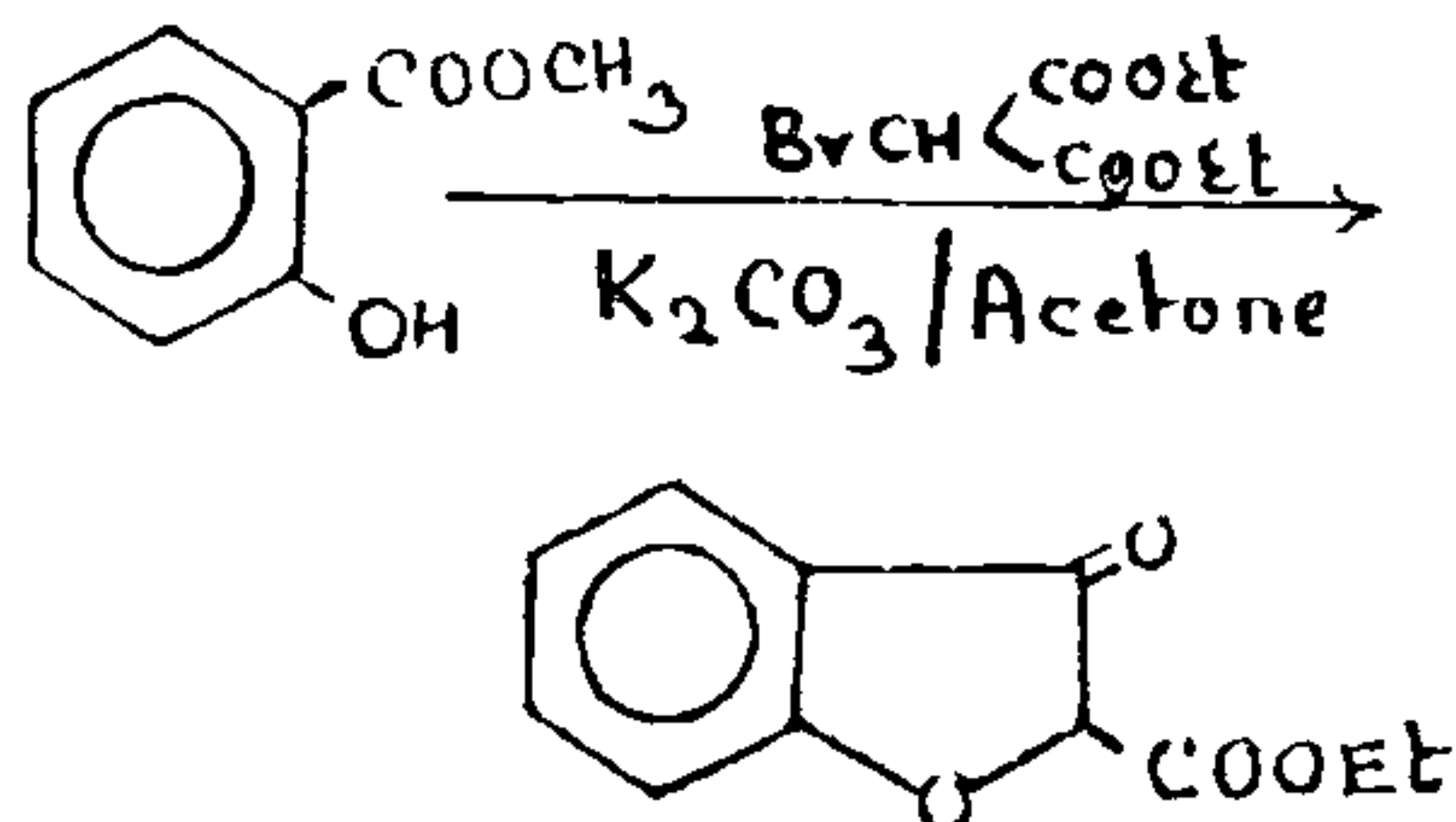


**A CONVENIENT METHOD FOR THE
SYNTHESIS OF 2-CARBETHOXY-3 (2 H)
BENZOFURANONE**

SCHRODLER *et al.*¹, have made an investigation of a number of available methods for the synthesis of 3 (2 H) benzofuranone and found that Dieckmann cyclisation of the ethyl *O*-carbethoxymethyl salicylate was the most effective method. This requires the initial preparation of *O*-carbethoxymethyl salicylate by the condensation of ethyl chloroacetate or ethyl bromoacetate with *n*-ethyl salicylate. We felt that both condensation and cyclisation may be effected in a single stage by the use of ethyl bromomalonate instead of ethyl bromoacetate. Because it is shown that the condensation of ethyl bromomalonate with salicylaldehyde in presence of anhydrous potassium carbonate in dry acetone resulted in the simultaneous condensation and cyclisation accompanied with the partial hydrolysis and decarboxylation giving benzofuran 2-carboxylate², in a single step. It is also reported that the condensation of chloroacetone with methyl salicylate in the presence of a large excess of anhydrous potassium carbonate gave some amount of cyclised product, *viz.*, 2-acetyl-3 (2 H) benzofuranone³. As we needed 2-carbethoxy-3 (2 H) benzofuranone in connection with our work, we have made an attempt to obtain it in a single step by condensing ethyl bromomalonate with methyl salicylate in presence of anhydrous potassium carbonate. As expected condensation, cyclisation, partial hydrolysis and decarboxylation occurred simultaneously and 2-carbethoxy 3 (2 H) benzofuranone was obtained 60% yield. The identity of the compound was established by its m.p. and superimposable ir and uv spectra with that of an authentic sample obtained by known method⁴.



Experimental

2-Carbethoxy-3 (2 H) benzofuranone.—A mixture of freshly distilled methyl salicylate (30.4 g), ethyl bromomalonate (48 g) and anhydrous potassium carbonate (60 g) in dry acetone (150 ml) was heated under reflux on a water bath while stirring magnetically for 12 hours. The reaction product

was filtered and potassium salts were washed with dry ether until colourless. The dry salt was suspended in water (200 ml) and cooled thoroughly in ice bath. The suspension was carefully acidified with dilute acid and the 2-carbethoxy-3 (2 H) benzofuranone which separated as a colourless solid was collected by filtration. On crystallisation from petroleum ether it was obtained as colourless needles. m.p. 63–64° (lit. m.p. 65°), yield, 25 g. (Found C, 63.81; H, 4.57; C₁₁H₁₀O₄ requires C, 64.08; H, 4.85%.)

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1. Schroeder, D. C., Corcoran, P. O., Holden, C. A. and Mulligen, M. C., *J. Org. Chem.*, 1962, 27, 586.
2. Kawase, Y., Nakayama, M. and Tamatskuri, P., *Bull. Chem. Soc.*, Japan, 1962, 35, 149.
3. Geissman, T. A. and Armen, A., *J. Am. Chem. Soc.*, 1955, 77, 1623.
4. King, A. I., Holland, R. A., Reed, F. P. and Robertson, A., *J. Chem. Soc.*, 1948, p. 1672.

**SPECTROPHOTOMETRIC STUDIES ON
Pd (II)-5-CHLORO-2-HYDROXY-4-METHYL
ACETOPHENONE OXIME COMPLEX**

5-CHLORO-2-hydroxy-4-methylacetophenone oxime (CHMAO) is a good complexing agent for a number of transition metal ions¹. The literature reveals that the spectrophotometric studies of its palladium chelate have not been carried out. In continuation^{2,3} of our work on disubstituted *o*-hydroxy acetophenone oximes, we now report the spectrophotometric studies of the palladium complex of CHMAO by its extraction into chloroform.

Experimental

Apparatus.—Optical density and pH measurements were carried out with the Systronic, Colorimeter type (103) and type (322) respectively.

Solution.—Standard solution of palladium (II) was prepared from palladium chloride, B.D.H. (A.R.) in dilute hydrochloric acid and standardized gravimetrically⁴. Other solutions were prepared from AnalaR reagents. Hydrochloric acid and ammonium hydroxide buffers of different pH values were used.

The reagent (CHMAO) was prepared as reported earlier¹. Freshly distilled chloroform (A.R. grade) was used for the extraction of the complex.

Procedure for the determination of palladium.—A suitable aliquot of palladium (II) solution

[(10–40 $\mu\text{g Pd (II)}$)] is mixed with CHMAO (2 ml., 0.01 M ethanolic solution). The mixture was buffered to pH 2–4 and the total volume made upto 10 ml with water. The mixture was allowed to stand for about 100 min. and then extracted into 8 ml. of chloroform by vigorous shaking. The chloroform solution was separated and the absorbance recorded against the reagent blank prepared under similar conditions at 400 nm. The palladium content was found from the calibration curve.

Interferences.—The following ions did not cause a deviation in absorbance of more than 2.5% at pH 2.5–4.0 when present in amounts (ppm) shown in parentheses: Co (II) (500), Ni (II) (500), Cu (II) (300), Zn (II) (800), Mg (II) (800); Cd (II) (1000), MoO_2 (II) (500), UO_2 (II) (500), VO (II) (500), Hg (II) (500), Mn (II) (500), Sb (III) (400), Bi (III) (400), As (III) (400), Cl^- , Br^- , I^- , NO_2^- , $\text{C}_2\text{O}_4^{2-}$, SO_4^{2-} , SO_3^{2-} and CO_3^{2-} upto (2000 each). But EDTA, Fe (III), and F^- interfere seriously even in small quantities.

Results and Discussion

Palladium forms yellow precipitate with CHMAO, which is extractable into chloroform easily. Vosburgh and Cooper's method⁵ shows the formation of only one complex and maximum absorbance lies at 400 nm. The absorbance *versus* pH plot shows that the absorption of the complex remains maximum and constant between pH 2.5–4.0 and pH 3.0 was maintained for these studies. Similarly absorbance *versus* reagent plot shows that at least four times excess of reagent is essential for complete precipitation.

The system obeys Beer's law upto 18 ppm of palladium and from Ringbom's plot is 5.00–16.20 ppm. The molar extinction coefficient is 2800 and its sensitivity is 0.038 $\mu\text{g Pd/cm}^2$.

Stoichiometry of the complex.—Job's method⁶, mole ratio method⁷ and slope ratio method⁸ showed that the metal and the ligand were present in 1 : 2 ratio in the complex.

Stability constant of the complex.—The conditional stability constant (27° C) was determined by (1) the mole ratio method and (2) Dey and Mukherji method⁹ and the log of stability constant was 8.44 and 8.76 respectively. The free energy of formation of the complex, $-\Delta F = RT \ln K$, was 11.86 Kcal/mole.

A number of oximes react with palladium (II) to give precipitate which are extractable into organic solvent like chloroform. Dimethylglyoxime¹⁰ is a selective reagent for separation of palladium (II) from other platinum metals. But the sensitivity is poor (0.06 $\mu\text{g Pd/cm}^2$) at 375 nm. α -Furil-

dioxime¹¹ (sensitivity 0.005 $\mu\text{g Pd/cm}^2$ at 380 nm) and phenyl- α -pyridyl ketoxime¹² (sensitivity 0.0036 $\mu\text{g Pd/cm}^2$ at 410 nm) are sensitive and selective reagents for palladium (II). However, CHMAO (sensitivity 0.038 $\mu\text{g Pd/cm}^2$ at 400 nm) is more sensitive than dimethylglyoxime but less sensitive and selective as compared with the other oximes.

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1. Saksena, R. N. and Panday, K. K., *J. Ind. Chem. Soc.*, 1972, 49, 779.
2. Gupta, S. P., Srivastava, S. K. and Lal, K., *Ind. J. Chem.*, 1975, 13, 297.
3. Lal, K. and Gupta, S. P., *Curr. Sci.*, 1975, 44, 178; 652. *Ind. J. Chem.*, 1975, 13, 973 (in press).
4. Vogel, A. I., *A Text Book of Quantitative Inorganic Analysis*, Longmans Green and Co., Ltd., London, 1962, p. 511.
5. Vosburgh, W. C. and Cooper, G. R., *J. Am. Chem. Soc.*, 1941, 63, 437.
6. Job, P., *Ann. Chim.*, 1928, 9, 113.
7. Goe, J. H. and Jones, A. L., *Ind. Eng. Chem., Anal. Ed.*, 1944, 16, 111.
8. Harvey, A. E. and Manning, D. L., *J. Am. Chem. Soc.*, 1950, 72, 4488.
9. Mukherji, A. K. and Dey, A. K., *J. Inorg. Nucl. Chem.*, 1958, 6, 314.
10. Peshkova, V. M., Shlenskaya, V. I. and Rashevskaya, A. I., *Anal. Abs.*, 1957, 4, 2623.
11. Menis, O. and Rains, T. C., *Anal. Chem.*, 1955, 27, 1932.
12. Sen, B., *Ibid.*, 1959, 31, 881.

PREPARATION MOLAR CONDUCTANCE AND INFRA RED SPECTRA OF SOME AROMATIC AMINE COMPLEXES OF COPPER (II) PHTHALIMIDE

Part I. Complexes of *o*-, *m*-, *p*-toluidines, piperidine and morpholine

THE above-mentioned amines have been used to prepare 5 new coordination complexes with copper (II) phthalimide, and their structures have been resolved on the basis of analysis, molar conductance and infra red measurements.

All the complexes were prepared by refluxing copper (II) phthalimide with amines in 1 : 2 ratio in acetone for 6 hours, and crystallising out the complex from solution by the addition of petroleum ether. These were recrystallised from methanol, dried and analysed.

(a) *Diphthalimidodipiperidine Copper (II)*—
[Cu (C₈H₇O₂N)₂ pip₂]^o. Found Cu = 13.90; C = 62.97; H = 5.89; N = 10.98%; Calculated Cu = 14.25; C = 63.34; H = 6.09; N = 11.34%.