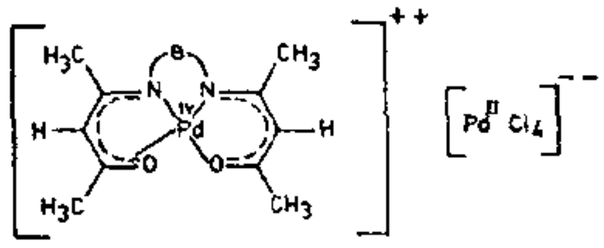
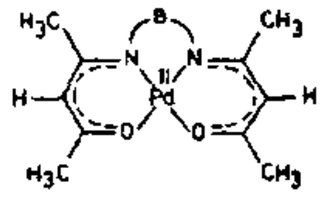
coordination is favoured. The results of these studies along with reactions of A with primary amines and nitrosating reagents will be published elsewhere.



A



B

(I) B = $-CH_2CH_2-$
(II) B = $-CH_2CH(CH_3)-$
(III) B = $-CH_2CH_2CH_2-$

Although four methyl proton signals are expected for the structure of the type A, the pmr spectrum of A(I) in $CDCl_3$ shows only three signals at 8·42, 8·00 and 7·94 τ with integrated intensities of 6 : 3 : 3, which are assignable respectively to $[-(CH_3)C(=N)-]$, $COCH_3$ (Oxygen-bonded ring) and $COCH_3$ (π-allylic bonded ring). The merging of the methyl proton signals in the vicinity of the ethylene skeleton may be attributed to their identical shielding parameters. The γ-CH proton gives a broad singlet at 5·12 τ. The complex multiplet centered at 6·52 τ is due to ethylene protons. The pmr spectrum of A(II) shows spectral features analogous to that of A(I).

In conclusion, at present, $[Pd^{IV}\ L]\ [PdCl_4]$ are the only known mixed-valent palladium complexes, in which Pd^{IV} shows oxo-π-allylic bonding.

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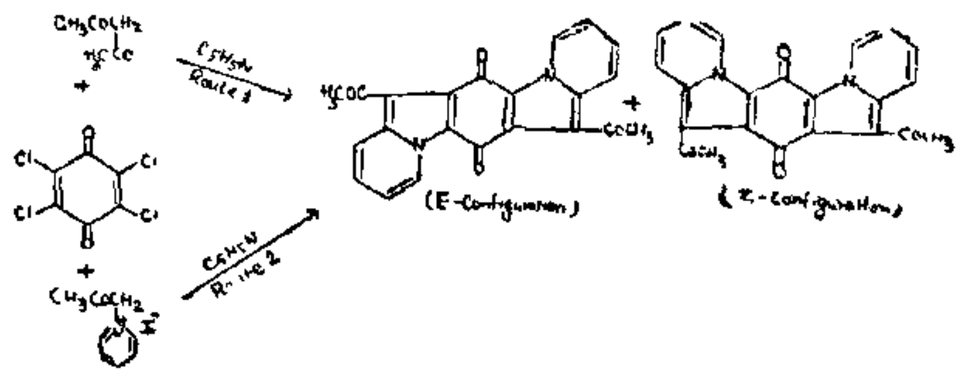
A NEW PROCEDURE FOR THE SYNTHESIS OF SUBSTITUTED PYRROCOLINE QUINONES

Introduction

THE synthesis of a number of 5 : 11 disubstituted and 5 : 7 disubstituted pyrrocoline quinones has been reported by Tilak *et al.*[1] ; by the oxidative condensation of chloranil with pyridine and active methylene compounds, like acetyl acetone, acetoacetic ester or malonic ester. That both malonic ester and acetoacetic ester gave the same products was explained on the basis that in the final stage the more electron withdrawing group was cleaved.

It was therefore thought logical to use some other compounds like acetonyl pyridinium iodide (CH_3–CO–CH_2–$N^+C_5H_5I^-$) and its analogues in which an active methylene group is situated between a carbonyl group and a strongly electron withdrawing $\rangle N^+-$ (quaternary nitrogen). It should be the strongly electron withdrawing $\rangle N^+-$ group which should be cleaved at the final stage. The resulting product in this particular case should be identical with the product obtained by the condensation of chloranil with acetyl acetone and pyridine as shown in the scheme below :



It may be seen that the use of acetonyl pyridinium iodide or acetonyl quinolinium iodide should give the same products and it is actually observed that the products of reaction (i) and (ii) are the same as verified through T.L.C. The nature of Z and E isomers of pyrrocoline quinones is ascertained through their characteristic colour reaction with sulphuric acid. In reaction (ii), if we take quinoline or isoquinoline instead of pyridine as the base, only E configuration benzo dibenz pyrrocoline quinone is obtained and is found to be identical with the compounds reported earlier[2]. The formation of compounds of Z configuration seems to be sterically hindered. The identity of the compounds prepared by both the routes was ascertained through T.L.C.

The use of the various substituted keto alkyl quaternary ammonium salts ($R\text{-}CO\text{-}CH_2\text{-}N\text{-}N\diagup\!\!\diagdown\ I^-$) should give different substituted derivatives of pyrrocoline quinones. This should be a general reaction for preparing such compounds. Further work in synthesising these compounds is in progress.

Experimental

All melting points have been determined on a Kofler instrument and are uncorrected.

N-Acetonyl pyridinium quinolinium iodide.—These compounds are prepared and purified by the known methods[1].

Benzo-dibenz (h, h')-pyrrocoline quinones—The following general procedure was adopted:—A mixture of chloranil (1 mole), N-acetonyl pyridinium iodide or N-acetonyl quinolinium iodide (1 mole) and quinoline (1 mole) in 25–30 ml ethanol was heated under reflux on a water bath for 4 hours, when all the chloranil dissolved and a deep red coloured reaction mixture was obtained. The product separated on cooling was filtered and washed with ethanol, ether, hot water and then dried. The product was recrystallised twice from pyridine. Benzo-dipyrrocoline quinones. Same procedure was adopted while using N-acetonyl pyridinium iodide, chloranil and pyridine. The E and Z products were separated through chromatography over alumina using benzene and methanol as eluants.

Compounds :

(1) 7:15-diacetyl-benzo (1:2-*b*, 4:5-*b'*)-dibenz (*h*, *h'*) pyrrocoline quinone—m.p. does not melt upto 356° (Found : C, 76·5; H, 3·8; N, 5·9; $C_{30}H_{18}N_2O_4$ requires C, 76·5 ; H, 3·8, N, 5·9%).

(2) 5:11-diacetyl-benzo (1:2-*b*, 4:5-*b'*)-dipyrrocoline quinone (E form)—m.p. does not melt upto 356° (Found : C, 71·1; H, 3·5 ; N, 7·4 ; $C_{22}H_{14}N_2O_4$ requires C, 71·3; H, 3·7; N, 7·5%).

(3) 5:11-diacetyl benzo (1:2-*b*, 4:5-*b'*)-dipyrrocoline quinone (Z form)—m.p. does not melt upto 356° (Found: C, 71·2 ; H, 3·4 ; N, 7·3 ; $C_{22}H_{14}N_2O_4$ requires: C, 71·3; H, 3·7 ; N, 7·5%).

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CHEMICAL EXAMINATION OF THE LEAVES OF *GUAZUMA TOMENTOSA* KUNTH

THE presence of friedelin 3β-ol, friedelin 3α-acetate, β-sitosterol besides a plant alcohol is reported from the leaves of *Guazuma tomentosa* Kunth.

Guazuma tomentosa Kunth (N.O. Sterculeaceae) is a moderate sized deciduous tree indigeneous to tropical America and introduced into India[1]. The presence of kaempferol, quercetrin and kaempferitrin were reported earlier from the flowers of *G. tomentosa* Kunth[2]. Isolation and characterisation of friedelin, β-sitosterol and betulin have been recently reported by us from the hexane extract of its bark[3]. Chemical examination of the leaves is now reported.

The air dried leaves (1·2 kg) were extracted with petroleum ether. The extract after concentration left a residue which resisted crystallisation. It was chromatographed over a column of silica gel. The first three fractions (500 ml) of the hexane eluate gave only waxes. The next two fractions gave Compound A (0·08 m). Further elution with hexane: benzene (9:1) gave Compound B (0·1 gm), with hexane-benzene (3:1) Compound C (0·5 gm), with hexane: benzene (7:3) Compound D (1·0 gm) and further elution with hexane: benzene (1:1) and benzene did not yield any crystalline compounds.

Compound A, $C_{32}H_{54}O_2$, crystallised from petroleum ether-chloroform as colourless shining needles, m.p. 306–8°, $[\alpha]_D^{30°} - 14°$. It gave Liebermann Burchard test positive for triterpenes. It indicated acetoxyl group (1730 and 1250 cm^{-1}) in I.R. Compound A on hydrolysis with 5% methanolic KOH furnished a compound, $C_{30}H_{50}O$, m.p. 300–301° which was identified as friedelin 3α-ol by direct comparison (m.m.p. and I.R.) with an authentic sample. Compound A is thus friedelin 3α-acetate.

Compound B, $C_{30}H_{50}O$, crystallised from chloroform-petroleum ether as colourless needles, m.p. 278–279°, $[\alpha]_D^{30°} + 14°$. It answered positive LB test for triterpenes and gave an acetate, m.p. 288–289°. Compound B was characterised as friedelin 3β-ol by direct comparison (m.m.p. and I.R.) and through its acetate with authentic samples.

Compound C, crystallised from methanol as colourless solid, m.p. 89–90° and was found to be a plant alcohol.

Compound D, $C_{29}H_{50}O$, crystallised from chloroform-methanol as colourless needles, m.p. 137–138°, $[\alpha]_D^{30°} - 36·5$. It gave positive LB test for steroids