

1.5 eV, in close agreement with the latest value of Eley *et al.*⁶. The specific conductivity of DPPH is $2.4 \times 10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 30° C. The specific conductivity of picryl N-amino carbazyl (PAC) at 30° C is $1.5 \times 10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$ with an E_g value of 0.9 eV. The value of E_g in this case is lower than that found in other free radicals³. The size and shape of the barrier between the molecules influences the mobility of the conduction electrons and the energy gaps. It is likely that in organic free radicals, the orbitals containing unpaired electrons are not favoring the tunnelling process. At this point, it appears that all the known organic free radicals have high E_g values comparable to those of molecular crystals⁷.

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TRICYCLOPENTADIENYL AND TRIINDENYL COMPOUNDS OF THALLIUM (III)

CYCLOPENTADIENYL thallium(III)^{1,2} and cyclopentadienyl thallium(III) dimethyl³ have already been reported. The present communication deals with a study on the preparation and characterization of tricyclopentadienyl thallium and triindenyl thallium by the direct reactions of thallium(III) oxide with cyclopentadiene as well as indene in tetrahydrofuran. These compounds were isolated by removing the solvent under reduced pressure and subsequent recrystallization from petroleum ether.

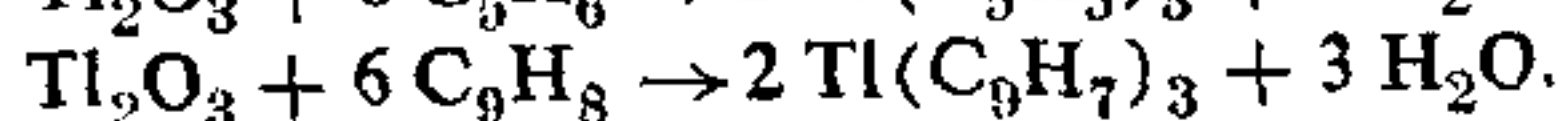
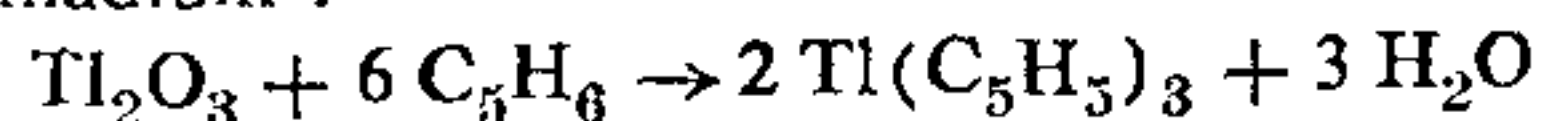
Experimental.—Operations were carried out under anhydrous conditions. A good grade of tetrahydrofuran was further purified by distillation over lithium aluminium hydride. Infrared spectra (KBr) were recorded on Perkin Elmer Infracord Model-137

spectrophotometer. Thallium was estimated as thallium(III) oxide while carbon and hydrogen were determined by microanalytical methods.

Preparation of Tricyclopentadienyl Thallium.—Cyclopentadiene (3.4 ml; 0.04 mole) was added to thallium(III) oxide (2.3 g; 0.005 mole) in tetrahydrofuran (150 ml). The mixture was refluxed for 35–40 hr at 80–85° C and filtered. The resultant orange yellow solution was freed from solvent by evaporation under reduced pressure (20–25 mm) leaving behind a brown paste. Repeated crystallization of this paste from petroleum ether (60–80° C) gave a red brown crystalline compound whose analysis corresponded with the formula $(C_5H_5)_3Tl$, yield 85% (Found: C, 44.9; H, 3.6; Tl, 50.9; $C_{15}H_{15}Tl$ calcd.: C, 45.07; H, 3.78; Tl, 51.14%). The compound is quite stable under dry and inert atmosphere and decomposes without melting at 94° C. It is soluble in acetone, chloroform, dichloromethane, carbon tetrachloride and insoluble in benzene, toluene and cyclohexane.

Preparation of Triindenyl Thallium.—Indene (3.5 ml; 0.03 mole) was added to thallium(III) oxide (1.8 g; 0.004 mole) in tetrahydrofuran (200 ml). The mixture was refluxed for 50–55 hr at 70–75° C and filtered. The solvent was removed by evaporation under reduced pressure (20–25 mm) and the brown pasty mass after repeated crystallization from petroleum ether (60–80° C) gave a red orange crystalline compound of $(C_9H_7)_3Tl$, yield 70% (Found: C, 58.8; H, 3.6; Tl, 37.1; $C_{27}H_{21}Tl$ calcd.: C, 58.98; H, 3.85; Tl, 37.17%). The compound is stable in dry and inert atmosphere and decomposes without melting at 72° C. It is immiscible with water and is fairly soluble in common organic solvents like dichloromethane, chloroform, carbon tetrachloride, acetone, dioxane, benzene and alcohol.

Discussion.—The preparation of tricyclopentadienyl and triindenyl thallium may be regarded as analogous to tricyclopentadienyl and triindenyl oxy vanadium⁴.



The infrared spectra in KBr show the following absorption peaks:

$(C_5H_5)_3Tl$: 2950, 2380, 1700 1570, 1460,

1350, 1160, 1050, 855, 780 cm^{-1} .

$(C_9H_7)_3Tl$: 3050, 2930, 2340, 1705, 1580,

1455, 1360, 1280, 1150, 1055, 800, 755

720 cm^{-1} .

(where: s = strong; w = weak; m = medium).

The infrared spectrum of tricyclopentadienyl thallium shows the usual peaks of the $C_5H_5^-$ group⁵, viz., the frequencies at 2950 cm^{-1} (C—H stretching), at 1460 cm^{-1} (C—C stretching), at $1160, 1050\text{ cm}^{-1}$ (C—H deformation) and at 855 cm^{-1} (C—H out of plane deformation). Infrared spectrum of triindenyl thallium shows the various absorption peaks due to phenyl group in addition to the usual peaks of the $C_5H_5^-$ group as discussed above, at 1360 cm^{-1} (C—H stretching), at 1580 cm^{-1} (C—C stretching) at 755 cm^{-1} (C—H out of plane bending) and at 720 cm^{-1} (methylene rocking vibration), since indene itself shows absorption band at $\sim 700\text{ cm}^{-1}$ ⁶.

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CHEMICAL EXAMINATION OF THE LEAF RESIDUES OF SKIMMIA LAUREOLA HOOK.

Skimmia laurela Hook. (Rutaceae) is a common fodder plant of India and its leaves have been found to contain the furano quinoline alkaloid skimmianine¹, the linear furano coumarins², bergapten and iso-pimpinellin and the simpler coumarins, umbelliferone, skimmian and scopoletin³. They are now used for large-scale extractions of essential oil which is an important commercial product. Large quantities of leaf residues are available for proper utilisation and therefore they have now been examined. The powdered dry leaf residues (600 g) were extracted in succession in a Soxhlet with (i) petroleum ether, (ii) acetone and (iii) alcohol.

The petroleum ether extract yielded a green oil (15 g), which was subjected to column chromatography over silica gel and three compounds A, B, C were obtained. Compound (A), 50 mg, crystallised from petroleum ether, m.p. $169-70^\circ$, $[\alpha]_D + 56.4^\circ$, it was identified as lupenone and

identity confirmed by comparison with an authentic sample (m.p., m.m.p., IR). Compound (B) after crystallisation from chloroform-methanol (40 mg), m.p. $212-13^\circ$. It gave positive Liebermann-Burchard test and its IR indicated characteristic bands at $\nu_{\text{max}}^{\text{KBr}}$ $3390(\text{OH})$, $2950(\text{C-H})$, 1350 (gem dimethyl), 1655 and 880 cm^{-1} ($\text{C}=\text{CH}_2$). It was identified as lupeol. Its identity was confirmed by comparison with an authentic sample and by the preparation of its acetate; m.p. and m.m.p. $214-16^\circ$. Compound (C) crystallised from methanol as colourless needles (70 mg), m.p. $135-36^\circ$, $[\alpha]_D - 30.6^\circ$. Its identity as β -sitosterol was confirmed by TLC comparison with an authentic sample and by mixed m.p. and also by the preparation of its acetate. The occurrence of these triterpenoid and steroid compounds was not recorded before.

Acetone extract.—From the acetone extract, was obtained an ether-insoluble and ether-soluble fractions. The former was similar to the alcoholic extract (see later) on TLC, with which it was mixed. The ether solution was extracted several times with 0.1% hydrochloric acid. The acid solution when neutralised yielded a very small amount of a base (10 mg), m.p. $175-77^\circ$, which gave alkaloid reaction and was identified as skimmianine.

The remaining ether solution when extracted with 10% sodium carbonate solution and the extract acidified yielded a mixture of two compounds (TLC). They were separated by column chromatography and marked D and E. Compound D crystallised from ethyl acetate as colourless needles (20 mg), m.p. $202-03^\circ$, $\lambda_{\text{max}}^{\text{MeOH}}$ 230 ($\log \epsilon 4.18$), 254 ($\log \epsilon 3.79$) and 345 nm ($\log \epsilon 4.0$); $\nu_{\text{max}}^{\text{KBr}}$ 3367 ($-\text{OH}$), 1681 (conjugated lactone), 1639 (unsaturation), 1613 cm^{-1} (phenyl nucleus). It was identified as scopoletin and confirmed by comparison with authentic sample. The compound E (50 mg), m.p. $231-32^\circ$ was found to agree in all respects with the synthetic sample of umbelliferone.

From the remaining neutral ether solution an oil was obtained which was saponified with 20% methanolic potassium hydroxide. On acidification and purification of the product by column chromatography, two major compounds F and G were obtained. The compound F, crystallised from methanol (23 mg), m.p. $187-89^\circ$; $\lambda_{\text{max}}^{\text{MeOH}}$ 222, 240, 245, 255, 265 and 308 nm . It was identified as bergapten and identity confirmed by direct comparison with an authentic sample. Compound G (18 mg), m.p. $150-51^\circ$, $\lambda_{\text{max}}^{\text{MeOH}}$ 220, 243, 270 and