[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, ILLINOIS INSTITUTE OF TECHNOLOGY]

Atmospheric Oxidation of 6-Dodecyne*

BY M. J. MURRAY AND FORREST F. CLEVELAND

During an investigation of the Raman spectra of disubstituted acetylenes, it was found that 6-dodecyne upon standing in contact with air is oxidized to give 6-dodecynone-5. The evidence which supports this conclusion is given below.

Spectroscopic Evidence.—After obtaining the Raman spectrum of 6-dodecyne,[1] the sample was stored in a cork-stoppered test-tube exposed to diffuse light. After three months it was noted that the still colorless liquid had acquired an odor different from the one previously observed. Consequently, the Raman spectrum was again obtained, without distillation, in an attempt to discover the source of this odor. Two strong lines at 1673 and 2212 cm.$^{-1}$, not present in the spectrum of 6-dodecyne, appeared.

Distillation of the aged sample in a 30-cm. Podbielniak-type column yielded fractions boiling at 62–63° and 89–90° (1–2 mm.), with a small quantity of residue. The Raman spectra of these fractions are given in columns one and two of Table I. The spectrum of the lower boiling sample is identical with that of 6-dodecyne. In addition to slight changes in some of the frequencies, the oxidation product gives a new line at 1673 cm.$^{-1}$ and only a single "triple bond" frequency at 2212.

The 1673 frequency could be attributed to an ethylenic or a carbonyl linkage, but reaction with phenylhydrazine indicated the latter. Absence of aldehyde was indicated by tests with Tollens and Fehling solutions, thus leaving a ketonic linkage as the only possibility. The low value of the characteristic ketone linkage (normal value near 1710) indicates conjugation. Acrolein, for example, gives 1685 as compared with 1718 for *n*-butyraldehyde. That the carbonyl bond is conjugated with the triple bond is further indicated by the low value of the triple bond frequency. An example of such conjugation is found in the case of vinylacetylene, for which this frequency is 20 cm.$^{-1}$ lower than the normal value for unconjugated monosubstituted acetylene.

Additional Evidence.—The Raman spectra having indicated the presence of a carbonyl group conjugated with a triple bond in the oxidation product, the question which then arose was whether the oxidation product was a diketone or a monoketone. Both microanalysis[2] and molecular refraction indicated the latter.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.9; H, 11.2. Found: C, 79.4; H, 11.6. $n^{20}{}_D$ 1.4510; $d^{20}{}_4$ 0.860; $M^{20}{}_D$ calcd. for $C_6H_{11}C{\equiv}CCOC_4H_9$, 55.7; found, 56.4.

The 2,4-dinitrophenylhydrazone after repeated crystallization from alcohol melted at 59°.

Raman Spectrum of 6-Dodecynone-5.—Having concluded from the foregoing evidence, that an oxidation product was 6-dodecynone-5, it seemed desirable to substantiate further the identity by synthesis of this compound and subsequent determination of its Raman spectrum.

TABLE I

RAMAN SPECTRA OF 6-DODECYNE, OF THE PRODUCT FORMED FROM IT ON STANDING, AND OF 6-DODECYNONE-5

6-Dodecyne		Product formed on standing		6-Dodecynone-5	
cm.$^{-1}$	I	cm.$^{-1}$	I	cm.$^{-1}$	I
373	3	364	2	361	1
383	1				
435	1				
842	2	835	1	832	2
887	1	900	1b	892	2
				908	1
970	1	968	0	969	0
1024	1	1030	2	1028	2
1067	3	1066	3	1062	3
1110	4	1107	4	1107	4
1221	1				
1271	1				
1300	3	1304	3	1303	3
1330	3	1325	2	1328	2
		1421	2	1421	2
1436	6	1444	6b	1446	7
1452	3	1454	3	1460	3
		1673	9	1673	6
2231	7	2212	10	2212	7
2248	2				
2294	4				
2852	6	2867	8	2865	8
2874	6				
2906	10	2908	10	2909	10
2934	8	2933	8	2937	10
2967	4	2967	4	2967	4

Synthesis.—6-Dodecynone-5 was synthesized by the action of heptynylmagnesium chloride and valeric anhydride. The details of the synthesis were those of Kroeger and Nieuwland[3] for acetylacetylenes, except that only a 20% excess of the anhydride was used.

The Raman spectrum of the 6-dodecynone-5 so obtained is given in column three of Table I. It is seen to be identical (within experimental error) with that of the oxidation product.

The melting point of the 2,4-dinitrophenylhydrazone of the synthetic compound was 65°. When mixed with the 2,4-dinitrophenylhydrazone of the oxidation product the melting point was 61°, thus indicating the presence of an impurity in the oxidation product. The 2,4-dinitrophenylhydrazone of this impurity is apparently difficult to separate from the derivative of the 6-dodecynone-5 by recrystallization.

The impurity must be such that it would have no additional strong lines in its Raman spectrum. For example, the presence of an unconjugated ketone or of an acetylenic

---

* Original manuscript received July 11, 1940.

[1] Forrest F. Cleveland and M. J. Murray, THIS JOURNAL, **62**, 3185 (1940).

[2] Microanalysis of sample by Dr. T. S. Ma.

[3] J. W. Kroeger and J. A. Nieuwland, THIS JOURNAL, **58**, 1861 (1936).

hydrocarbon (such as 6-dodecyne) would show a line near 1710 or 2231 cm.$^{-1}$, respectively. This suggests that the impurity may be the diketone, with both carboxyl groups in conjugated positions, since this compound would probably have little effect on the frequencies at 1673 or 2212.

It was thought that the semicarbazone of the impurity might be separable from that of the 6-dodecynone-5 but when preparation of this compound was attempted the semicarbazone would not crystallize.

Preliminary experiments indicate that atmospheric oxidation to produce ketones is not specific for 6-dodecyne. 7-Tetradecyne, 5-decyne, 2-octyne, and 3-octyne oxidize in a manner similar to that of 6-dodecyne. In all cases the frequencies at 1673 and 2212 cm.$^{-1}$ are absent from the spectra of the freshly distilled samples but appear on spectrograms of the compounds taken after a few days standing in contact with air. Both frequencies are remarkably constant in all the samples studied. Spectroscopic evidence for ketone formation could not be obtained for a sample of 1-heptyne which had been exposed to air for several months.

The ketones formed from disubstituted acetylenes are of interest spectroscopically because the displacement of two hydrogen atoms by oxygen in the otherwise unchanged molecule causes the *three* Raman frequencies near 2200 cm.$^{-1}$ observed for the hydrocarbons to be replaced by a *single* line. If the multiplicity of lines in the hydrocarbons is caused by Fermi resonance interactions of overtones or of combination frequencies with the fundamental expected near 2200, then this simplification of the spectrum would be understandable on the basis that the 2200 fundamental is lowered by conjugation and is no longer in sufficiently exact coincidence with such overtones or combinations to permit resonance interaction. Consistent with this is the observation made in the case of phenyliodoacetylene[1] for which the authors found in the triple bond region only a single line at 2183, considerably below that for other disubstituted acetylenes.

Acknowledgment.—The authors wish to express their thanks to Dr. G. F. Hennion and to the Union Carbide and Carbon Research Laboratories for furnishing the acetylenes used in this investigation.

Summary

6-Dodecyne in contact with air at room temperature oxidizes to form 6-dodecynone-5. Preliminary experiments indicate that other disubstituted acetylenes react in a similar way.

CHICAGO, ILL. RECEIVED FEBRUARY 26, 1941

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates. XXI. Isolation and Synthesis of 2,3,4-Trimethyl-8-*i*-propylquinoline

BY LESLIE M. SCHENCK AND J. R. BAILEY

Introduction

From 13.5 liters of kero bases of b. p. 320–330° and $n^{20}\mathrm{D}$ 1.5698, exhaustively processed through fractional distillation,[1] there has been reported the isolation of 2,3,4-trimethyl-8-*n*-propylquinoline (b. p. 330°)[2]; 2,3,4-trimethyl-8-ethylquinoline (b. p. 320)[3] and 2,4-dimethyl-8-*s*-butylquinoline (b. p. 310°).[4]

In addition to the three quinoline homologs above, three new products have recently been obtained from the same crude material in the 320–330° range, including 2,3-dimethyl-4,8-diethylquinoline (I, b. p., 319°)[5]; 2,3-dimethyl-4-ethyl-8-*n*-propylquinoline (II, b. p. 327°)[5]; and 2,3,4-trimethyl-8-*i*-propylquinoline (b. p. 327°). The separation of these six bases solely through fractional distillation under reflux is apparently impractical for two reasons: (1) the presence of azeotropic mixtures and (2) admixture of other quinoline homologs which await isolation. It may be emphasized that, of the numerous base-types in petroleum, quinolines are best adapted to separation in pure form, proof of structure and synthesis.

The structure of 2,3,4-trimethyl-8-*i*-propylquinoline follows from chromic acid oxidation yielding 2,3,4-trimethylquinoline-8-carboxylic acid,[6] like all 2,3,4-trimethyl-8-alkylquinolines. Synthesis of the base was effected through the same general procedure[7] previously employed in preparation of its analogs, the intermediates used being methylacetylacetone and *o*-cumidine. No other petroleum base with an *isopropyl* substituent has been reported.

---

(1) This material was furnished by the Union Oil Co. of California.

(2) Schenck and Bailey, THIS JOURNAL, **61,** 2613 (1939).

(3) Ref. 2. Credit is due Glenn and Bailey for the synthesis of this base, *ibid.*, **61,** 2612 (1939).

(4) Schenck and Bailey, *ibid.*, **62,** 1967 (1940).

(5) For bases I and II, see *ibid.*, **63,** 1365 (1941).

(6) Refs. 2, 3; Axe and Bailey, *ibid.*, **60,** 3028 (1938).

(7) Combes, *Bull. soc. chim.*, (2) **49.** 91 (1888).