1-Propyl-2-iodoacetylene

By Thomas H. Vaughn

When the densities and indices of refraction of the alkyl iodoacetylenes are plotted against molecular weight it becomes apparent that the values for these constants reported for propyl iodoacetylene by Grignard and Perrichon [*Ann. chim.*, **5**, 5–36 (1926)] are seriously in error.

This compound has been prepared in this Laboratory in 77% yield by the action of iodine on pentinylmagnesium bromide according to the procedure outlined by Grignard and Perrichon and has been found to possess the following properties: b. p. 67.0–67.5° at 35 mm.; 75–77° at 51 mm.; γ_{25} 34.22 dynes/cm. (maximum bubble pressure method); [P], obs., 283.3; calcd., 281.3; n^{25}_{D} 1.52231, n^{10}_{D} 1.5310; d_{25} 1.6557; MR'_{D} calcd., 36.54; obs., 35.73. These values for the index of refraction and density lie on their curves as determined from the other members of the series.

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COMMUNICATIONS TO THE EDITOR

HYDROGENOLYSIS OF ALCOHOLS TO HYDROCARBONS

Sir:

Recently we have found a method for the preparation of certain hydrocarbons which were not readily available. The reaction involved is the hydrogenolysis of a primary alcohol according to the equation $RCH_2OH + 2H_2 = RH + CH_4 + H_2O$. The reaction proceeded smoothly with duodecanol-1, tetradecanol-1, octadecanol-1 and 3-cyclohexylpropanol-1, from which were obtained *n*-undecane [b. p. 189–190° (740 mm.), n^{25}_{D} 1.4164], *n*-tridecane [b. p. 84–85° (3 mm.), n^{25}_{D} 1.4250, m. p. −7–8°], *n*-heptadecane [b. p. 290–292° (738 mm.), n^{25}_{D} 1.4360, m. p. 20–21°], and ethylcyclohexane [b. p. 127–128° (738 mm.), n^{25}_{D} 1.4310]. Similarly the diprimary glycol, decanediol-1,10, by the removal of both carbinol groups was converted into *n*-octane [b. p. 121–123° (742 mm.), n^{25}_{D} 1.3975].

Hydrogenolysis was accomplished by subjecting 40 to 50 g. of the alcohol or glycol for about five hours to the action of hydrogen (100 to 200 atmospheres) at 250° over a nickel catalyst. The reaction proceeded almost quantitatively and no product other than the indicated hydrocarbon was found in any case. In some experiments a small amount of the original alcohol or glycol was recovered. [The catalyst and apparatus have been described in THIS JOURNAL, **54,** 4116 (1932), and *Ind. Eng. Chem., Anal. Ed.*, **4,** 342 (1932).]

Secondary alcohols also undergo hydrogenolysis but in this case the reaction involves the cleavage of a carbon to oxygen rather than a carbon to carbon bond, *i. e.*, $R_2CHOH + H_2 = R_2CH_2 + H_2O$. This type of reaction giving a hydrocarbon of the same carbon content as the alcohol is not novel; in fact it has been regarded as the normal reaction for primary as well as secondary and tertiary alcohols. The reaction proceeds smoothly under the conditions described above. For example, cyclohexane (m. p. 4–5°, n_D^{25} 1.4260) and *n*-octane were the only hydrocarbons obtained by the hydrogenolysis of cyclohexanol and octanol-2.

The primary–secondary glycol octadecanol-1,12, $CH_3(CH_2)_5CHOH-(CH_2)_{10}CH_2OH$, as would be anticipated from the results stated above, underwent carbon to oxygen cleavage at the secondary carbinol, and carbon to carbon cleavage at the primary carbinol, with the formation of *n*-heptadecane, $C_{17}H_{36}$. The glycol [293 g., m. p. 67–69°, b. p. 200–208° (4 to 5 mm.)] was obtained by hydrogenation of castor oil (500 g.) over copper–chromium oxide catalyst (35 g.) for nine hours at 250° under 200–300 atmospheres pressure. The product so obtained was not completely homogeneous, as evidenced by its physical constants and the fact that in addition to the main product, *n*-heptadecane, a small amount of an unidentified hydrocarbon was obtained in its hydrogenolysis.

The primary alcohols and decanediol-1,10 subjected to hydrogenolysis were prepared from the ethyl esters of the corresponding acids through the action of hydrogen over a copper–chromium oxide catalyst [THIS JOURNAL, **54,** 4678 (1932)]. Both of the steps in the conversion of an ester to a hydrocarbon containing one less carbon atom than the acyl group of the ester can be accomplished by using a mixture of the two catalysts, *i. e.*, copper–chromium oxide and nickel. However, our experience indicates that it is preferable to carry out the operation in two stages since the water formed in the second step prevents the completion of the first reaction.

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RECEIVED JANUARY 23, 1933 PUBLISHED MARCH 7, 1933

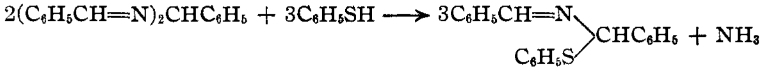
A NEW CONDENSATION REACTION OF THE THIOPHENOLS

Sir:

In view of the recent increase of interest in mercaptan chemistry, both in this country and abroad, we should like to report briefly upon a new reaction of the thiophenols, the investigation of which has been carried forward in this Laboratory during the past two years.

We have found that phenyl mercaptan itself, and many substituted thiophenols, as well as benzyl mercaptan, undergo condensation in boiling 1,4-dioxane solution with such condensed ammonia-aldehydes as hexamethylenetetramine and hydrobenzamide, only part of the nitrogen of the base being eliminated as ammonia. The products are crystalline substances (except in a very few cases) which may be considered as substituted trimethylamines. The following typical examples of the reaction will serve to illustrate

$$(CH_2)_6N_4 + 6C_6H_5SH \longrightarrow 2N(CH_2SC_6H_5)_3 + 2NH_3$$



$$2(C_6H_5CH{=}N)_2CHC_6H_5 + 3C_6H_5SH \longrightarrow 3\left.\begin{matrix}C_6H_5CH{=}N\\ C_6H_5S\end{matrix}\right\rangle CHC_6H_5 + NH_3$$

The only analogous reactions which we have been able to find reported in the literature are those of hexamethylenetetramine with such weak acids as HCN [Eschweiler, *Ann.*, **278**, 230 (1894)] and N-nitromethylamine [Franchimont, *Rec. trav. chim.*, **29**, 355 (1910)], where a similar condensation takes place.

We are continuing our investigations and hope very shortly to be able to publish a detailed report of the work.

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RECEIVED JANUARY 28, 1933 PUBLISHED MARCH 7, 1933

ON THE MAXIMUM ROTATIONS IN THE HOMOLOGOUS SERIES OF α-BROMO ACIDS

Sir:

In the course of our work on the shift of the molecular rotations of members of homologous series, we were in need of resolving α-bromobutyric and α-bromocaproic acids to the maximum. The α-bromopropionic acid had already been resolved to the maximum of $[M]_D^{25}$ −43.6° by Ramberg [*Ann.*, **370**, 234 (1909)] through the cinchonine salt.

We succeeded in resolving the α-bromobutyric acid through its brucine salt to $[M]_D^{25}$ +59.62° and α-bromocaproic acid through its strychnine salt to $[M]_D^{25}$ −71.45°, thus showing that in this homologous series the values of the rotations of the individual members increase progressively. The progress in the case of the methyl esters was similar, being 83, 92 and 104°, respectively, for the three esters.

These results were obtained nearly a year ago and remained unpublished for the reason that they were intended to be part of a comparative study of the rotations of the corresponding α-hydroxy and α-amino acids.

We wish to record the results at this time for the reason that in the current number of the *Journal für praktische Chemie* there appeared an article by Ahlberg [*J. prakt. Chem.*, **135**, 335 (1932)] devoted exclusively to the resolution of α-bromobutyric acid. The author failed to accomplish resolution by means of the brucine salt, but by means of the strychnine salt obtained a value for the maximum rotation lower than ours and of opposite sign, namely, $[M]_D^{25}$ −54.0°.

It is interesting to note that through the strychnine salts both acids lead to active acids rotating in the same direction.

It may also be mentioned that α-bromobutyric acid had previously been resolved by Levene, Mori and Mikeska [*J. Biol. Chem.*, **75**, 337 (1927)] to a degree somewhat higher than that of Ahlberg.

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RECEIVED FEBRUARY 2, 1933 PUBLISHED MARCH 7, 1933

THE ROTATION OF MOLECULES OR GROUPS IN CRYSTALLINE SOLIDS

Sir:

In continuation of earlier studies of the possibility of rotation of molecules or groups in crystalline solids [Smyth and Hitchcock, THIS JOURNAL, **54**, 4631 (1932); *ibid.*, **55**, in press (1933); Kamerling and Smyth, *ibid.*, **55**, 462 (1933)], the dielectric constants of hydrogen sulfide, ammonia and methyl alcohol have been measured from −190° to a few degrees above the melting points over a frequency range of 300 to 60,000 cycles. In solid hydrogen sulfide two sharp transitions are shown by the dielectric constant at −146.7° and −170.0°, in excellent agreement with the values just reported by Kemp and Denison [THIS JOURNAL, **55**, 251 (1933)]. The dielectric constant of the solid, higher than that of the liquid, shows almost free molecular rotation above the lower transition. Below it, there appears to be practically no dipole rotation. The behavior of hydrogen sulfide is thus similar to that of the hydrogen halides and in marked contrast to that of ice.

The low dielectric constant of solid ammonia in contrast to the high value of the liquid and its small decrease with decreasing temperature show that the molecule behaves like large molecules, such as those of nitrobenzene, in possessing little or no rotation in the solid, thus differing from all the small molecules previously investigated by means of dielectric constants. The dielectric constant of solid methyl alcohol near the melting point is much lower than that of the liquid but high enough to give evidence of some dipole rotation, which decreases sharply at a transition point −114.0°, a value close to the average of those found from specific heat measurements, −115.7° by Kelley [THIS JOURNAL, **51**, 180 (1929)], and −112.0° by Parks [*ibid.*, **47**, 338 (1925)]. Under conditions such that a glass is probably formed, a change of dielectric constant with frequency is found. Higher alcohols are being investigated in order to learn whether the dipole rotation is a limited rotation of the entire molecule or merely of the hydroxyl group.

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RECEIVED FEBRUARY 8, 1933 PUBLISHED MARCH 7, 1933

THE ACTION OF BROMINE AND BUTADIENE

Sir:

Dr. H. Eyring has presented calculations in a paper given before the Section of Chemistry of the American Association for the Advancement of Science which indicated that addition of bromine to butadiene should be 1–4 rather than 1–2. The high energy of activation also indicated that the reaction should not occur in the gas phase. At the request of Doctors Taylor and Eyring, experiments have been made which show that on mixing gaseous butadiene and bromine in the ratio of 1–1 or 1–0.5 with from 15–20 volumes of nitrogen a reaction occurs and that crystals of the 1,4-dibromo-2-butene are formed. The melting point of the unpurified crystals was 53° (very sharp), which is identical with that reported in the literature. A mixture of the product with 1,2,3,4-tetrabromobutane melted from 30 to 48°. On carrying out the reaction in the same bulb which had been previously coated with paraffin, the rate of the reaction was very markedly reduced. This fact together with the observation that no fog or smoke formed in the uncoated reaction sphere leads to the conclusion that the reaction occurs on the surface. The kinetics of the reaction on glass and surfaces are being studied and details of the experiments will be reported later.

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RECEIVED FEBRUARY 20, 1933 PUBLISHED MARCH 7, 1933

THE ISOTOPE OF HYDROGEN

Sir:

With the aid of Dr. R. T. Macdonald I have been attempting to isolate various isotopes. Less than a month ago we turned our attention to the isotope of hydrogen. Our first experiments, employing a difference in overvoltage suggested by the work of Washburn and Urey, were so promising that we at once planned a systematic series of concentrations which has just been completed. This yielded water of specific gravity 1.035, which means that the heavy isotope constitutes one-third of all the water present. The refractive index of this heavy water is considerably lower than that of ordinary water, but exact figures cannot be given until the concentration has been accurately determined.

The separation of any isotope in sufficient quantity to permit investigation not only of its spectroscopic but also of its other chemical and physical properties suggests a wide range of interesting experiments but the isotope of hydrogen is, beyond all others, interesting to chemists. I believe that it will be so different from common hydrogen that it will be regarded almost as a new element. If this is true the organic chemistry of compounds containing the heavy isotope of hydrogen will be a fascinating study.

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RECEIVED FEBRUARY 23, 1933 PUBLISHED MARCH 7, 1933

NEW BOOKS

Life and Experiences of a Bengali Chemist. By PRAFULLA CHANDRA RÂY. Chuckervertty, Chatterjee and Co., Ltd., 15 College Square, Calcutta, India, 1932. x + 557 pp. 14 × 22.5 cm.

This is an interesting and inspiring account of what a chemist's life can be. The first half of the book (Part I) is explicitly autobiographical. It describes in nearly chronological order: the author's early years on his father's estate in Bengal and at school in Calcutta; his student days under Crum Brown at Edinburgh; his return to become a professor of chemistry at Presidency College at Calcutta; his life as a teacher; his establishment during his spare time of the Bengal Chemical and Pharmaceutical Works, Ltd., now one of the great industrial concerns of India; his studies in the history of Hindu chemistry; his extensive experimental researches; finally, his manifold and multifarious activities in the public service.

The second half of the book (Part II) is only autobiographical; it contains numerous essays on educational, industrial, economic and social subjects. They not only serve to define the author's personality and point of view but they are also of the greatest interest, particularly to a far-away American, for the light they throw on the problems of present-day India. The author attacks scathingly the caste system that hangs as a millstone about India's neck and the ignorance and superstition of many of the Hindus. But his fiercest invective is launched against the spiritlessness and supineness of his fellow Bengali. As regards the British-Indian government he reaches, although by a different route and disagreeing with him in many vital points, the same position of non-coöperation championed by his compatriot Gandhi.

To the readers of this autobiography it is clear that, while Sir P. C. Rây has been a great scholar, chemist, teacher and administrator, these activities have been to him of secondary importance; he has been first, last and all the time a patriot—a Hindu and a Bengali. And he dedicates this account of his life, his opinions and his hopes for his country "To the Youth of India."

ARTHUR B. LAMB