

hydrocarbon (such as 6-dodecyne) would show a line near 1710 or 2231  $\text{cm}^{-1}$ , 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  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  observed for the hydrocarbons to be replaced by a *single* line. If the multiplicity of lines in the hydrocar-

bons 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<sup>1</sup> 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.

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[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  $n_D^{20}$  1.5698, exhaustively processed through fractional distillation,<sup>1</sup> there has been reported the isolation of 2,3,4-trimethyl-8-*n*-propylquinoline (b. p. 330°)<sup>2</sup>; 2,3,4-trimethyl-8-ethylquinoline (b. p. 320°)<sup>3</sup> and 2,4-dimethyl-8-*s*-butylquinoline (b. p. 310°).<sup>4</sup>

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°)<sup>5</sup>; 2,3-dimethyl-4-ethyl-8-*n*-propylquinoline (II, b. p. 327°)<sup>5</sup>; and 2,3,4-trimethyl-8-*i*-propylquinoline (b. p. 327°).

(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).

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,<sup>6</sup> like all 2,3,4-trimethyl-8-alkylquinolines. Synthesis of the base was effected through the same general procedure<sup>7</sup> 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.

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

(7) Combes, *Bull. soc. chim.*, (2) **49**, 91 (1858).

### Experimental

Fractions 3 and 4 previously obtained (ref. 4, Table I) were combined and fractionated into 12 cuts of 12 ml. each. Their boiling points at 2 mm. increased regularly from 145.0 to 155.5°, and the refractive indices  $n_D^{16}$  of the first and last samples were 1.5845 and 1.5890, respectively. Those of the other fractions varied irregularly within the narrow limits of 1.5870 and 1.5879, respectively.

**2,3,4-Trimethyl-8-*i*-propylquinoline.**—On cooling to -10° a solution of fractions 5 to 9, inclusive, in six volumes of methanol, 3 g. of this base separated. It was recrystallized from the same solvent in small needles of m. p. 106-107° and b. p. 327° (750 mm.).

*Anal.* Calcd. for  $C_{18}H_{19}N$ : C, 84.45; H, 8.98; N, 6.57. Found: C, 84.31; H, 9.00; N, 6.49.

**2,3,4-Trimethylquinoline-8-carboxylic Acid.**—The base (0.5 g.) in dilute sulfuric acid was oxidized with the calculated quantity of potassium dichromate in 6 *N* sulfuric acid to 2,3,4-trimethylquinoline-8-carboxylic acid, which was identified by the usual comparison with an authentic sample.<sup>6</sup>

**Picrate.**—This salt was prepared in the usual way and recrystallized from alcohol in yellow needles melting at 165-166°. In comparison with picrates of other petroleum quinolines, it is more readily soluble in organic solvents.

*Anal.* Calcd. for  $C_{21}H_{22}O_7N_4$ : C, 57.07; H, 5.01. Found: C, 57.05; H, 5.03.

**Nitrate.**—The calculated amount of concentrated nitric acid added to an acetone-ether solution of the base precipitated the nitrate which was recrystallized from water in long needles melting with decomposition at 143-144°.

*Anal.* Calcd. for  $C_{18}H_{19}N \cdot HNO_3$ : C, 65.18; H, 7.23;  $NO_3$ , 22.44. Found: C, 65.05; H, 7.41;  $NO_3$ , 22.54.

**Acid Sulfate.**—The salt was formed on addition of the calculated volume of concd. sulfuric acid to the base in acetone, and crystallizes from absolute alcohol in irregular platelets melting at 204-205° undecomposed.

*Anal.* Calcd. for  $C_{18}H_{19}N \cdot H_2SO_4$ :  $SO_4$ , 30.86. Found:  $SO_4$ , 30.71.

**Synthesis of 2,3,4-Trimethyl-8-*i*-propylquinoline.**—Cumene was nitrated at 0° with a mixture of concd. nitric and sulfuric acids to *o*- and *p*-nitrocumene, which were segregated by fractional distillation. A quantitative reduction of the *o*-isomer to *o*-cumidine in one-half hour was effected through hydrogenation over Raney nickel catalyst at 70° and 2600 lb. pressure. The quinoline base was synthesized by condensation of methylacetylacetone and *o*-cumidine.<sup>7</sup> Here is involved elimination of two molecules of water in a double phase reaction. As concerns the present preparation, it was found advantageous in the initial condensation to reflux the intermediates only a few minutes rather than to follow the standard procedure of prolonged heating at steam-bath temperature. A mixed melt of the synthetic and petroleum base showed no depression.

### Summary

The isolation of 2,3,4-trimethyl-8-*i*-propylquinoline from California petroleum is reported. Its structure was established through chromic acid oxidation to the known 2,3,4-trimethylquinoline-8-carboxylic acid and was confirmed by synthesis from methylacetylacetone and *o*-cumidine.

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## The Nitrogen Compounds in Petroleum Distillates. XXII. Isolation and Synthesis of 2,3-Dimethyl-4,8-diethylquinoline (I) and 2,3-Dimethyl-4-ethyl-8-*n*-propylquinoline (II)

BY LESLIE M. SCHENCK AND J. R. BAILEY

### Introduction

For isolation of base I, highly processed fractions of aromatic kero bases in the 320-330° range were employed.<sup>1</sup> Initially, the bases were precipitated in acetone-ether solution as nitrates which were converted to picrates. Purification was effected by recrystallization of the picrates in alcohol, followed by conversion to acid sulfates, then back to picrates, the procedure being repeated until the preparation had a constant melting point.

(1) This material was furnished the Texas Laboratory by the Union Oil Company of California; Schenck and Bailey, *THIS JOURNAL*, **61**, 2613 (1939).

Three specific properties of II contributed to a segregation from admixtures: (1) in contrast to I it separated as acid sulfite<sup>2</sup> in the form of an oil when base fractions suspended over sodium sulfite, chloride or nitrate brine were salified with sulfurous acid; (2) from acetone-ether solution of the base, liberated by degassing the acid sulfite,<sup>3</sup> concentrated nitric acid precipitated the

(2) Through employment of so-called sulfating over sodium chloride brine, C. O. Edens and J. R. Bailey in unpublished research discovered that a series of 2,3-dimethyl-8-alkylquinolines, in contrast to 2,4-dimethyl-8-alkyl analogs, are precipitated as base hydrochlorides. Where nitrate brine was used, only base-acid sulfites separated.

(3) Cf. Stiles M. Roberts and J. R. Bailey, *THIS JOURNAL*, **60**, 3025 (1938).