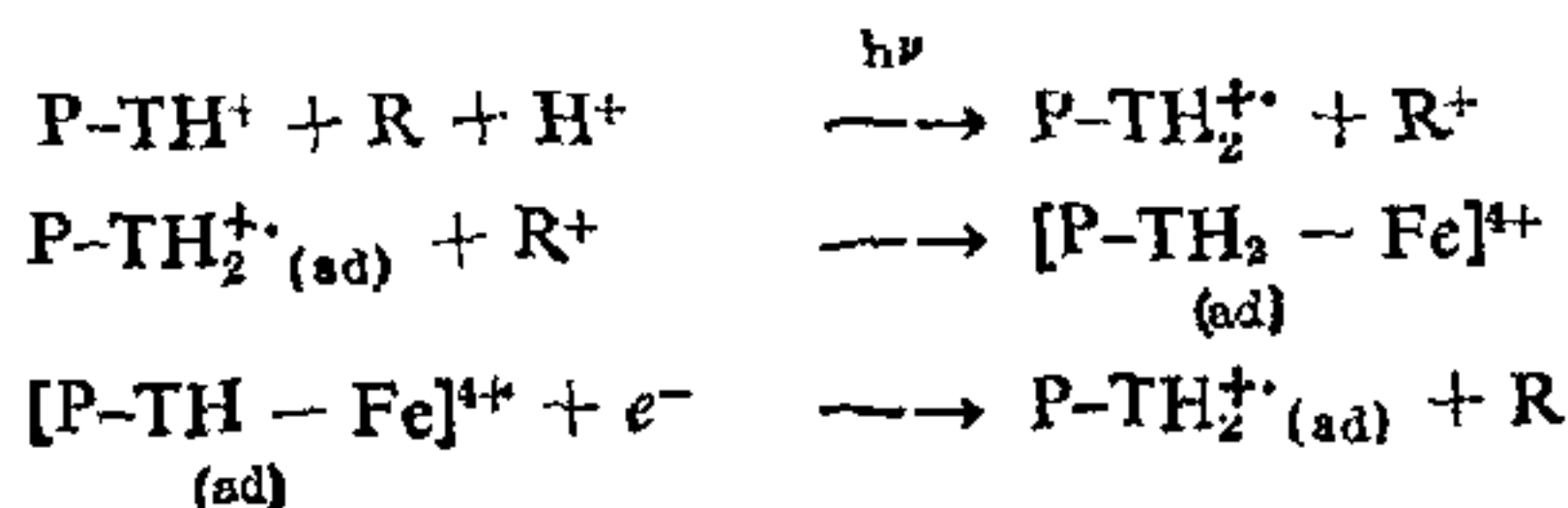
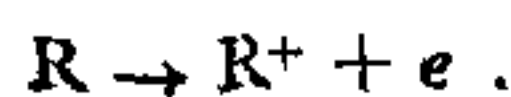


The reaction scheme at the illuminated polymer-bound thionine coated platinum electrode is proposed to be as shown below:



where R represents Fe(II), hydroquinone or $\text{Fe}(\text{CN})_6^{4-}$

Polymer-bound semithionine and Fe^{3+} are produced photochemically and Fe^{3+} ion forms a complex with the polymer-bound semithionine adsorbed at the surface. This complex undergoes reduction at the platinum electrode. The reaction at the other electrode is proposed to be



Among the various reductants used in the Totally Illuminated Thin Layer Cell with one of the platinum electrodes coated with polymer-bound thionine, ferrous sulphate gives the maximum power output which is ~ 10 times higher than the power output of polymer-bound thionine-Iron(II) system in this cell with one clean platinum electrode and another SnO_2 electrode.

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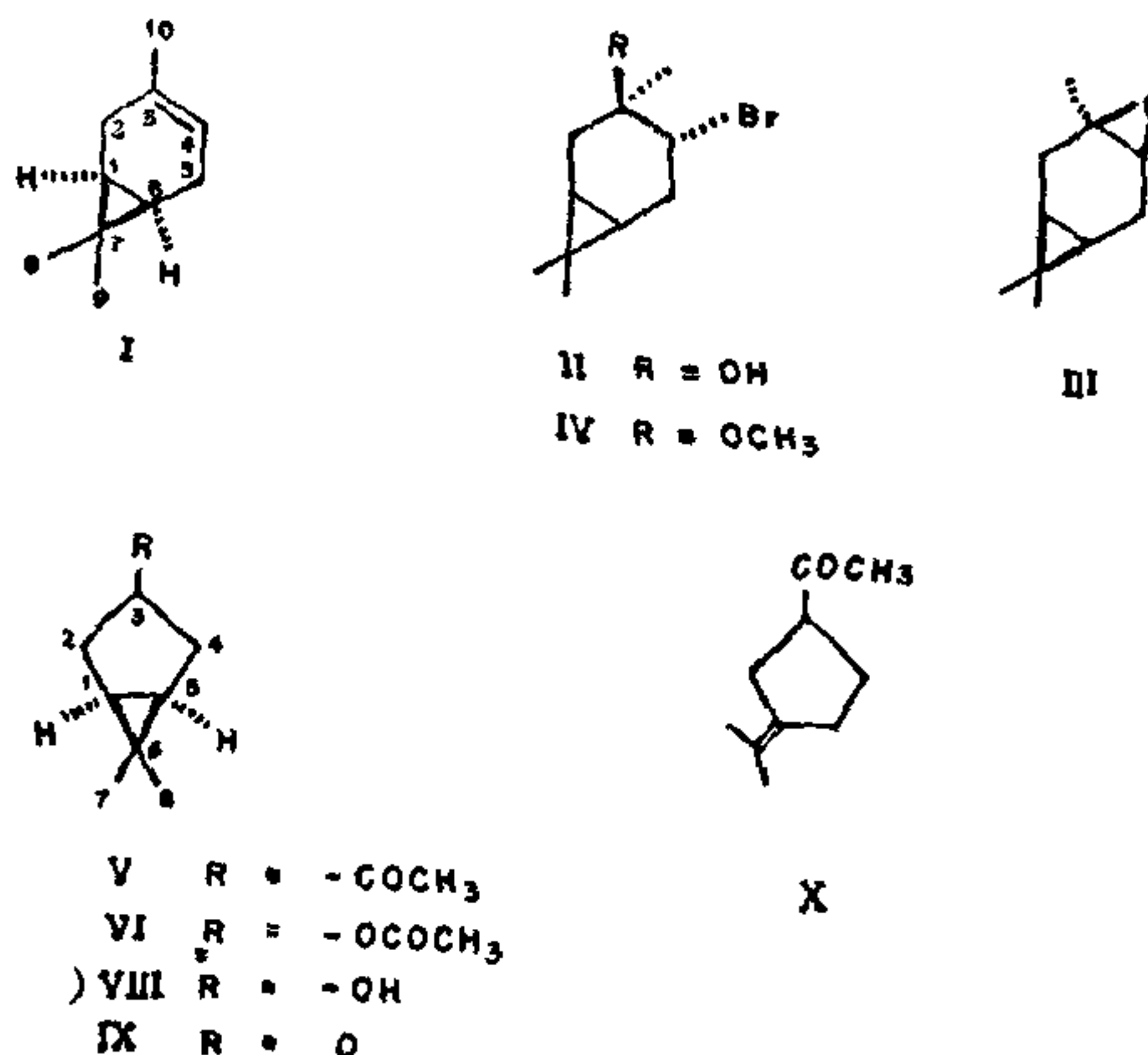
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REACTION OF N-BROMOSUCCINIMIDE ON (+)-3-CARENE

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The reaction of N-bromosuccinimide on (+)-3-carene(I) has been reported¹ to give the *trans*-bromohydrin(II). The latter was also converted into the carene- β -epoxide (III). In this communication we report the



reaction of N-bromo-succinimide on (I) in different solvents and also report some interesting transformations of (II), leading to some useful intermediates.

Treatment of (I) with aqueous N-bromosuccinimide in tertiary butanol, afforded as the major product the bromohydrin (II), $\text{C}_{10}\text{H}_{17}\text{OBr}$, m.p. 60–62°; identified by spectral data; IR* bands at 3,390, 1,100 (tertiary-OH); PMR* (CCl_4) signals at: 9.3 (2H, *m*, C_1 and C_6 -H), 8.98, 8.95 (3H each, *s*, C_7 -methyls), 8.68 (3H, *s*, C_8 - CH_3), 7.6 (4H, *m*, C_2 and C_5 -H) and 6.07 (1H, *t*, $J = 9$ Hz, C_4 -H). However, when (I) is treated with aqueous N-bromosuccinimide in methanol, a different bromocompound, $\text{C}_{11}\text{H}_{19}\text{OBr}$ was obtained as a liquid to which structure (IV) has been assigned on the basis of spectral data; PMR (CCl_4): 9.28 (2H, *m*, C_1 and C_6 -H), 9.0, 8.97 (3H each, *s*, C_7 -methyls), 8.73 (3H, *s*, C_8 - CH_3), 7.83 (4H, *m*, methylene protons at C_2 and C_5), 6.87 (3H, *s*, $-\text{OCH}_3$ at C_3) and 6.10 (1H, *t*, $J = 9$ Hz, C_4 -H).

Treatment of the compound(II) with aq. silver nitrate in acetone solution gave a mixture of three compounds (TLC), from which the major product was isolated by fractional distillation, followed by chromatography to give the ketone(V), $\text{C}_{10}\text{H}_{16}\text{O}$, M^+ 152, b.p. 85–90°/4 mm, $(\alpha)_D^{25} \pm 0$ (*c*, 3), identified by spectral data; IR: 1,709 ($>\text{C}=\text{O}$); PMR (CCl_4): 9.05 (6H, *s*, *gem*-dimethyl), 8.77 (2H, *m*, cyclopropane protons), 8.27 (4H, *m*, methylene protons), 7.97 (3H, *s*, $-\text{COCH}_3$) and 7.43 (1H, *m*, $\overset{\text{O}}{\underset{|}{\text{C}}}\text{H}$, α to $>\text{C}=\text{O}$). It gave a semicarbazone, $\text{C}_{11}\text{H}_{19}\text{ON}_3$, m.p. 162–163°.

* IR bands are expressed in ν (cm^{-1}) and PMR chemical shifts on τ -scale with TMS as internal standard.

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*, -OCOCH₃) and 5.17 (1H, *m*, C₈-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*, C₈-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-CH₂); PMR (CCl_4): 9.13, 8.9 (3H each, *s*, gem-dimethyl), 8.73 (2H, *m*, C₁ and C₅ 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*, COCH₃), 7.67

(4H, *m*, allylic methylenes) and 7.2 (1H, *m*, CH₂- α to >C=O).

Ketone (IX) is an important intermediate in the synthesis³ of some substituted chrysanthemoid 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