

values chosen by Eastman as representing the heat capacity of all three halide gases has been included for comparison.

It will be seen that the agreement between Eastman's selected figures and the calculated values for HCl is satisfactory, the maximum deviation being approximately 1.5%. It is perhaps worth noting that above 2000° Eastman's values run higher than the calculated ones and that this is the same direction in which Eastman's values deviate from the best of the experimental observations.

For HBr and HI differences as great as 5% exist between the results of the calculations and the data of Eastman. Unfortunately there appear to be no experimental observations on which to check the calculations but in view of the agreement found with HCl it seems probable that the calculated values are not much in error and almost certainly give a closer description of the true heat capacity of these gases than is obtained by assigning the same figure to all.

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THE CHLORINATION OF NEOPENTANE

Sir:

All recorded methods of making neopentane failed to give appreciable yields except that of Lwow [*Z. Chem.*, 520 (1870)] involving dimethyl zinc and a tertiary butyl halide. The iodide, bromide and chloride gave 42, 46 and 51% yields, respectively. The hydrocarbon froze and boiled at approximately -20 and $+10^{\circ}$, respectively.

The chlorination of neopentane was very easy. At room temperature in diffused light the color of chlorine disappeared in fifteen minutes. The chloride boiled at 24° (80 mm.) and froze at -20° . The analysis for chlorine was 1.5% low for an amyl chloride. Tertiary amyl chloride showed b. p. 23.5° (8 mm.) and m. p. -73° . A small amount of a dihalide, b. p. 35° (8 mm.), was also obtained. The monochloride when shaken with cold water for thirty minutes showed the presence of 6% of tertiary halide (Michael). The amount of tertiary halide was increased only slightly, if at all, by heating the chloride at 140° for one and one-half hours. All known methods of converting a halide to a Grignard reagent failed. These facts indicate that the halide obtained is neopentyl chloride.

Neopentane is being prepared in larger amounts to make possible a more thorough study of its chlorination in relation to the mechanism of rearrangements. The limited amount of tertiary amyl chloride formed and the surprising stability of the neopentyl chloride carry implications of great

significance in this field [Whitmore, *THIS JOURNAL*, **54**, 3274 (1932); Whitmore and Rothrock, *ibid.*, **54**, 3431 (1932)].

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DEHYDRATION OF DIETHYLCARBINOL

Sir:

By dehydrating diethylcarbinol in a flow reactor at 40 lb. pressure and at 365–410° with a phosphoric acid catalyst on silica gel we have obtained a mixture of olefins of b. p. 65–70° which on ozonolysis gives formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde. The first two were identified by the resorcinol-sulfuric acid test and as acetaldehyde-ammonia, respectively. The last two were converted to the 2,4-dinitrophenylhydrazones, which were identified by melting point and mixed melting point determinations. Small amounts of impure 2,4-dinitrophenylhydrazones probably corresponding to methyl ethyl ketone and diethyl ketone were also obtained. These results show that the dehydration of diethylcarbinol gives both the normal and rearranged products. This study is to be continued on a larger scale in an endeavor to determine quantitatively the various modes of dehydration.

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THE REACTION OF ACID IODIDES WITH ETHERS

Sir:

In a recent paper by Meerwein and Maier-Hüser [*J. prakt. Chem.*, **134**, 51 (1932)] on the cleavage of ethers by acid halides and anhydrides in the presence of catalysts, these workers have called attention to the isolated observation of Kishner [*J. Russ. Phys.-Chem. Soc.*, **41**, 651–659 (1909); *Chem. Zentr.*, II, 1132 (1909)] that benzoyl iodide is capable of splitting primary aliphatic ethers at 100° without the presence of a catalyst, giving alkyl iodides and benzoates. This work has not previously received the further study which its suggestive character would indicate.

With the hope that aliphatic acid iodides might prove more reactive, permitting the cleavage of ethers at ordinary temperatures, we have investigated the behavior of acetyl iodide and the chloro substituted acetyl iodides with a number of aliphatic ethers, thio ethers and oxides. This