

(or 2.70 if CH_3 vibrates as a single unit of mass 15). If now the amyl group vibrates as a unit the force constant for amyl bromide would be 7.0×10^5 dyne/cm., or more than two and a half times larger than for methyl bromide. This is much too large.

If the force constant in all of the normal bromides is assumed to be constant and equal to 2.60×10^5 dyne/cm., the effective mass of the portion of the hydrocarbon chain which vibrates (with respect to the bromine) is 17. This indicates that the CH_2 group adjacent to the bromine possesses most of the mass which is effective. That is, the CH_2 group vibrates, but its effective mass is increased by the constraint due to its union with the rest of the hydrocarbon chain, and is influenced by the vibration of this part of the molecule.

The writers have determined the frequencies of the Raman lines of nine organic bromides. These give a large number of characteristic frequency differences as, for example, 1639 cm.^{-1} for the double bond of allyl bromide, but only the values characteristic of the carbon-bromine and other carbon-halogen bonds can be discussed here. The variation in the wave number corresponding to this bond is usually not more than one unit of wave number for any one compound, and the maximum variation for any compound is two units.

The equation for the force constant (k) is

$$\nu_0 = \omega_0 (n' - n'') = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} (n' - n'')$$

in which n represents a quantum number, μ the mutual mass, ν_0 the fundamental frequency of the radiation, and ω_0 the fundamental mechanical frequency. A further discussion will be presented in the final paper.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

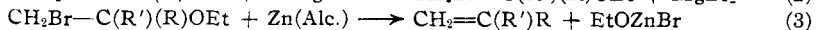
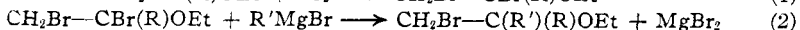
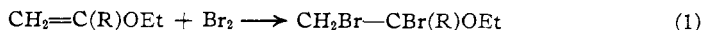
WILLIAM D. HARKINS
HAROLD E. BOWERS

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PREPARATION OF UNSYMMETRICAL DIALKYL ETHYLENE DERIVATIVES

Sir:

The recent description of the preparation of α, β -unsaturated ethers by Lauer and Spielman [THIS JOURNAL, **53**, 1533 (1931)] makes possible an extension of our nuclear synthesis of olefins [*ibid.*, **52**, 3396 (1930); **53**, 1505 (1931)] to include the unsymmetrical dialkyl derivatives of ethylene. The essential steps in the process are clearly represented by the scheme.



Three hexenes have been prepared by this method, with the physical constants indicated.

| Olefin | B. p. (760 mm.) | D_D^{20} | n_D^{20} | MR (Fd.) | MR (Calcd.) |
|-----------------------|-----------------|------------|------------|----------|-------------|
| 2-Methyl-1-pentene | 61.5-62.0 | 0.6831 | 1.3921 | 29.34 | 29.44 |
| 2-Ethyl-1-butene | 66.2-66.7 | .6938 | 1.3990 | 29.31 | 29.44 |
| 2,3-Dimethyl-1-butene | 56.0-56.5 | .6827 | 1.3905 | 29.55 | 29.44 |

The method is being extended to the preparation of other olefins and diolefins.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO
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CLAUDE G. SCHMITT
CÆCIL E. BOORD

THE DECOMPOSITION OF SODIUM AZIDE BY CONTROLLED ELECTRON BOMBARDMENT

Sir:

The decomposition of solid sodium azide has been achieved by subjecting a thin film to bombardment by electrons of known velocity. The reaction was carried out in a high vacuum using an oxide filament as the source of electrons and suitable electrodes for controlling the velocity. Impacts in the gas phase were shown to be absent. The nitrogen resulting from the decomposition was detected and measured by an ionization manometer. The gas evolved was shown to be nitrogen by critical impact measurements. Rate curves taken at various electron velocities gave a sharp intercept on the voltage axis, setting the minimum potential at 12 ± 1 volts. The rate curves showed discontinuities in the region of the critical potentials of nitrogen, thus affording additional proof of the nature of the gas. At no time was any thermal decomposition observed, nor any effect at or below 11.5 volts.

These measurements are being continued with slightly improved technique. The photochemical decomposition is being studied as well and will be the subject of a later communication.

DEPARTMENT OF CHEMISTRY
WASHINGTON SQUARE COLLEGE
NEW YORK UNIVERSITY
NEW YORK CITY
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RALPH H. MÜLLER
G. CALVIN BROUS