differ slightly in hydrogen-ion concentration. However, since the difference in potential between the hydrogen and quinhydrone electrodes in the same solution is not a function of the hydrogen-ion concentration but of the total electrolyte present, little difference between the values in the two series would be expected. This proved to be the case. The mean values at 25 ± 0.01° were: for (a) 0.69903 ± 0.00002 volt, for (b) 0.69898 ± 0.00002 volt. When the quinhydrone electrode is part of a cell involving liquid junction 0.6990 volt should be used for both (a) and (b). Due to its reproducibility and constancy we are convinced that in all around qualifications this standard quinhydrone electrode excels either the 0.1 *N* or saturated calomel electrode.

The above potentials differ appreciably from the ideal value for the cell Pt/H_2, electrolyte, quinhydrone/Au because of the salt error. This will be considered in a later report.

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FRANK HOVORKA
WM. C. DEARING

RECEIVED NOVEMBER 17, 1933

ADDITION OF HYDROGEN BROMIDE TO 4,4-DIMETHYLPENTENE-1

Sir:

The addition of halogen acids to substituted ethylenes has been under investigation in our laboratory for some time, particularly as regards the effects of peroxides and antioxidants on the direction of addition. For certain theoretical reasons these studies included the addition of halogen acids to 4,4-dimethylpentene-1.

In view of the recent publication of Whitmore and Homeyer [THIS JOURNAL, **55,** 4555 (1933)] it appears desirable to publish some of our pertinent findings.

Our results indicate that the direction of addition of hydrogen bromide to 4,4-dimethylpentene-1 is governed by the peroxide content of the material or reagents. From that standpoint the compound 1-bromo-4,4-dimethylpentane, the product first isolated by Whitmore and Homeyer, is what we define the "abnormal" product of the reaction. This product is formed whenever the addition of halogen acid is carried out in air, or when the mixture contains peroxides. On the other hand, if the addition of hydrogen bromide is carried out *in vacuo* in the presence of good antioxidants, the isomeric 2-bromo-4,4-dimethylpentane is obtained. It is this last product that we consider the "normal" product of the reaction.

In conformity with what we have just stated, we find that if the addition of hydrogen bromide to 4,4-dimethylpentene-1 is carried out *in vacuo* (instead of in air) 50% of the 2-bromo-4,4-dimethylpentane is obtained. The physical constants of the hitherto unknown 2-bromo-4,4-dimethylpentane are: b. p. 59.4° at 34 mm.; n^{20}_{D} 1.4463; while those of the 1-bromo-4,4-dimethylpentane under the same experimental conditions are: 68.8° and 1.4485. The table summarizes some of our results. The yields were excellent in all cases.

No.	Mole of olefin	Mole HBr	Reagent added, in mole
1	0.046	0.075	Ascaridole, 0.0012
2	.046	.075	None
3	.045	.079	Acetic acid, 0.075
4	.048	.077	*p*-Thiocresol, 0.0024
5	.049	.088	Diphenylamine, 0.0030

No.	Gas in bombs	n^{20}_{D}	2-Isomer, % ± 10%
1	Air (R. T.)	1.4483	0
2	Vac. (0°)	1.4474	50
3	Vac. (0°)	1.4479	27
4	Vac. (R. T.)	1.4469	73
5	Vac. (R. T.)	1.4463	100

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RECEIVED NOVEMBER 20, 1933

THE RULE OF SHIFT (VERSCHIEBUNGSGESETZ)

Sir:

Efforts to discover an indirect method for the correlation of the configurations of structurally similar substances have led to the enunciation of several rules all of which may be classed under the general heading of the "Rules of Shift." The earliest of these is perhaps that of Tschugaeff[1] stating that in homologous series the rotations of individual members increase asymptotically to a maximum value. To the same group belong the "Lactone Rule" of Hudson,[2] the "Phenylhydrazide Rule" of Levene,[3] etc. In its most comprehensive form (presented by K. Freudenberg[4]) the rule states that in similar, configurationally-related substances an identical substitution on identical groups produces a shift of rotation in the

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[1] Tschugaeff, *Ber.*, **31**, 360 (1898); *Chem. Zentr.*, I, 93 (1905); *Trans. Faraday Soc.*, **10**, 70 (1914).

[2] Hudson, THIS JOURNAL, **40**, 813 (1918); **40**, 1141 (1919).

[3] Levene, *J. Biol. Chem.*, **23**, 145 (1915).

[4] Freudenberg, *Ber.*, **66**, 177 (1933).