of IV with acetic anhydride in pyridine yielded V, m.p. 263–265° (Calcd. for $C_{14}H_{13}NO_6$: C, 57.73; H, 4.50; N, 4.81. Found: C, 57.45; H, 4.12; N, 5.10). The infrared absorption spectrum and melting point of the synthetic product and of the compound obtained by degradation of novobiocin were identical. 2,2-Dimethylchroman-6-carboxylic acid[3,4] was converted with thionyl chloride into 2,2-dimethylchroman-6-carbonyl chloride, m.p. 95–97°. Treatment of the amine hydrochloride IV with this acid chloride in pyridine gave cyclonovobiocic acid (VI), m.p. 280–284°. A mixture of this product and VI obtained by degradation of novobiocin melted at 280–286°, and the infrared absorption spectra of the two were identical.

4-Acetoxy-3-(3-methylbutyl)-benzoic acid,[4] m.p. 147–149°, was converted with thionyl chloride into 4-acetoxy-3-(3-methylbutyl)-benzoyl chloride. Upon treatment of IV with this acid chloride in pyridine, followed by hydrolysis, dihydronovobiocic acid (VII) was obtained, m.p. 237–239°. A mixture of this product and VII obtained by degradation of novobiocin melted at 237–239°. The identity was confirmed by the infrared absorption spectra.

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RECEIVED MAY 9, 1956

POLYMERIZATION INITIATED BY ELECTRON TRANSFER TO MONOMER. A NEW METHOD OF FORMATION OF BLOCK POLYMERS[1]

Sir:

Aromatic hydrocarbons react with metallic sodium in suitable solvents yielding colored and soluble complexes of composition 1 Na to 1 hydrocarbon[2] which initiate polymerization of conjugated olefinic hydrocarbons.[3] Their structure has been elucidated by Weissman and Lipkin,[4] who showed them to be composed of negative aromatic hydrocarbon ions and Na^+ ions. They have shown also that the negative hydrocarbon ions act as electron transfer agents, *e.g.*

$$\text{Naphthalene}^- + \text{Phenanthrene} \rightleftarrows \text{Phenanthrene}^- + \text{Naphthalene} \quad (1)$$

We postulate the same type of electron-transfer process to be responsible for the initiation of polymerization by sodium-naphthalene complex, *e.g.*

$$\text{Naphthalene}^- + \text{Styrene} \longrightarrow \text{Styrene}^- + \text{Naphthalene} \quad (2)$$

The negative monomer ions formed by reaction (2) may be represented formally by I or Ia.[5]

$$:\mathrm{CHX{-}CH_2}\cdot \quad (\mathrm{I}) \qquad \cdot\mathrm{CHX{-}CH_2}: \quad (\mathrm{Ia})$$

With excess of monomer both ends of I or Ia propagate polymerization, each by a different mechanism, one end growing as a radical, the other as a carbanion. After addition of the first monomeric unit to *either* end, structures I or Ia become perfectly legitimate, *i.e.*, a true separation of electrons takes place and species like II are formed.

$$:\mathrm{CHX{-}CH_2{-}CHX{-}CH_2}\cdot \text{ or } :\mathrm{CHX{-}CH_2{-}CH_2{-}CHX}\cdot \quad (\mathrm{II})$$

The radical ends do not long exist. At low temperature they dimerise, and consequently species III are formed

$$:\mathrm{CHX{-}CH_2{-}CH_2{-}CHX}: \quad (\mathrm{III})$$

Inspection of species III suggests that they do not terminate, and thus propagation should continue until all the monomer is consumed, and eventually a "living" polymer is produced.

The correctness of all these assumptions has been tested. Polymerization, if carried out correctly, always goes to completion. The green color of naphthalene$^-$ ion instantaneously changes into deep red on addition of styrene, the latter color due to styrene$^-$ ends. After completion of polymerization the red color persists, indicating no reverse of reaction (2). If an additional amount of styrene is added after completion of the polymerization of the first portion, the polymerization starts again, and the reaction goes again to completion.

The viscosity of the polymer solution can be measured without withdrawing the solution out of the reaction vessel. Addition of further amounts of styrene and of solvent, quantities of which are adjusted in such a way that the ratio styrene: solvent remains unaltered, leads to an increase in the viscosity of the solution. For example, styrene (9.2 g.) was added to 60 cc. of tetrahydrofuran containing 3.3×10^{-4} mole of sodium naphthalene. Polymerization was carried out at −80° and after completion the viscosity of the solution was determined at room temperature (1.2–1.5 sec.). The solution was recooled to −80°, and an additional 7.7 g. of styrene in 50 cc. of tetrahydrofuran was added. After completion of the reaction the viscosity was found to increase to 18–20 sec. at room temperature. The final yield was 16.6 g. of polystyrene, *i.e.*, about 100% conversion. This proves conclusively the existence of living ends in these polymers, and suggests an interesting and novel method for preparation of block polymers. After completion of the first polymerization process, a second monomer is added to the still living polymers formed from the first monomer. Thus, block polymers of the type A.A···A.B.B···B.A.A···A are produced. For example, styrene (5.7 g.) was polymerized by 0.3 millimole of catalyst in the usual way and then 3.6 g. of isoprene was added. After precipitation 8.8 g. of polymer was obtained. The polymer solution in toluene could not be precipitated by isoöctane, proving the absence of pure polystyrene. On the other hand, the polymer is not extractable by isoöctane, proving the absence of pure polyisoprene. Thus, the nature of the

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[1] This research was partially supported by a grant from the Office of Naval Research Contract Nonr-134091.

[2] N. D. Scott, J. F. Walker and V. L. Hansley, THIS JOURNAL, **58**, 2442 (1936).

[3] N. D. Scott, U. S. Patent 2,181,771 (1939).

[4] D. E. Paul, D. Lipkin and S. I. Weissman, THIS JOURNAL, **78**, 116 (1956).

[5] This is only a formal notation. Styrene$^-$ should be visualized as a species possessing an additional electron in the lowest π orbital which is unoccupied in the ordinary molecule of styrene.

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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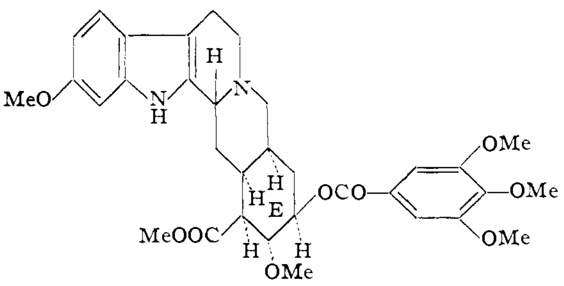
RECEIVED MARCH 29, 1956

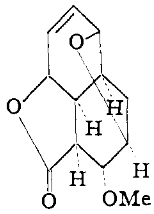
A SIMPLIFIED ROUTE TO A KEY INTERMEDIATE IN THE TOTAL SYNTHESIS OF RESERPINE

Sir:

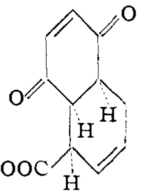
Recently we recorded[1] the total synthesis of reserpine (I), through a route involving the methoxy-ether (II), which was prepared from the *p*-benzoquinone–vinylacrylic acid adduct (III, R = H) by a five-stage process. We now wish to report that the key intermediate (II), *which contains all five of 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.



I

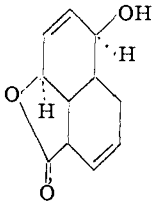


II



III

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



IV

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RECEIVED APRIL 19, 1956

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

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[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).