

An attempt to recover the hydrocarbon from the picrate by means of activated alumina and super-cel was unsuccessful. The process finally adopted was to decompose a benzene solution of the picrate at room temperature with dilute ammonium hydroxide. The benzene extract was washed, dried, and evaporated *in vacuo* at room temperature, as rapidly as possible. This afforded a yellow solid, m. p. 52–54° with preliminary shrinkage and softening.

*Anal.*¹⁰ Calcd. for C₁₃H₁₈: C, 92.26; H, 7.74. Found: C, 91.94; H, 7.84.

Subsequent analyses¹⁰ at Alberta gave slightly lower carbon values (C, 91.46, 91.39; H, 7.64, 7.73). The sample having the analysis reported above when analyzed ten days later at Harvard gave values indicating the absorption of oxygen (C, 88.79, 88.93; H, 7.64, 7.83). The deteriorated sample melted unsharply at 80°, and gas was evolved at a temperature of 120°; the fluores-

(10) Semi-microanalyses performed by one of us (R. K.), N. M. Perkins and J. C. Nichol.

cence in solution was markedly diminished. Attempts to crystallize fresh samples of the hydrocarbon from dilute acetic acid, 95% ethanol, benzene or petroleum ether were unsuccessful. Once the hydrocarbon was obtained as long yellow needles, m. p. 47–50°, from an alcoholic solution of the picrate treated with ammonium hydroxide. Attempts to purify these crystals further by the use of alumina resulted in the loss of the material.

Summary

1,2,9,10-Tetramethylanthracene, of interest as a model of a potent carcinogen, has been synthesized and characterized in the form of the picrate, trinitrobenzene complex, and two methoxy derivatives. The hydrocarbon is very sensitive to air.

EDMONTON, ALBERTA

CAMBRIDGE, MASSACHUSETTS RECEIVED JULY 13, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Hydrogenation of the Triple Bond¹

BY ALBERT L. HENNE AND KENNETH W. GREENLEE

Monoalkylacetylenes, treated with sodium in liquid ammonia, are one-third hydrogenated to the corresponding olefins, and two-thirds metalated. Dialkylacetylenes are reduced to the *trans* olefins whose physical properties are markedly different from those of the olefin obtained by catalytic hydrogenation. The latter have been labeled as *cis* compounds and claimed to be pure by Campbell and Eby.²

We have found that monoalkylacetylenes can be reduced quantitatively by the theoretical amount of sodium in liquid ammonia containing an ammonium salt, and that no hydrogen escapes. Under the same circumstances, dialkyl acetylenes are inefficiently reduced, hydrogen is evolved, and more than the theoretical amount of sodium is consumed. Ammonium chloride, which is appreciably soluble in liquid ammonia, gives off some hydrogen and causes an inefficient reduction in every case, while ammonium sulfate, which is nearly insoluble, proved almost 100% efficient in the reduction of monoalkylacetylenes. From these results, it is deduced that the hydrogen re-

leased from the acetylene molecule is more effective for reduction than the hydrogen from the ammonium ion, and that the function of the ammonium salt is to regenerate the acetylene from its sodium derivative.

A similar mechanism might be proposed for the reduction of dialkyl acetylenes, if the assumption is accepted that hydrogen on the carbon atoms adjacent to the triple bond has become acidic enough to react with sodium. This, however, is ruled out by the inefficiency of the reduction in the presence of ammonium sulfate. The formation of a disodium derivative of dialkyl acetylenes by addition of sodium to the triple bond seems more plausible; if this is accepted, a simple explanation can be given³ for the formation of the *trans* olefin exclusively on the basis of repulsion between electrical charges. In contrast, when a triple bond is reduced to a double bond on a catalyst the mechanism consists merely in the breakage of one of the bonds with automatic set-up of the *cis* configuration, so long as molecular hydrogen only is involved.

Monoalkylacetylenes

I. Hydrogenation with Sodium Alone

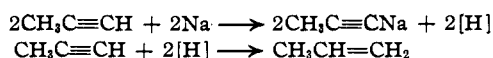
(1) The detailed preparation of acetylenic compounds in better yields and purity than recorded in the literature has been submitted to the Editor of *Industrial and Engineering Chemistry*. Practical directions for making sodium amide and sodium acetylide efficiently and handling them safely are described by us in "Inorganic Syntheses," Vol. 11 (in press), John Wiley and Sons, Inc., New York, N. Y.

(2) Campbell and Eby, *THIS JOURNAL*, **63**, 216, 2683 (1941).

(a) Propyne.—To 5 moles of sodium acetylide in two liters of ammonia was added 5 moles of dimethyl sulfate,

(3) Greenlee and Fernelius, *ibid.*, **64**, 2505 (1942).

and a total reaction time of three hours under ammonia reflux was allowed. The propyne thus produced was boiled off together with ammonia and liquefied into another reactor. Sodium was added from a side-flask until the blue color persisted. This end-point was difficult to judge precisely because adequate stirring brought about excessive foaming. The sodium used amounted to 3.44 gram atoms and no hydrogen was evolved. This is well in line with Picon's observations,⁴ as a consumption of 3.33 gram atoms would be required to satisfy the equations



(b) 1-Octyne.—Sodium was added to one mole of 1-octyne in one liter of ammonia. No hydrogen was evolved and the permanent blue color appeared after 0.674 gram atoms of sodium had been consumed.

II. Hydrogenation with Sodium and Ammonium Sulfate

1-Octyne (0.75 mole) was added with stirring to one liter of ammonia containing 1.25 moles of ammonium sulfate. Then small cubes of sodium were slowly dropped from a side-flask. The blue color spread somewhat around each lump of sodium but did not color the whole solution; when it spread throughout the solution, hydrogen made its appearance. This was taken as the end-point, and coincided with the consumption of 1.5 gram atoms of sodium. The resulting octene was recovered in the usual way, with a 90% yield; it failed to give a coloration with ammoniacal cuprous reagent. It was easily purified by a single distillation through a 10 plate column.

Dialkylacetylenes

I. Hydrogenation with Sodium in Ammonia

(a) 2-Octyne.—In a two-liter flask, 2.05 gram atoms of sodium was dissolved in one liter of ammonia, and 0.90 mole of 2-octyne was added slowly with stirring. A vigorous reaction occurred which subsided soon after completion of the addition. Reflux was allowed for two hours longer, then the excess of sodium was titrated by adding small crystals of ammonium nitrate until the blue color disappeared. This required 0.05 mole of nitrate, corresponding to 0.15 gram atom of excess sodium, and indicated that 1.90 gram atoms of sodium had been used to reduce the octyne, instead of the theoretical 1.80 gram atoms. Water was then added very cautiously, as it reacted exceedingly vigorously with the sodamide by-product. The hydrocarbon layer (94 g. = 93% yield) was decanted, washed, dried, and rectified. The pure compound amounted to 81% net.

(b) 3-Octyne.—A number of large scale runs were made, similar to the preceding case. Eight moles of 3-octyne was added to an excess of sodium dissolved in 5 liters of ammonia contained in a 12-liter flask. The rate of addition had to be slow: the reaction was so vigorous that mechanical stirring sometimes had to be discontinued. The yields of 3-octene averaged from 97 to 99%, from which redistillation through a 25-plate column removed very small amounts of heads and of a polymer.

(c) 4-Octyne.—The reduction of 1.76 moles of 4-octyne consumed 3.71 gram atoms of sodium and yielded

97% of octene, from which distillation through a 10-plate column gave 90% of pure 4-octene, net. On the larger scale 98 to 99% yields were obtained. Unlike the preceding case, the addition could be done rapidly, and the rate of reaction was regulated easily by adjusting the speed of stirring.

Catalytic Hydrogenation

Hydrogenation of a triple bond with the aid of a catalyst does not stop sharply at the olefin stage, unless the catalyst is only mildly active. This can be brought about by "poisoning" a colloid-supported catalyst⁵ like palladium black which operates at room temperature, or by using a catalyst of the nickel type at as low a temperature and low hydrogen pressure as possible. Raney nickel has been used by Campbell and Eby.² We have used nickel supported on kieselguhr, which is still less active. At the low temperature and pressure used, there was little tendency to hydrogenate further than the olefin, and the absorption of hydrogen slowed almost to a stop as the amount used approached one mole per mole of alkyne. Furthermore, in order to minimize the formation of paraffin, the hydrogenation was systematically interrupted with the absorption of only 0.8 mole of hydrogen per mole of alkyne.

(a) 3-Octyne.—Three-tenths of a mole was added to 100 cc. of absolute alcohol containing 5 g. of nickel on kieselguhr triturated in alcohol. The hydrogenation was carried out at pressures of one to three atmospheres and at temperatures of 30 to 80° in a Burgess-Parr hydrogenator. The same catalyst was used for several successive batches, and hydrogenation was always interrupted about 20% short of completion. After throwing the hydrocarbon out of the alcohol with water and drying the product, distillation gave an apparently pure compound, but with an index differing from that of the literature, and with a melting point very difficult to determine.

(b) 4-Octyne, treated in the same way, was found somewhat more sluggish to reduce. A similar variation in reactivity had been observed in the sodium reduction of these two acetylenes. The 4-octene after distillation gave a fairly good freezing curve, yet the physical properties differed significantly from those of Campbell and Eby.

(c) 2-Octyne was studied more intensively, because the wide separation between its boiling point (138.0°) and that of the olefin made purification easier. The product was divided into 12 fractions by distilling through a 25-plate column. Some of the data obtained are presented here.

Fraction	B. p., °C.	d_{20}^{20}	n_D^{20}	Freezing pt., °C.	Freezing range, °C.
II	124.5-125.1	0.7216	1.4133	-105.2	5
V	125.46	0.7228	1.4141	-102.39	1.43
VII	125.6	..	1.4145
IX	125.57	0.7236	1.4148	-101.08	0.89
XII	125.62	0.7243	1.4150	-100.47	0.59

This slow but steady trend indicates a mixture. To ascertain that one of the constituents was not unreduced 2-octyne, fractions VIII and IX were united and treated with sodium in liquid ammonia. The freezing point did not change significantly, showing the absence of 2-octyne.

(4) Lebeau and Picon, *Compt. rend.*, **157**, 137 (1913).

(5) Bourguet, *Bull. soc. chim.*, [4] **45**, 1067 (1929).

To the composite of VIII and IX, freezing at -101.17° , was added pure *trans*-2-octene amounting to 1.0% of the resultant mixture. The freezing point fell to -101.34° . When the percentage of added *trans*-2-octene was raised to 10.3%, the freezing point became -103.04° . The drop (dT) per 1% added was 0.17 and 0.18°, respectively. Plotting the freezing points of fractions V, IX, and XII against corresponding freezing ranges gives nearly a straight line which extrapolated to zero freezing range gives a "true" freezing point of -99.0° . Using this and the calculated dT , the approximate content of *trans*-2-octene in the various fractions can be computed if it is assumed to be the only impurity.

Fraction	Freezing point °C.	ΔF , °C.	dT , °C.	% <i>trans</i> - 2-octene
II	-105.2	-6.2	0.18	35
V	-102.4	-3.4	.18	19
IX	-101.1	-2.1	.17	12
XII	-100.5	-1.5	.17	9

These experimental results were communicated to Drs. Campbell and Eby, who kindly sent us their own samples of *cis* olefins to permit us to determine the freezing points and freezing ranges. Some of these data are included in the table.

PHYSICAL CONSTANTS OF MONOOLEFINS

Compound	B. p., °C.	Mm.	F. p. (m. p.), °C.	F. range, °C.	d_{20}^4	n_D^{20}	Source
1-Octene	121.27	760	-102.56	0.1	0.7160	1.4088	Pres. res.
	120.75	742	-102	..	.7155	1.4081	C. and E.
"cis-2-Octene"	125.62	760	-100.5	0.59	.7243	1.4150	Pres. res.
	124.6	750	-104 (-102.0)	(1.36)	.7229	1.4139	C. and E.
<i>trans</i> -2-Octene	124.94	760	-87.8	0.10	.7199	1.4132	Pres. res.
	123.55	750	-88	..	.7184	1.4128	C. and E.
"cis-3-Octene"	122.7	760	-137 to -138	1-2	.7223	1.4140	Pres. res.
	122.3	741	-126	..	.7189	1.4125	C. and E.
<i>trans</i> -3-Octene	123.29	760	-110.05	0.17	.7149	1.4129	Pres. res.
	122.4	741	-108	..	.7173	1.4124	C. and E.
"cis-4-Octene"	122.8	760	-120.2	0.52	.7228	1.4147	Pres. res.
	121.7	739	-118 (-121.2)	(3.5)	.7205	1.4136	C. and E.
<i>trans</i> -4-Octene	122.37	760	-93.80	0.05	.7139	1.4122	Pres. res.
	121.4	739	-94	..	.7147	1.4116	C. and E.

A satisfactory freezing point could not be determined on the *cis*-3-octene sample of Campbell and Eby and our own sample gave very erratic results. Other Campbell and Eby samples were studied. On *cis*-3-hexene the amount was so small that the freezing range could not be ascertained, but it was probably some degrees wide.

Alkene	Freezing point, °C. (by C. and E.)	Freezing point, °C. (our measurement)	Freezing range, °C.
"cis-2-Hexene"	-146	-141.4	0.4
"cis-3-Hexene"	-135	-143.3	..
"cis-5-Decene"	-112	-112.8	0.53

It was held possible that the Campbell and Eby samples had deteriorated while standing in sealed tubes under nitrogen for 18-20 months. To rule this out the freezing point was redetermined on our best sample of *cis*-2-octene which had stood for five months without special precautions. The change was only 0.04° or nearly insignificant

The freezing point of the Campbell and Eby sample of *cis*-2-octene indicates (by the empirical method described above) a purity of only 83%.

The Reduction of Diacetylenes

Since the reduction of diacetylenes has not been reported in the literature, the experimental details are given below. The diacetylenes used were 1,6-heptadiyne and 2,7-nonadiyne.

I. Reduction by Sodium Alone.—A solution of 0.424 mole of 2,7-nonadiyne (it freezes at $+4.3^\circ$) in 200 cc. of dry ether was added to 800 cc. of ammonia containing 2.13 gram atoms of sodium. A vigorous reaction took place without evolution of gas. After stirring for one hour longer, the excess sodium was "back-titrated" with ammonium nitrate. This showed that 1.83 gram atoms of sodium had been consumed, 8% in excess. Fractionation under reduced pressure gave 72% of a cryoscopically pure diene, presumably the *trans-trans* derivative.

II. Reduction by Sodium and Ammonium Sulfate

(a) 1,6-Heptadiyne.—To one liter of ammonia in a 3-liter flask was added 5 equivalents (14% excess) of ammonium sulfate and 1.10 moles of 1,6-heptadiyne. While stirring, sodium was added from a side-flask until a semi-

permanent blue color appeared. The sodium used to this point was 102 g. or 101%. The crude product recovered (87%) was distilled to give pure 1,6-heptadiene in 61% yield.

(b) 2,7-Nonadiyne.—To one liter of ammonia was added 2.72 equivalents of ammonium sulfate (10% excess) and 0.62 mole of diyne dissolved in 200 cc. of ether. Sodium was added with stirring. The semi-permanent blue color did not appear at the equivalence point, but after a 68% excess of sodium had reacted. Hydrogen was evolved throughout. The ethereal product was recovered and distilled under reduced pressure. The part boiling in the range of 2,7-nonadiene amounted to 79% yield. Its density, refractive index, and Cottrell boiling point were significantly lower than those of the pure diene (*vide infra*); its freezing point was 3.7° lower and the range was many degrees. The impurity was believed to be diene with the *cis-trans* or *cis-cis* configuration, produced in the random hydrogenation by nascent hydrogen.

PHYSICAL CONSTANTS OF DIOLEFINS						
Compound	B. p. (760 mm.), °C.	F. p. (m. p.), °C.	F. range, °C.	d_4^{20}	n_D^{20}	Source
1,6-Heptadiene	90.01	-129.35	0.16	0.7142	1.4142	Pres. res.
	89.77134	1.4142	Frank ⁶
" <i>cis-cis</i> -2,7- Nonadiene"	151.0	glass	..	.7582	1.4368	Pres. res.
<i>trans-trans</i> -2,7- Nonadiene (by sodium alone)	150.3	-72.46	0.08	.7499	1.4358	
<i>trans-trans</i> -2,7- Nonadiene (by sodium and (NH ₄) ₂ SO ₄)	150.5	-76.2	55	.7515	1.4360	

III. Catalytic Hydrogenation.—2,7-Nonadiene was treated with hydrogen in presence of nickel as described under dialkylacetylenes. Since it would be hard to separate a diene from the corresponding enyne, exactly one equivalent of hydrogen was supplied. The last 10% was absorbed but slowly. The purified product gave indications of being a mixture and no freezing point could be determined, but its other constants varied in the direction expected from those of the pure *trans-trans* compound. The *cis* configuration probably predominated in this diene but did not exclude the *trans*.

Summary

Monoalkylacetylenes were quantitatively reduced to the corresponding olefins by reaction with sodium in liquid ammonia containing am-

(6) Frank, Dissertation, The Ohio State University, 1938.

monium sulfate; the use of soluble ammonium salts caused inefficient reduction.

Dialkylacetylenes were quantitatively reduced (in liquid ammonia) by sodium alone to pure *trans* olefins; ammonium salts led to mixtures of geometric isomers presumably due to the intervention of nascent hydrogen. Catalytic hydrogenation of dialkylacetylenes produced olefins in which the *cis* configuration predominated.

Diacetylenes were similarly treated. 1,6-Heptadiene was reduced to 1,6-heptadiene by sodium and ammonium sulfate. 2,7-Nonadiene was reduced by sodium to pure *trans-trans*-2,7-nonadiene, while catalytic hydrogenation yielded a substance which was obviously a mixture.

COLUMBUS, OHIO

RECEIVED MAY 22, 1943

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, HAVERFORD COLLEGE]

The Molal Depression Constant for Camphor

By W. B. MELDRUM, L. P. SAXER AND T. O. JONES

Probably no solvent has been more used by organic chemists as a means of finding the molecular weights of newly-prepared substances by the cryoscopic method than camphor. Hence the establishment of the numerical value of the molal depression constant for this solvent is a matter of considerable importance. Of the several values extant in the literature the one which has been most generally accepted is that of Rast, 39.7.¹ Of the values in disagreement with that obtained by Rast and others² the outstanding ones are those of Jounieaux, 49.5,³ Efremov, 48.7,⁴ and Durand, 49.7.⁵ The calculations of Jounieaux have been shown to be

- (1) Rast, *Ber.*, **55**, 3727 (1922).
- (2) Smith and Young, *J. Biol. Chem.*, **75**, 289 (1927); LeFèvre and Tidemann, *J. Chem. Soc.*, **107**, 1729 (1931).
- (3) Jounieaux, *Bull. soc. chim.*, **11**, 546 (1912).
- (4) Efremov, *Bull. acad. scie. Russ.*, 765 (1919).
- (5) Durand, *Bull. soc. chim.*, **57**, 67 (1937).

unreliable,⁶ but the values of the latter two still stand. Bohme and Schneider⁷ have given, without experimental data, several isolated values which suggested to the authors of this paper that the cryoscopic constant for camphor might vary with the concentration. It was to test this hypothesis that the present investigation was undertaken. Such a variation has been noted by Pirsch in the case of camphene dibromide as solvent.⁸ Using various solutes, Pirsch obtained values for the molal depression constant which, although quite discordant for solutions of less than about 8 mole-per cent. solute, showed a regular decrease between 9 and 21 mole-per cent. from about 116 to about 45.

- (6) LeFèvre and Tidemann, *Nature*, **127**, 972 (1931).
- (7) Bohme and Schneider, *Angew. Chem.*, **52**, 58 (1939).
- (8) Pirsch, *Ber.*, **69**, 1229 (1932).