIS JOURNAL, **69**, 2523 (1947); H. Faraggi, *Ann. Phys.*, **6**, 325 (1951).

(5) By *synthesis* we mean any product formed which has *one carbon more* than the parent compound exclusive of the carbon analog of the parent compound. See also A. G. Schrodt and W. F. Libby, THIS JOURNAL, **76**, 3100 (1954); L. J. Sharman and K. J. McCallum, *ibid.*, **77**, 2989 (1955).

(6) E. F. Phares, *Arch. Biochem. Biophys.*, **33**, 173 (1951).

(7) J. E. Willard, *Ann. Rev. Phys. Chem.*, **6**, 141 (1955).

(8) J. F. Hornig, G. Levey and J. E. Willard, *J. Chem. Phys.*, **20**, 1556 (1952).