chloride was refluxed for four and one-half hours with 25 g. of flowers of sulfur and distilled rapidly through a 30-bulb Snyder column attached to an all-glass setup. A 94% yield of colored product was taken overhead. The distillate was fractionated through the 30-bulb column, about twelve hours being needed to remove the colored forerun. The colorless portion was taken overhead in about two hours and distilled over no range with a thermometer that was graduated in degrees. The yield in the second step was 88% making an 82% over-all yield. The product was colorless when viewed crossways in a liter graduate and very slightly yellow when viewed from the top. The still went to dryness and the residue was yellow with some black material reminiscent of organic matter. No attempts to improve the above procedure were made.

The sulfur probably aids in changing the sulfuryl chloride to sulfur dioxide and sulfur chlorides. The sulfur monochloride, b. p. 135.6°, presumably is left behind in the first distillation and sulfur dichloride, b. p. 69°, is the forerun of the fractionation which gives the colorless thionyl chloride, b. p. 78.8°. It is probably impractical to try removing both sulfur chlorides in one distillation because of the equilibrium between sulfur monochloride on the one hand and sulfur dichloride and sulfur on the other.

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The Molecular Refractions of the Higher Acetylenic Hydrocarbons[1]

BY G. F. HENNION AND T. F. BANIGAN, JR.

It is well known that the calculated molecular refractivities of organic compounds usually do not agree exactly with the observed values given by the Lorenz–Lorentz equation. In the absence of structural complications, *e. g.*, conjugate unsaturation, the agreements are on the whole remarkably good for pure liquids. Notable exceptions to this fact are found among the higher acetylenic hydrocarbons. The treatises of organic chemistry uniformly cite the (D-line) value, 2.398, as the atomic correction factor for the triple bond, even though there is good evidence that this value is not entirely trustworthy. Auwers,[2] among others, called attention to this some years ago after examination of selected literature data. He suggested a triple bond correction of 2.325 for terminal acetylenes, R—C≡CH, and 2.573 for the non-terminal ones, R—C≡C—R′. Campbell and Eveslage[3] very recently showed that these values also are not fully reliable and recommended a new set of increments for 1-, 2-, 3-, 4-, and 5-acetylenes, respectively. Actually none of these approaches are accurate. This was brought to our attention recently during a study of di-*t*-butylacetylene.[4] Using the accepted value for the triple bond, 2.398, the calculated and observed refractions were 46.378 and 47.641, respectively, thus showing an apparent exaltation of 1.263 units. Campbell's increment for 3-acetylenes, 2.696, improves the agreement insufficiently. A study has therefore been made of the refractions of twenty purified acetylenes reported in the literature (Table I). In order to obtain exact agreement between the calculated and observed refractions of these compounds, twenty different triple bond increments are needed. They range from 2.219 for 1-pentyne to 3.661 for 2,2,5,5-tetramethyl-3-hexyne (di-*t*-butylacetylene). The required correction increases with alkyl chain lengthening on each side of the triple linkage and with chain branching nearby. The triple bond increment therefore depends upon the number of carbon (?) atoms which come under the influence of the triple linkage and it seems impossible to assign any satisfactory value or values to the triple bond, *per se*.

In order to estimate the expected refractions more closely, an entirely different method of cal-

TABLE I

PHYSICAL CONSTANTS AND MOLECULAR REFRACTIONS OF HIGHER ACETYLENES

Compound	Formula	d^{20}	n^{20}_D	MR_D obsd.	MR_D calcd. Present method	Old method
2-Butyne[a]	C_4H_6	0.6913	1.3921	18.637	18.638	18.670
1-Pentyne[a]	C_5H_8	.6908	1.3852	23.118	23.100	23.288
2-Pentyne[a]	C_5H_8	.7104	1.4039	23.444	23.443	23.288
1-Hexyne[a]	C_6H_{10}	.7156	1.3990	27.766	27.736	27.906
3-Hexyne[b]	C_6H_{10}	.7231	1.4110	28.204	28.248	27.906
3,3-Di-Me-1-butyne[c]	C_6H_{10}	.6686	1.3744	28.083	28.074	27.906
1-Heptyne[a]	C_7H_{12}	.7325	1.4088	32.444	32.336	32.524
5-Me-1-hexyne[a]	C_7H_{12}	.7274	1.4059	32.467	32.336	32.524
1-Octyne[a]	C_8H_{14}	.7460	1.4159	37.060	36.954	37.142
2-Octyne[a]	C_8H_{14}	.7596	1.4278	37.308	37.315	37.142
3-Octyne[a]	C_8H_{14}	.7522	1.4250	37.458	37.502	37.142
4-Octyne[a]	C_8H_{14}	.7509	1.4248	37.508	37.520	37.142
3-Nonyne[d]	C_9H_{16}	.7616	1.4295	42.090	42.120	41.760
3,3-Di-Me-4-heptyne[e]	C_9H_{16}	.7610	1.4360	42.679	42.494	41.760
5-Decyne[b]	$C_{10}H_{18}$	.7688	1.4332	46.746	46.756	46.378
3-Me-3-Et-4-heptyne[e]	$C_{10}H_{18}$	.7714	1.4386	47.104	47.130	46.378
2,2-Di-Me-3-octyne[e]	$C_{10}H_{18}$	.7491	1.4270	47.382	47.112	46.378
2,2,5,5-Tetra-Me-3-hexyne[f]	$C_{10}H_{18}$	.7120	1.4055	47.641	47.468	46.378
5-Undecyne[d]	$C_{11}H_{20}$	.7760	1.4360	51.306	51.374	50.996
3,3-Di-Me-4-nonyne[g]	$C_{11}H_{20}$	.7667	1.4317	51.480	51.748	50.996

[a] Henne and Greenlee, THIS JOURNAL, **67**, 484 (1945). [b] Campbell and Eby, *ibid.*, **63**, 2684 (1941). [c] Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Co., New York, N. Y., 1939, Vol. I, p. 367. [d] Campbell and O'Connor, THIS JOURNAL, **61**, 2898 (1939). [e] Campbell and Eby, *ibid.*, **62**, 1800 (1940). [f] Hennion and Banigan, *ibid.*, **68**, 1202 (1946). [g] Eveslage, M.S. Dissertation, University of Notre Dame, 1945.

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(1) Paper I. on the chemistry of the substituted acetylenes; previous paper, THIS JOURNAL, **68**, 1202 (1946).

(2) Auwers, *Ber.*, **68**, 1635 (1935).

(3) Campbell and Eveslage, THIS JOURNAL, **67**, 1851 (1945).

(4) Hennion and Banigan, previous paper, ref. 1.

culation was undertaken. From the numerous examples in Table I, it is possible to calculate approximate contributions of acetylenic carbon ($C^{\equiv}$) and of the α, β, γ, ..., ω carbon atoms combined thereto, assuming only that hydrogen is normal, *i. e.*, contributes 1.100 per atom. On this basis there is obviously no correction for the triple bond. The various calculations are best explained by the following examples. The observed refraction for 1-pentyne less 1.100 gives 22.018 as the value for the group $CH_3—CH_2—CH_2—C{\equiv}C—$; one-half the observed value for 4-octyne, 18.754, is the contribution of $CH_3—CH_2—CH_2—C{\equiv}$. Thus one $C^{\equiv}$ contributes 3.264, the difference between 22.018 and 18.754. Similar calculations made by comparison of 1-hexyne with 5-decyne and of 3,3-dimethyl-1-butyne with 2,2,5,5-tetramethyl-3-hexyne give $C^{\equiv}$ values of 3.293 and 3.163, respectively. The maximum deviation is only 0.130 and the average of the three values, 3.240, is now taken as the mean contribution of one acetylenic carbon atom, $C^{\equiv}$.

The value for *alpha* carbon atoms, C^{α}, was calculated from the data for 2-butyne: *MR* (obsd.), 18.637; $C^{\equiv}$, 3.240; H, 1.100; C^{α} (calcd.), 2.779.

In a similar way the average contribution of *beta* carbon atoms was obtained from the data for 2-pentyne, 3-hexyne, 3,3-dimethyl-1-butyne, and 2,2,5,5-tetramethyl-3-hexyne. The values so found are 2.606, 2.583, 2.608, and 2.624, respectively; average 2.605.

Using these average values, the increment for each C^{γ} was estimated from the observed refractions of 1-pentyne, 4-octyne, and 3-methyl-3-ethyl-4-heptyne. The agreement is again surprisingly good, the values being 2.454, 2.430, and 2.423, respectively; average, 2.436.

It is seen immediately that the succeeding carbon atoms rapidly approach the normal mean value, 2.418, and it may be assumed that the $C^{\delta \cdots \omega}$ increments are, indeed, 2.418 units each. Not only is it likely that the atomic exaltations induced by the triple bond should be largely dissipated at the *delta* carbon atoms, it is possible to justify this assumption by noting the increments for succeeding methylene units in the symmetrical dialkylacetylenes: $C_2H_5—C{\equiv} > CH_3—C{\equiv}$, 4.783; n-$C_3H_7—C{\equiv} > C_2H_5—C{\equiv}$, 4.652; n-$C_4H_9—C{\equiv} > n$-$C_3H_7—C{\equiv}$, 4.619; n-$C_5H_{11}—C{\equiv} > n$-$C_4H_9—C{\equiv}$, 4.616; accepted, $—CH_2—$, 4.618.

The final atomic refractions recommended for alkyl and dialkylacetylenes are, therefore, $C^{\equiv}$ 3.240; C^{α}, 2.779; C^{β}, 2.605; C^{γ}, 2.436; $C^{\delta \cdots \omega}$, 2.418; H, 1.100.

The comparison of molecular refractions, observed and calculated on the old and present basis, is made in Table I. The agreements for the present method are uniformly quite good, the maximum deviation being about 0.5%. The normal acetylenes check particularly well; the highly branched isomers deviate slightly in proportion to the extent of branching.

An alternative method of calculation which has been employed commonly with other types of compounds is the use of alkyl group values determined from known compounds. The examples in Table I make possible the assignment of group values for methyl, ethyl, *n*-propyl, *n*-butyl, *t*-butyl, and a few others in the usual manner. Unfortunately, however, such group values taken from several examples frequently disagree. Thus the contribution for *t*-butyl calculated from *t*-butylacetylene is 19.749; taken from di-*t*-butylacetylene it is 20.204, both values based on 2.398 for the triple bond correction. It seems better, therefore, to calculate the expected molecular refraction by summation of the average contributions of the various types of atoms in the molecule.

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The Preparation of Some Tertiary Alcohols by the Addition of Organic Acids to Grignard Reagents

BY RALPH C. HUSTON AND DONALD L. BAILEY

In 1904, Grignard[1] prepared 2-methyl-5-ethyl-5-heptanol by passing carbon dioxide into isoamylmagnesium bromide and adding ethylmagnesium bromide to the reaction mixture. He also prepared 2,7-dimethyl-5-isobutyl-5-nonanol from isobutylmagnesium bromide and isoamylmagnesium bromide. Later Iwano[2] used the method to prepare 5-butyl-5-nonanol.

A patent[3] issued to Bayer and Company in 1906 covered the preparation of tertiary alcohols from organic acids (or their potassium salts) but gave little detail as to procedure or yield.

We have prepared the following sixteen tertiary alcohols in 40–60% yield by slowly adding one mole of organic acid in ether to 3.3 moles of primary Grignard reagent[4] and refluxing on a water-bath for two hours: 2-methyl-2-pentanol, 2-methyl-2-hexanol, 3-ethyl-3-hexanol, 2-methyl-3-ethyl-3-pentanol, 3-ethyl-3-heptanol, 3-ethyl-5-methyl-3-hexanol, 3-ethyl-3-octanol, 6-methyl-6-undecanol, 6-ethyl-6-undecanol, 6-propyl-6-undecanol, 6-isopropyl-6-undecanol,[5] 6-butyl-6-undecanol, 6-isobutyl-6-undecanol,[6] 6-amyl-6-undecanol and 5-butyl-5-nonanol. (The yield of 2-methyl-2-propanol was 4% and that of 3-methyl-3-pentanol was 32%.)

It was found that yields of the alcohols could be increased by adding the acid in benzene solution

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(1) Grignard, *Compt. rend.*, **138**, 154 (1904).

(2) Iwano, *Bull. soc. chim.*, **32**, 244 (1925).

(3) German Patent 166,898–99 (1906).

(4) Whitmore and Badertscher, THIS JOURNAL, **55**, 1561 (1933).

(5) B. p. 104–106° (2 mm.); d^{20}_4 0.8425; n^{20}_D 1.4477. Calcd. for $C_{14}O_{30}O$: C, 78.5; H, 14.02. Found: C, 78.41; H, 14.17.

(6) B. p. 116–118° (3 mm.); d^{20}_4 0.8367; n^{20}_D 1.4464. Calcd. for $C_{15}H_{32}O$: C, 78.95; H, 14.04. Found: C, 78.63; H, 14.14.