

### Structure of Ketoyobyrine

THE recent publication of a paper by Woodward and Witkop<sup>1</sup> suggesting a new structure for ketoyobyrine, based on degradative evidence, and of another by Schlittler and Speitel<sup>2</sup>, claiming the synthesis of this substance, prompts us to point out that on May 28, 1948, we submitted to the Chemical Society a paper describing the synthesis of ketoyobyrine. This has been accepted for publication in the *Journal*; but unfortunately its appearance cannot be expected for many months.

In the main, our work is along similar lines to that of Schlittler and Speitel; but differs in certain details.

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<sup>1</sup> *J. Amer. Chem. Soc.*, **70**, 2409 (1948).

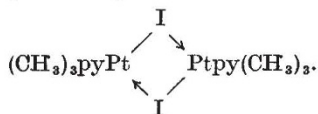
<sup>2</sup> *Helv. Chim. Acta*, **31**, 1199 (1948).

### Trimethylplatinum Derivatives

Lile and Menzies<sup>1</sup> report some new derivatives in the trimethylplatinum series, the first members of which were prepared from platinum tetrachloride some forty years ago by Pope and Peachey<sup>2</sup>. Since we are similarly engaged in investigating these compounds, it is desirable to record some of our observations on this subject.

(a) *Cis*-dipyridinetetrachloroplatinum,  $\text{PtPy}_2\text{Cl}_4$ , which unlike platinum tetrachloride is not hygroscopic, is a very good source of trimethylplatinum derivatives, just as pyridinetrichlorogold,  $\text{AuPyCl}_3$ , is the most convenient starting material for the preparation of dialkylgold compounds<sup>3</sup>.

(b) Methylmagnesium iodide and *cis*- $\text{PtPy}_2\text{Cl}_4$  gives in excellent yield the compound  $(\text{CH}_3)_3\text{PtPyI}$ , which decomposes slowly at temperatures above 150°. It is soluble in pyridine chloroform and in benzene, in which it is dimeric by the freezing-point; thus the 6-covalency of the platinum is maintained as in



(c) By treatment with further pyridine, this new compound is converted into  $(\text{CH}_3)_3\text{Pt}(\text{py})_2\text{I}$ , m.p. 168°, without decomposition. The complex formed from  $(\text{CH}_3)_3\text{PtI}$  and pyridine, described by Lile and Menzies, has the same composition and melting point and is presumably identical with ours. It is of interest that the same isomer is formed by the two alternative routes. In the tetrameric  $(\text{CH}_3)_3\text{PtCl}$  (in which the platinum has an octahedral configuration<sup>4</sup>), the three methyl groups are all *cis* to one another, and it may well be that this same arrangement persists throughout.

We have also observed that the dipyridine complex undergoes dissociation in benzene solution, probably into pyridine and the dimeric complex mentioned in (b) above.

(d) The other molecule of pyridine is certainly much more firmly held and cannot be removed by dilute acids and alkalis. It is displaced with ease, however, when ethylene diamine is added to a cold

chloroform solution of the dimer, and the compound  $2(\text{CH}_3)_3\text{PtI} \cdot 3\text{en}$  (see also Lile and Menzies, *loc. cit.*) separates in crystalline condition.

(e) Although methylmagnesium iodide reacts so readily, no product has been obtained from ethyl magnesium iodide and *cis*- $\text{PtPy}_2\text{Cl}_4$ . This recalls Pope and Peachey's inability to prepare ethyl derivatives from platinum tetrachloride<sup>5</sup>.

(f) *Trans*- $\text{PtPy}_2\text{Cl}_4$  has so far given no alkyl derivative with methylmagnesium iodide. It undergoes reduction and halogen exchange with formation of *trans*- $\text{PtPy}_2\text{I}_2$ .

Work in this field is proceeding, and a fuller account will be given elsewhere in due course.

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<sup>1</sup> Lile and Menzies, *Nature*, **162**, 299 (1948).

<sup>2</sup> Pope and Peachey, *J. Chem. Soc.*, 571 (1909).

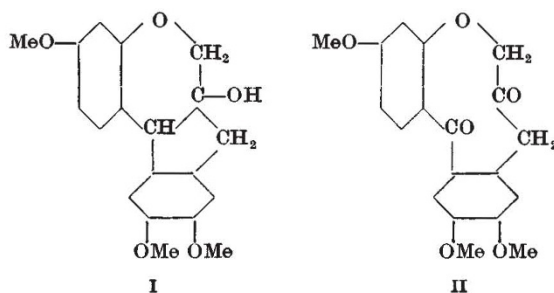
<sup>3</sup> Gibson *et al.*, *J. Chem. Soc.*, 219 (1935) *et seq.*

<sup>4</sup> Rundle and Sturdivant, *J. Amer. Chem. Soc.*, **69**, 1561 (1947).

<sup>5</sup> Private communication (C. S. G.).

### Structure of O-Trimethylbrazilone

OXIDATION of O-trimethylbrazilin (I)<sup>1</sup> yields O-trimethylbrazilone (II), the proposed structure<sup>2</sup> of which is satisfactory in most respects. Nevertheless, the explanation of the unusual loss of two atoms of oxygen which occurs when it is converted into deoxytrimethylbrazilone (anhydrotrimethylbrazilin) by interaction with phenylhydrazine is not apparent.



It was therefore thought desirable to examine the infra-red absorption spectra of (I) and (II). The spectra were measured in a double-beam spectrometer, using a very dilute solution in carbon tetrachloride at  $3\mu$  and a solid suspension in 'Nujol' at  $6\mu$ . As was to be expected, (I) exhibited an absorption band at a frequency of  $3,610\text{ cm}^{-1}$  and no marked absorption in the  $1,720\text{ cm}^{-1}$  region, indicative of the presence of the hydroxyl group and the absence of any ketonic grouping respectively; (II), on the other hand, showed no absorption in the region of  $3,610\text{ cm}^{-1}$ , but exhibited a strong band at  $1,720\text{ cm}^{-1}$ . This is consistent with the absence of a hydroxyl and the presence of a ketone group. Moreover, it follows that if there is a ketone group present any modified structure such as  $\text{>C-C-}$  is untenable, and



it therefore appears that the proposed large ring diketone structure is correct.