

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

## The Nitrogen Compounds in Petroleum Distillates. V. The Use of Sulfur Dioxide in the Separation of Petroleum Bases

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**Introduction.**—Although the behavior of organic bases toward sulfur dioxide has been studied quite extensively,<sup>1</sup> apparently this reaction has not been employed as an agency in separation of mixtures of amines.

Sulfur dioxide forms addition compounds with both aromatic and non-aromatic bases, but it remains to be determined whether all kero bases enter into such combinations. Some of these products are stable at temperatures as high as 100°, while others have been found to dissociate quite rapidly at room temperature. Advantage has been taken of the differences in the relative stability and solubilities of these sulfur dioxide addition compounds to effect a partial separation of the kero bases.

The sulfur dioxide process is unsatisfactory, in that it does not effect quantitative separations. Also addition products of some of the non-aromatic bases layer out, and subsequent separation of individual aromatic bases in the form of picrates is retarded through the formation of smears.

### Experimental Part

A 2000-cc. fraction of bases of b. p. 263–267° was dissolved in an equal volume of anhydrous ether, and sulfur dioxide was led in at room temperature to saturation. At first a small amount of oil separated which later redissolved. The excess of sulfur dioxide, along with part of the solvent, was allowed to evaporate to the point where a heavy viscous oil layered out, and then sufficient ether was added to restore the original volume. The supernatant layer was decanted and the viscous residue was washed with ether, dissolved in a little alcohol and treated with a slight excess of an alcoholic solution of picric acid. After complete precipitation, the picrates were washed with sufficient alcohol to remove smeary admixtures.

The alcoholic filtrate contained a considerable amount of non-aromatic picrates of a greater solubility in organic solvents than the aromatic salts. It may be that here the relative concentration of the various non-aromatics was decidedly different from that in the original fraction of bases, and in that event there is suggested an application of the sulfur dioxide reaction in partial resolution of non-aromatic mixtures.

**Isolation of 2,4-Dimethylquinoline.**—When the crystalline picrates were treated with an amount of hot glacial acetic acid sufficient to leach out the more soluble portion, 2,4-dimethylquinoline picrate separated from the filtered solution in long orange colored needles and was recrystallized several times from 95% alcohol, with filtration carried out around 40° to avoid the separation of admixtures. Finally a product melting at 194° was obtained.

2,4-Dimethylquinoline, synthesized according to Otto Fischer,<sup>2</sup> proved identical with the base obtained from the picrate of m. p. 194°. Furthermore, the kero base

(1) Schiff, *Ann.*, **140**, 125 (1866); **144**, 49 (1867); Michaelis, *Ber.*, **24**, 749 (1891); Glebocka and Korczynski, *Gazz. chim. Ital.*, **50**, 378 (1920); Woroshtzow, *Ber.*, **63**, 2354 (1930); Hill, *This Journal*, **53**, 2598 (1931).

(2) Otto Fischer, *Ber.*, **19**, 1037 (1886).

and the synthetic product were shown to be identical through comparison of several salts. Both the synthetic and the kero base boiled at 274° at 756 mm.<sup>3</sup>

**Isolation of 2,3-Dimethylquinoline.**—The picrates, referred to above as difficultly soluble in glacial acetic acid, were recrystallized from this solvent in the form of microscopic hexagonal prisms melting at 231°. The base, liberated from the purified picrate, proved identical with 2,3-dimethylquinoline, synthesized by the method of Eliasberg and Friedländer.<sup>4</sup> Several salts made from both the kero and the synthetic base were compared. The base itself is a white crystalline solid melting at 67° and boiling at 273° (750 mm.).<sup>5</sup>

All the filtrates obtained in the separation of the 2,3- and 2,4-dimethylquinoline picrates were combined and concentrated to a small volume, when a third picrate melting at 160° separated in radiating clusters of needles. This product is referred to in Paper IV by Perrin and Bailey, who find that, when pure, it melts at 174°.

#### ANALYTICAL DATA ON THE TWO KERO BASES AND THEIR SALTS

	Calcd.			Found		
	C	H	N	C	H	N
2,3-Dimethylquinoline	84.08	7.01	8.92	84.08	7.15	8.98
2,4-Dimethylquinoline	84.08	7.01	8.92	83.83	7.10	9.05
2,3-Dimethylquinoline picrate	52.85	3.63	14.51	52.80	3.66	14.52
2,4-Dimethylquinoline picrate	52.85	3.63	14.51	52.89	3.64	14.74
2,4-Dimethylquinoline chloroplatinate	...	..	3.86	...	..	3.84
2,3-Dimethylquinoline acid sulfate	...	..	5.49	...	..	5.25

### Summary

The additive reaction of sulfur dioxide on amines has been applied to the isolation of 2,3- and 2,4-dimethylquinoline from a distillation fraction of kero bases in the 263–267° range.

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(3) C. Beyer, *J. prakt. Chem.*, **33**, 401 (1885), reports a b. p. of 264–265° (uncorr.) with no mention of pressure.

(4) J. Eliasberg and P. Friedländer, *Ber.*, **25**, 1754 (1892).

(5) G. Rohde, *ibid.*, **22**, 269 (1889), reports an uncorrected b. p. of 261° at 729 mm.