

Compound (V) has been reported³ to be formed by treatment of carane-3,4-dibromide (VII) with silver oxide (Lit.³ records m.p. 165° for semicarbazone of V).

The structure of (V) has been confirmed by the following sequence of reactions. Baeyer-Villiger oxidation of (V) (perbenzoic acid, 1N, 72 hr) gave in 85% yield the acetate (VI) as a liquid $C_{10}H_{16}O_2$, M^+ 168, IR: 1,739, 1,227 (acetate); PMR (CCl_4): 9.12, 9.02 (3H each, *s*, *gem*-dimethyl), 8.83 (2H, *m*, cyclopropane protons), 8.13 (4H, *m*, methylene protons), 8.08 (3H, *s*, $-OCOCH_3$) and 5.17 (1H, *m*, C_3-H). Saponification of the acetate (VI) with methanolic potash (10%) gave the alcohol (VIII), $C_8H_{14}O$, M^+ 126 as a liquid; IR: 3,636, 1,047 (secondary-OH); PMR (CCl_4): 9.18, 9.03 (3H each, *s*, *gem*-dimethyl), 8.83 (2H, *m*, cyclopropane protons), 8.25 (4H, *m*, methylene protons, and 5.95 (1H, *m*, C_3-H).

Jones chromic acid oxidation of (VIII) afforded a liquid ketone, identified as (IX), $C_8H_{12}O$, M^+ 124, b.p. 130°/15 mm; IR: 1,748 (cyclopentanone), 1,405

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($-C-CH_2$); PMR (CCl_4): 9.13, 8.9 (3H each, *s*, *gem*-dimethyl), 8.73 (2H, *m*, C_1 and C_5 protons) and centered at 7.77 (4H, *m*, methylenes α to $>C=O$).

The bromo compound (IV), on treatment with silver nitrate under identical conditions, gave as one of the products the methyl ketone (V), identified by spectral data.

The ketone (V) on treatment with a mineral acid like sulphuric acid in methanol rearranges to give another ketone (X), $C_{10}H_{16}O$ identified by spectral data; IR: 1,705 ($>C=O$); PMR (CCl_4): 8.4 (6H, *s*, vinyl methyls), 7.93 (3H, *s*, $COCH_3$), 7.67

(4H, *m*, allylic methylenes) and 7.2 (1H, *m*, CH_2 , α to $>C=O$).

Ketone (IX) is an important intermediate in the synthesis³ of some substituted chrysanthemic acid analogues.

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STUDIES ON THE PREPARATION AND PROPERTIES OF SOME NEW PHENOLIC DERIVATIVES OF BIS- η^5 -METHYLCYCLOPENTADIENYL TITANIUM(IV) DICHLORIDE

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THE present communication describes the preparation and characterisation of some new phenolic derivatives of $(\eta^5-C_5H_5)_2TiCl_2$ (I). These derivatives have been prepared by reacting (I) with various phenols like phenol, resorcinol, phloroglucinol, catechol and α -naphthol in THF medium.

All reactions were carried out in strict dry conditions. Conductance measurements were made in nitrobenzene at $30 \pm 0.5^\circ C$ on Beckmann RC-18 conductivity bridge. C and H were estimated micro-analytically and Ti as TiO_2 gravimetrically. IR spectra of these derivatives were recorded on Perkin Elmer Model 621 in KBr pellets, in the region $4000-250\text{ cm}^{-1}$. Molecular weights were determined ebullioscopically.

Compound (I) was prepared by literature method¹, 0.554 g (0.002 mole) of (I) was refluxed with 0.376 g (0.004 mole) of freshly distilled phenol in 150 ml dry THF for 6 hr and filtered. Filtrate was evaporated under vacuo and precipitated by petroleum ether ($60-80^\circ C$) to give reddish crystals of $(\eta^5-C_5H_5)_2Ti(OC_6H_5)_2$. Yield -60%.

The other derivatives were similarly prepared, by using appropriate quantities of corresponding phenols.

These complexes are soluble in common organic solvents. They vary in colour from reddish brown to greenish blue. They are monomeric and non-electrolytes as inferred from conductance measurements and molecular weights. The analytical data is in good agreement with formulae suggested for them (Table I).

The presence of methylcyclopentadienyl group in these compounds is shown by following bands in their i.r. spectra: C-H stretching $\sim 3100\text{ cm}^{-1}$, C-C asymmetric ring breathing $\sim 1430\text{ cm}^{-1}$, C-H deformation in-plane bending $\sim 1120-1040\text{ cm}^{-1}$ and C-H bending out of plane deformation at $800-820\text{ cm}^{-1}$. These bands also suggest a π -bonded $CH_2 \cdot C_5H_4$ group in these compounds².

In the case of phloroglucinol derivative, only two of the three hydrogen atoms are replaced and the presence of third hydroxyl group (phenolic is indicated by the appearance of bands at $\sim 3500\text{ cm}^{-1}$,³. This peak is absent in other derivatives. This observation is further confirmed by appearance of a band at $\sim 1180\text{ cm}^{-1}$ (due to hydroxyl deformation)⁴. The

TABLE I
Analytical data and physical characteristics of phenolic derivatives of $(\eta^5\text{-CH}_3 \cdot \text{C}_6\text{H}_4)_2 \text{TiCl}_2$

Compound	Colour	M.wt. found (calc.)	Analysis (Found/Calc.)		
			C	H	Ti
$(\eta^5\text{-CH}_3 \cdot \text{C}_6\text{H}_4)_2 \text{Ti}(\text{OC}_6\text{H}_5)_2$ Phenol	Reddish	375 (392)	73.39 (73.47)	6.08 (6.12)	12.18 (12.25)
$(\eta^5\text{-CH}_3 \cdot \text{C}_6\text{H}_4)_2 \text{Ti}(\text{OC}_{10}\text{H}_7)_2$ -Naphthol	Reddish brown	478 (492)	77.95 (78.03)	5.61 (5.69)	9.70 (9.75)
$(\eta^5\text{-CH}_3 \cdot \text{C}_6\text{H}_4)_2 \text{Ti}(\text{O}_2\text{C}_6\text{H}_4)$ Resorcinol	Green	302 (314)	68.72 (68.80)	5.65 (5.73)	15.21 (15.29)
$(\eta^5\text{-CH}_3 \cdot \text{C}_6\text{H}_4)_2 \text{Ti}(\text{O}_2\text{C}_6\text{H}_4)$ Catechol	Green	300 (314)	68.70 (68.80)	5.68 (5.73)	15.20 (15.29)
$(\eta^5\text{-CH}_3 \cdot \text{C}_6\text{H}_4)_2 \text{Ti}(\text{O}_3\text{C}_6\text{H}_4)$ Phloroglucinol	Greenish blue	310 (330)	65.40 (65.46)	5.38 (5.45)	14.47 (14.54)

bands at 1410 cm^{-1} are due to M-O-C stretching frequencies⁵.

Various phenoxy groups in these are attached to the metal atom by covalent bonds.

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RAPID SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM WITH PERAZINE

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Introduction

THE coloured reaction between selenium(IV) and perazine (PZ), 10-[3-(4-methyl-1-piperazinyl)propyl]phenothiazine dimalonate has not been previously

studied. The authors have now developed PZ as a selective and sensitive reagent for the spectrophotometric determination of selenium(IV). The proposed method offers the advantages of simplicity, sensitivity, selectivity, rapidity and determination at room temperature without the need for extraction.

Experimental

Reagents

The stock solution of selenium(IV) was prepared by dissolving a known amount of selenium dioxide in 500 ml of doubly distilled water containing 5 ml of conc. hydrochloric acid and standardised by the gravimetric method¹. The stock solution was further diluted as needed. A 0.2% (w/v) aqueous solution of PZ was prepared and stored in an amber coloured bottle in a refrigerator. Beckman model DB spectrophotometer with matched 1 cm silica cells was used for absorbance measurements.

Procedure

1 ml of the stock solution, containing 1.2–45 μg of selenium(IV), 5–15 ml of 10 M hydrochloric acid and 1 ml of 0.2% PZ solution were transferred to a 25 ml volumetric flask. The solution was mixed thoroughly and diluted to the mark with doubly distilled water. The absorbance was measured at 514 nm against a corresponding reagent blank. The amount of selenium in the sample was deduced from the standard calibration curve.

Results and Discussion

PZ reacts with selenium(IV) to form a pink coloured species in hydrochloric, sulphuric or phosphoric acid