

Structure of the Complex : The palladium chelate was analysed for its carbon, hydrogen, and nitrogen contents. The composition corresponds to the formula $\text{Pd}(\text{C}_9\text{H}_5\text{O}_2\text{NCl})_2$ (Calc. C, 42.95%; H, 3.6%; N, 5.55%. Found C, 42.91%; H, 3.56%; N, 4.99%)

The normal oximes^{7,8} have ir absorption bands at $3300\text{--}3150\text{ cm}^{-1}$ (OH str.), $1690\text{--}1510\text{ cm}^{-1}$ (C=N str.) and around 950 cm^{-1} (N-O str.). In the present investigations, HMCAO has shown prominent bands at 3077 cm^{-1} , 1587 cm^{-1} and 996 cm^{-1} assignable to intramolecular hydrogen bonded (OH), C=N and N-O str. frequencies.

The broad weak band at 3077 cm^{-1} due to intramolecular hydrogen bonded OH in the reagent is not observed in the complex. The band due to phenolic C-O vibrations at 1361 cm^{-1} in the ligand is observed at 1389 cm^{-1} in the complex. These observations suggest that ortho-hydroxy group of the base has taken part in the bond formation.

The C=N str. at 1587 cm^{-1} in the free ligand is found at 1530 cm^{-1} in the complex and can be interpreted as a consequence of coordination of nitrogen with the metal.

On the basis of above results structure (Fig. 1) is assigned to the complex.

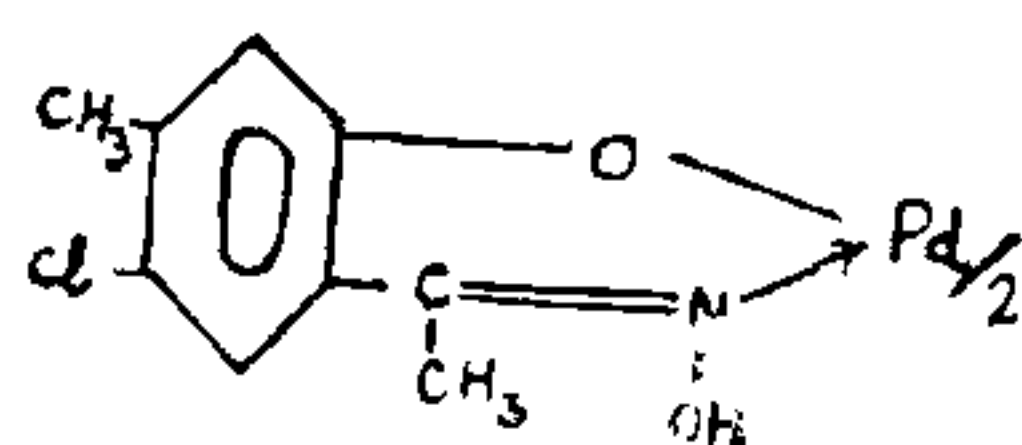


FIG. 1

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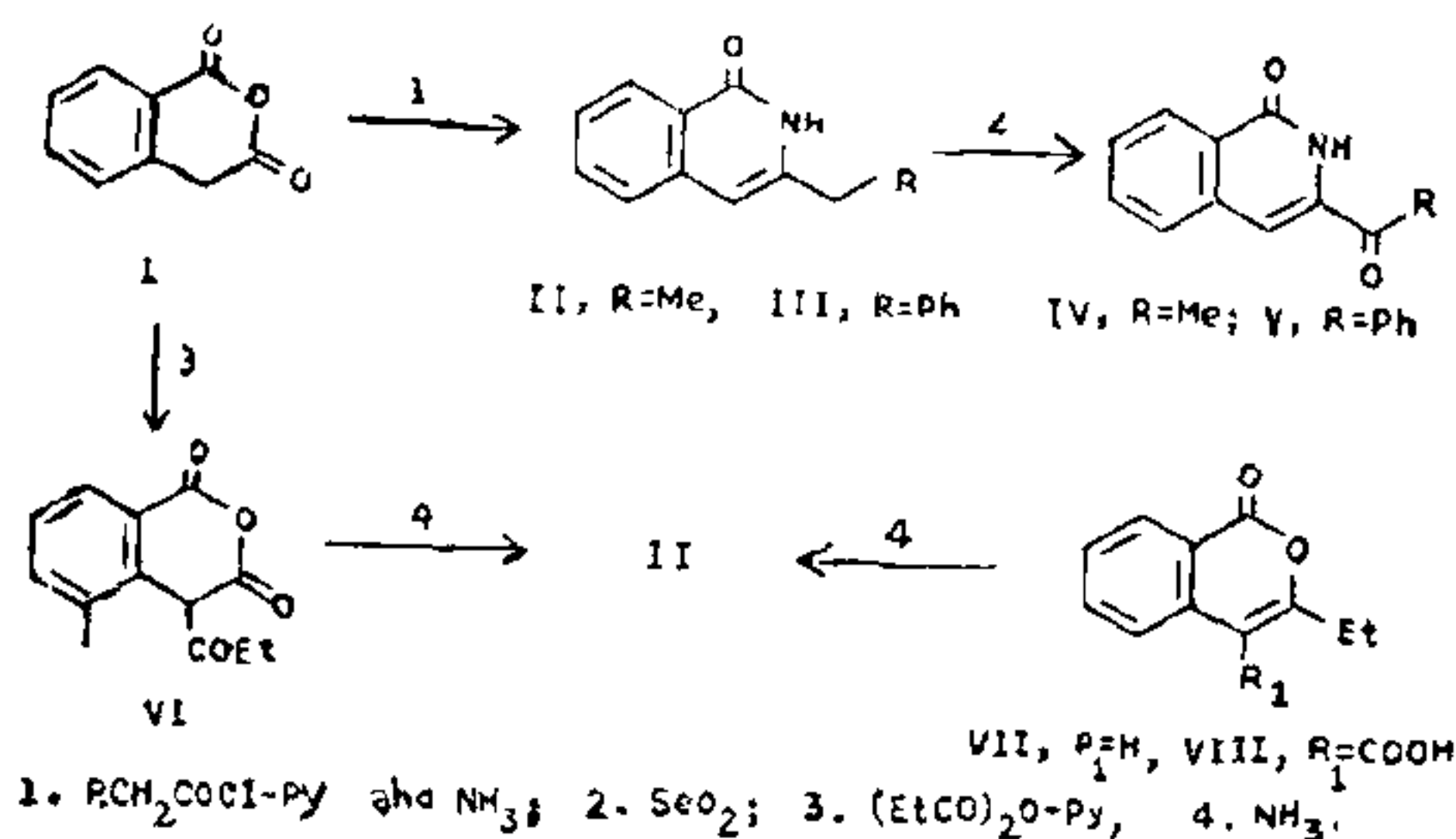
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ISOQUINOLONES - AN ELEGANT SYNTHESIS FOR 3-ACETYL AND 3-BENZOYL- ISOQUINOLONES

ISOQUINOLONES are growing in importance because of medicinal activity¹⁻⁷ and also because of their potentiality as good intermediates for synthesis of isoquinoline alkaloids. We report easy synthesis for two such potentially useful compounds, viz, 3-acetyl- and 3-benzoyl-1(2H)-isoquinolones (IV and V) from homophthalic anhydride in two steps schematically shown below. 3-Acetyl-1(2H)-isoquinolone was obtained¹² before by action of ammonia on 3-acetyl-isocoumarin. The latter compound was obtained¹² with difficulty by condensing potassium salt of phthalaldehydic acid with chloroacetone and cyclising the resulting acetonyl ester. The ease of oxidation of II and III by SeO_2 suggests the same mechanistic course as proposed¹³ before for oxidation of 3-methyl-isoquinoline to 3-formylisoquinoline.



3-Ethyl-1(2H)isoquinolone (II) is obtained in one step from homophthalic anhydride (I) (1 g) by stirring it in pyridine (3 ml) with propionyl chloride (1.3 ml) in chloroform (4 ml) which was added slowly drop by drop at 0° . The reaction mixture was stirred at 0° for 1.5 hr and then mixed with ammonia (25 ml) and heated on a boiling water bath for 2 hr and left aside at room temperature when 3-ethyl-1(2H)-isoquinolone (II) separated out as crystalline solid (0.2 g) [Crystallised from ethanol as colourless leaflets, m.p. $143\text{--}44^\circ$ Yield: 0.18 g. Found C, 76.3; H, 6.7; N, 8.2. $\text{C}_{11}\text{H}_{11}\text{ON}$ requires C, 76.3; H, 6.3 and N, 8.1. UV (MeOH) 224, 280, 330 nm; $\log \epsilon$: 4.32; 4.06; 3.78].

3-Ethyl-1(2H)isoquinolone (II) is obtained, however, in much better yield (0.5 g) by acylating homophthalic anhydride (1 g) with propionic anhydride (1.6 ml) and pyridine (1.2 ml), isolating the crude 4-propionyl-isochroman-1,3-dione (VI) (0.8 g) crude, m.p. $110\text{--}12^\circ$, needles from benzene-petrol ether, m.p. $113\text{--}15^\circ$ (Lit.⁸ m.p. of pure $113\text{--}15^\circ$) and then heating the crude product with liquor ammonia (10 ml) on boiling water

bath for 3 hr. 3-Ethyl-1(2H)isoquinolone (II) (0.4 g) separates out from the reaction mixture in pure state which is filtered and additional amount (0.1 g) is obtained by acidification of the filtrate. Synthesis of the compound VI by acylation is described⁸ before, but a modification of it improves the yield considerably. The modification consists of use of homophthalic anhydride in place of homophthalic acid, use of less amount of propionic anhydride and slightly different work up. The modified procedure is as follows: Homophthalic anhydride (I) is added slowly to a mixture of propionic anhydride and pyridine with stirring at room temperature and stirring is continued further for 2 hr. The compound VI that separates as yellow solid is filtered after stirring the reaction mixture with ether (14 ml).

The reaction that gave II in one step from I has thus proceeded through the intermediate VI and the conversion of VI to II takes place by the mechanism published earlier (The Tirodkar-Usgaonkar isoquinolone synthesis⁹). The compound II is also obtained in good yield by heating 3-ethylisocoumarin⁸ (VII) and 4-carboxy-3-ethylisocoumarin (VIII) with ammonia in boiling water bath as above. In case of VIII, replacement reaction of lactonic oxygen by NH is accompanied by decarboxylation (see ref. 9).

3-Ethyl-1(2H)isoquinolone (II, 1 g) is oxidised by refluxing it with selenium dioxide (1 g) in dioxane (40 ml) for 9 hr to furnish 3-acetyl-1(2H)isoquinolone (IV, 0.4 g) in good yield [colourless needles from ethanol, m.p. 182–83°. Lit.¹² m.p. same. Found C, 71.1; H, 5.1; N, 7.6. $C_{11}H_9O_2N$ requires C, 70.6; H, 4.8 and N, 7.5. UV (MeOH) 212, 250, 337 nm, $\log \epsilon$ 4.22, 4.0 and 4.01]. The product is isolated by filtering the reaction mixture hot from precipitated selenium and concentrating the solution when the compound crystallises out. 3-Benzoyl-1(2H)isoquinolone (V) is similarly synthesised by oxidation of 3-benzyl-1(2H)isoquinolone (III, 1 g) by SeO_2 (1 g) in dioxane (40 ml) for 4.5 hr in excellent yield [colourless needles from ethanol, m.p. 186–87°. Found C, 76.8; H, 4.4; N, 5.7. $C_{16}H_{11}O_2N$ requires C, 77.1; H, 4.4 and N, 5.6. UV 215, 257, 342; $\log \epsilon$: 4.3, 4.04 and 4.05]. The constitution got confirmed from its IR and NMR Spectra. It gave IR bands at 1670 ($C=O$ of ketone), 1650 ($C-O$ of lactam), 1610, 1570 (aromatic) and NMR ($CDCl_3$) gave signals at δ 7.13 (1H, s, H-4), 7.7 (8H, m, aromatic protons except H-8), 8.5 (1H, m, H-8), 9.8 (1H, NH). The aromatic proton H-8 resonated downfield due to $C-O$ in proximity. The compound gave 2,4-DNP (yellow prisms from ethanol, m.p. 283–84°; Found N, 16.5; $C_{22}H_{15}O_5N_2$ requires N, 16.3) and an Oxime (needles from benzene, m.p. 264–65°; Found C, 73.1; H, 5.0; N, 10.8; $C_{16}H_{12}O_2N_2$ requires C, 72.7; H,

4.5 and N, 10.6). 3-Benzylisoquinolone (III) was synthesised before from homophthalic anhydride by one step method¹⁰ and by a two step method¹¹ in very good yields. The latter was via 3-benzylisocoumarin.

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