

**THE SPECIFIC NATURE OF ENERGY EXCHANGE IN UNIMOLECULAR REACTIONS***Sir:*

Since the energy of activation in unimolecular reactions is undoubtedly obtained by collision, the velocity constants fall off at low pressures. It is well known that certain inert gases will prevent this falling off by furnishing the necessary collisions. The specific nature of this effect is, however, very remarkable. In general, hydrogen and the products of the reaction are effective, while other inert gases are usually ineffective. Rice has recently discussed the question from the point of view of quantum mechanics [O. K. Rice, *Chem. Reviews*, **10**, 125 (1932)].

In the past most of the inert gases employed have been of comparatively simple structure. It seems desirable to obtain information regarding the behavior of gases which are as complicated as the reactant, and which resemble the reactant as much as possible. The series of ether decompositions investigated by Hinshelwood and his co-workers are ideal for the purpose. Accordingly an investigation has been undertaken on the rate of decomposition of mixtures of aliphatic ethers. Mixtures of dimethyl and diethyl ether have already been investigated. These ethers decompose in an almost identical way, and have a pronounced resemblance in physical properties, and in the manner in which the velocity constants fall off with diminishing pressure. Each might therefore be expected to show a high efficiency in activating the molecules of the other.

The surprising result has been obtained that the two gases have absolutely no activating effect on each other. A mixture of the two (at pressures where the falling-off is large) decomposes at a rate which is exactly the mean of those of its components (within an experimental error of about three per cent.). This appears to be the most pronounced example of the specificity of energy transfer which has yet been observed.

The decomposition of mixtures of methyl ethyl ether with both diethyl and dimethyl ether is being investigated. A full account of the work will appear later.

PHYSICAL CHEMISTRY LABORATORY  
MCGILL UNIVERSITY  
MONTREAL, CANADA  
RECEIVED MARCH 7, 1932  
PUBLISHED APRIL 6, 1932

E. W. R. STEACIE

---

**THE PREPARATION OF AN OPTICALLY ACTIVE TRIARYLCARBINOL***Sir:*

A survey of the chemical literature shows that many primary and secondary alcohols containing an asymmetric carbon atom have been successfully resolved. However, all previous attempts to resolve asymmetrically substituted tertiary alcohols have failed. In an article published

in the *Proceedings of the National Academy of Sciences*, 16, 215 (1930), I described a method for preparing an optically active triarylcarbinol in the form of its thioglycolic acid derivative. *l*-Phenylbiphenyl- $\alpha$ -naphthylmethylthioglycolic acid,  $(C_6H_5)(C_6H_5C_6H_4)(C_{10}H_7)CSCH_2COOH$ , was prepared and resolved by means of its brucine salt. It was found to have the specific rotation in carbon tetrachloride,  $[\alpha]_D^{20} -13.63^\circ$ ; in ether,  $[\alpha]_D^{20} -12.93^\circ$ . The dextro modification obtained by working up the residues from the fractional crystallization of the brucine salt gave an acid with  $[\alpha]_D^{20} +10.6^\circ$  in ether.

Many experiments have been carried out on these compounds in order to convert them into the corresponding optically active triarylcarbinols. This has finally been accomplished. Under proper conditions the levo modification of the acid gives a *d*-phenylbiphenyl- $\alpha$ -naphthylcarbinol of the specific rotation in carbon tetrachloride,  $[\alpha]_D^{20} +5.8^\circ$ . The dextro modification of the acid yields a levorotatory-carbinol,  $[\alpha]_D^{20} -5.4^\circ$ . The corresponding ethyl ethers have been prepared. The levo acid produces a levorotatory ether,  $(C_6H_5)(C_6H_5C_6H_4)(C_{10}H_7)C-OC_2H_5$ ,  $[\alpha]_D^{20} -22.7^\circ$  in ether. The dextro acid gives a dextrorotatory ether,  $[\alpha]_D^{20} +21.6^\circ$ . Other asymmetrically substituted tertiary alcohols are being prepared in order to study their possibilities of resolution by this method. Further investigations on the above optically active compounds are in progress with a view of answering the question of the spatial arrangement of the valences of the trivalent carbon atom. At present this is completely unexplained, and has been but superficially investigated. A report of this work will be published later.

FRICK CHEMICAL LABORATORY  
PRINCETON UNIVERSITY  
PRINCETON, NEW JERSEY  
RECEIVED MARCH 9, 1932  
PUBLISHED APRIL 6, 1932

EVERETT S. WALLIS

---

#### BETA-SUBSTITUTED FURANS

Sir:

Absolute orientation studies of nuclear substituted furans are circumscribed by the paucity of simple *beta*-substituted furans, which are uncommonly difficult of synthesis. 3-Furancarboxylic acid is now accessible by the preferential pyrolytic decarboxylation of 2,4-furandicarboxylic acid. Although the halogen in 3-iodofuran is extremely inert, particularly toward magnesium and sodium, 2,5-dimethyl-3-iodofuran readily forms an organomagnesium iodide. The iodofurans were prepared from the furan-mercurials.

DEPARTMENT OF CHEMISTRY  
IOWA STATE COLLEGE  
AMES, IOWA  
RECEIVED MARCH 10, 1932  
PUBLISHED APRIL 6, 1932

HENRY GILMAN  
ROBERT R. BURTNER  
GEORGE F. WRIGHT