

A NEW ANTHRAQUINONE FROM THE ROOTS OF *MORINDA CITRIFOLIA* LINN.

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MORINDA CITRIFOLIA Linn. (N. O. Rubiaceae) is used in the Indian system of medicine¹. This anthraquinone has not been reported so far from this plant. We report here the isolation and characterization of a new anthraquinone (7-hydroxy-8-methoxy-2-methyl anthraquinone) by its colour reactions, spectral data and chemical methods.

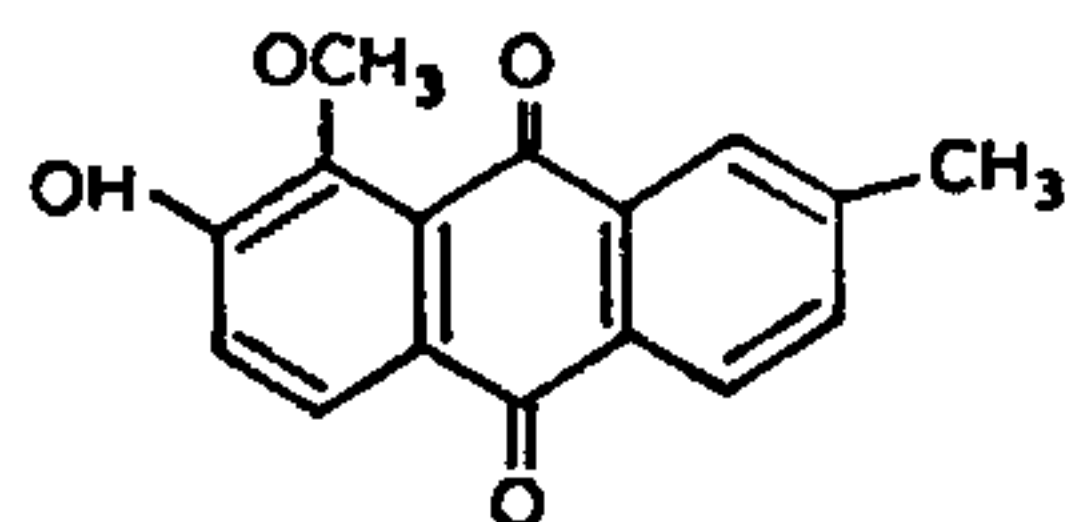
The powdered roots of *M. citrifolia* (3 kg) was extracted with ethanol under reflux for 180 h on a water bath. The ethanol from the percolates (20 l) was removed under reduced pressure on a water bath to get a solid mass which was then successively extracted with petroleum ether and benzene.

The benzene extract was concentrated and examined by thin layer chromatography, which showed the presence of a single entity. It was then passed through a column of neutral alumina and eluted with benzene:chloroform (5:5 v/v) and crystallized as red colour needles from ether:chloroform mixture (yield 900 mg).

The new anthraquinone, m.p. 240–241°, C₁₆H₁₂O₄ (M⁺268) showed uv-visible maxima at 225, 255, 385 and 410 nm and gave a positive Borntrager reaction², a characteristic for an anthraquinone. The IR (KBr) spectrum of (1) showed characteristic absorptions for hydroxyl (3560–3320), methoxyl (2860 and 1170), methyl (2920 and 1460) and unchelated carbonyl (1680) cm⁻¹ respectively. The ¹H-NMR spectrum (DMSO-*d*₆, δ, 90 MHz) of the compound displayed signal for a unchelated hydroxyl (11.0, s, 1 × OH), one methoxyl (3.88, s, 3H, 1 × OMe) and one methyl (2.70, s, 3H, 1 × Me). Further, the compound showed three ortho coupled doublets at δ 8.16, 8.08 and 7.80 for one proton each at positions H-4, H-5 and H-6 respectively and a meta coupled doublet at δ 7.04 for one proton at position H-1 and a double doublet centred at δ 6.80–6.90 for one proton at position H-3.

The compound formed a monomethyl ether (Me₂SO₄-K₂CO₃), m.p. 120–122° [found C, 72.33; H, 4.95; (OMe Zeisels method) 21.97; calculated for C₁₇H₁₄O₄: C, 72.34; H, 4.96; (OCH₃) 21.98%] and monoacetate (Ac₂O C₅H₅N), m.p. 127–128 [found: C, 69.63; H, 4.50; calculated for C₁₈H₁₄O₅: C, 69.67; H, 4.51%] confirming the presence of one hydroxyl

and one methoxyl group in the compound. Chromic acid oxidation of methylated compound gave 3,4-dimethoxy phthalic acid, m.p. 174–175° (lit m.p. 177°, m.m.p. and Co-TLC)³ as one of the oxidation products showing the presence of OMe at C-8 and hydroxyl at C-7 positions in the compound. The major MS fragment ions of the compound were as follows: MS: m/z: 268 (M⁺), 253, 251, 250, 240, 239, 212, 156, 151, 123, 119 and 91 respectively, which confirms the structure of the new anthraquinone:



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LITHIATION OF AROMATIC ETHERS WITH ULTRASOUND: SOME SYNTHETIC APPLICATIONS

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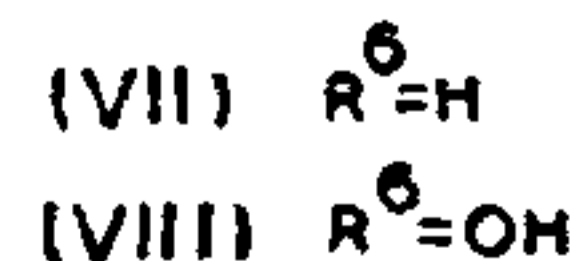
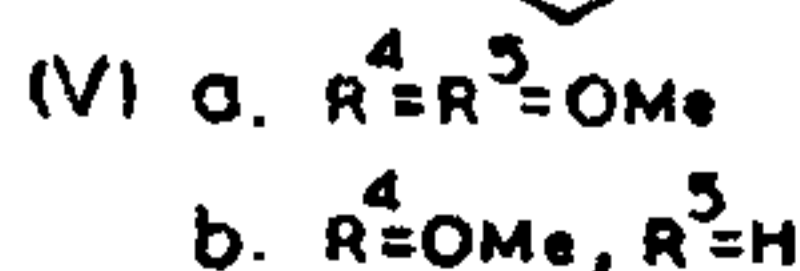
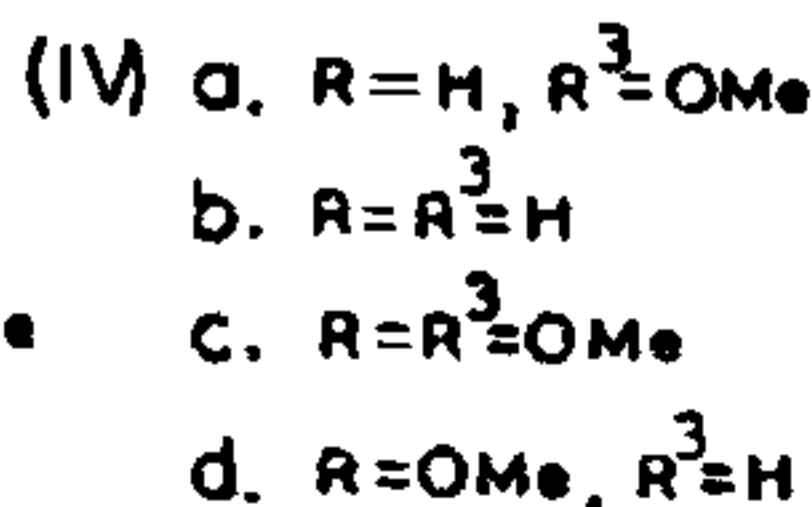
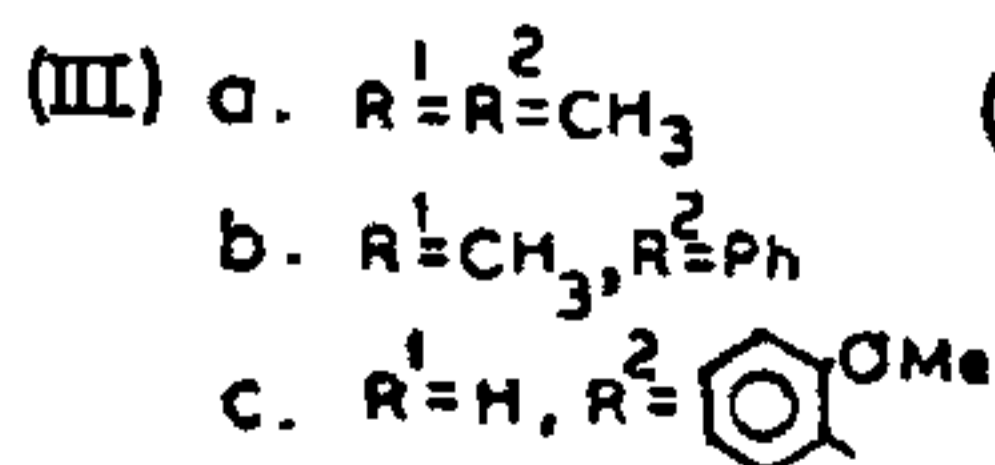
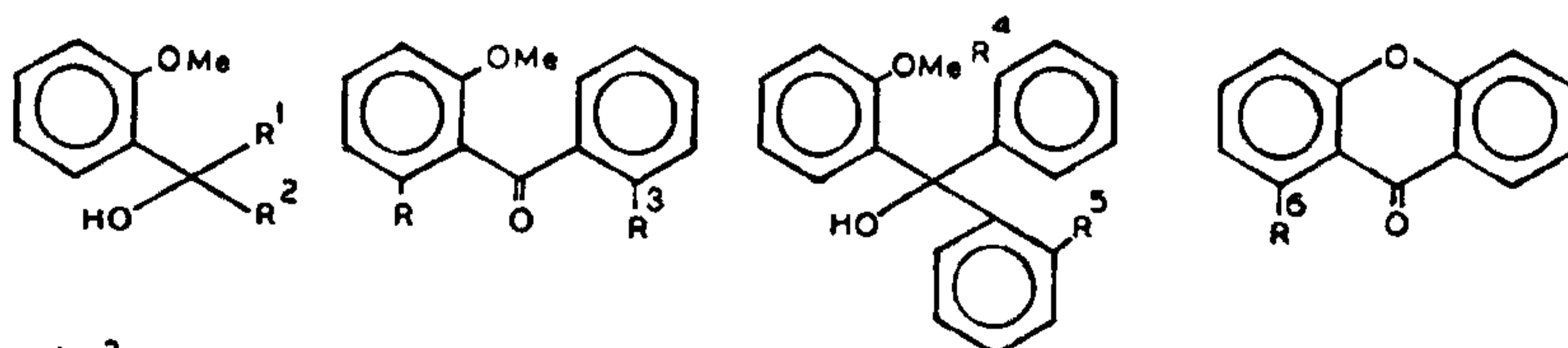
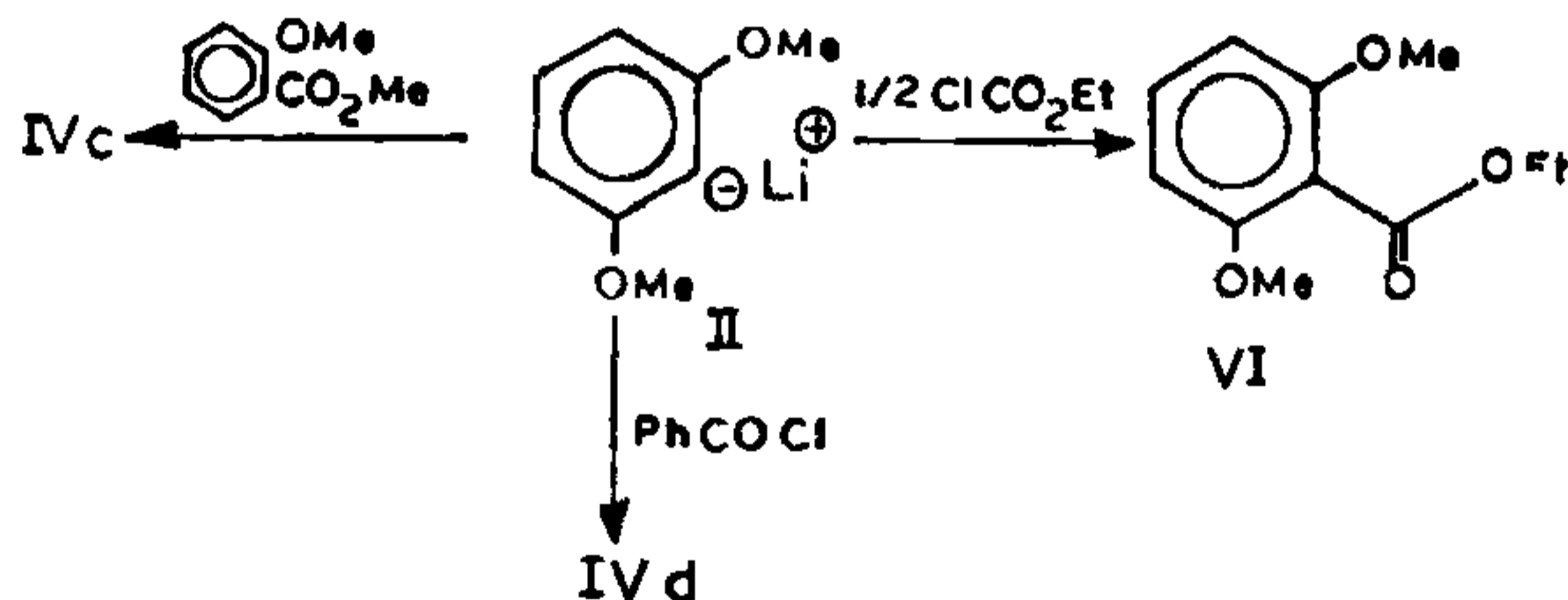
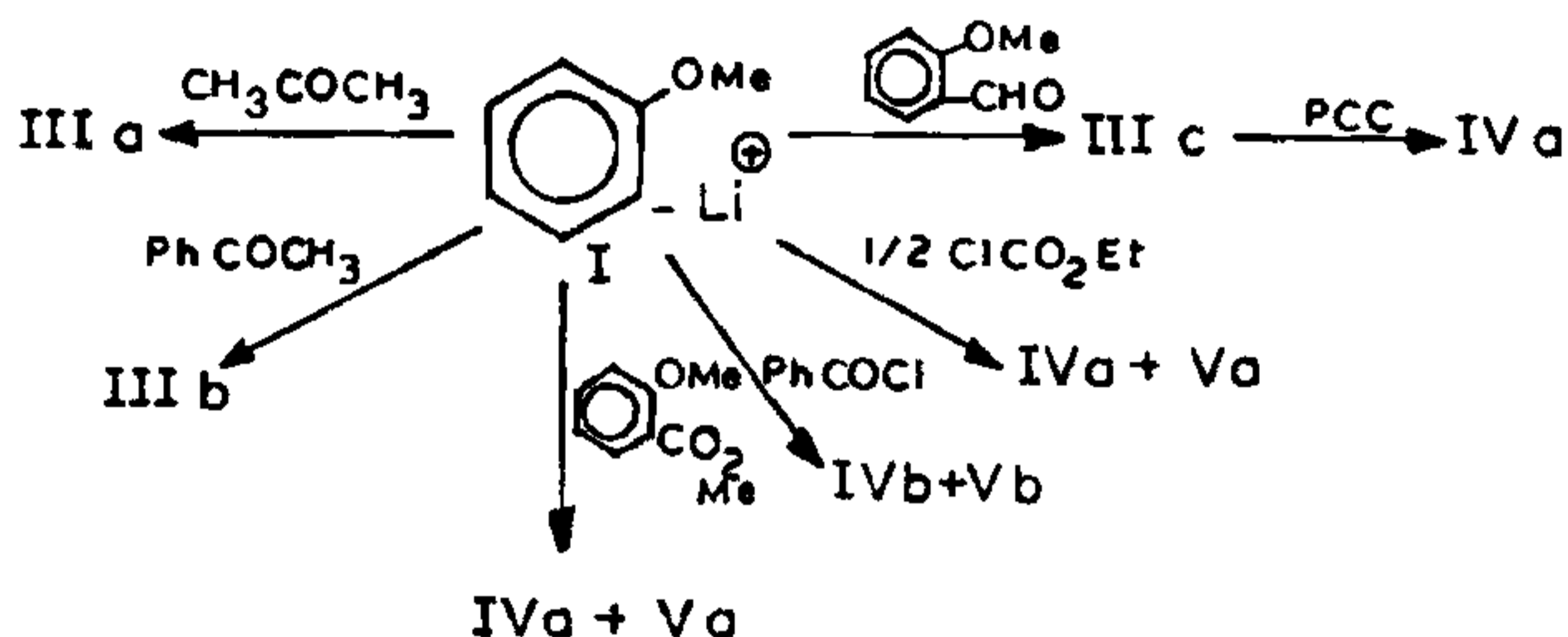
IN recent years dramatic effects of ultrasound on several chemical reactions have been reported¹. We have observed significant increase in the yields under ultrasonic irradiation in reactions of synthetic importance, such as *O*-alkylation of phenols, Reformatsky reaction, oxidative degradation, etc.² A recent communication³ on lithiation of different substrates using ultrasound prompts us to report

our results on the use of ultrasound in *ortho*-lithiation of alkyl aryl ethers.

Lithiation of alkyl aryl ethers is the key step in our programme on the synthesis of bioactive compounds. Effects of ultrasound irradiation on *o*-lithiation of anisole and 1,3-dimethoxybenzene are reported here. A mixture of lithium metal, butyl chloride and aromatic ether in tetrahydropyran at 20°C was irradiated with ultrasound under dry and inert atmosphere. Initiation of the reaction was indicated by the slow disappearance of lithium. The progress of the lithiation could be monitored by quenching aliquots with acetone and analysing the

products by thin layer chromatography. Under similar conditions but in the absence of ultrasound, no lithiation took place. Reactions of lithiated aromatic ethers with different electrophiles such as dialkyl and alkyl aryl ketones, acyl chlorides, alkyl chloroformate, aryl esters, aryl aldehydes, etc. have been studied and the products analysed in the usual way.

Anisole was lithiated in 30 min to 2-methoxyphenyllithium (I) at 20°C. Carbinol IIIa⁴ was obtained in 75% yield when acetone was added to I at -78°C. Similarly, good yields of carbinol IIIb⁵ were obtained using acetophenone. Reaction of I with



aromatic esters in 1:1 proportion gave mixtures of benzophenones and triarylmethanols (Va and Vb). Formation of V suggests that benzophenone formed in the first step reacts further with I to give carbinol. Thus, a mixture of IVa⁶ and Va⁷ was obtained when methyl *o*-methoxybenzoate was added to I at -78°C . Similarly reaction of I with benzoyl chloride gave benzophenone (IVb)⁸ and carbinol (Vb)⁹ in the ratio of 1:1. Formation of Va and Vb necessarily means that a part of the electrophile remains unreacted. In fact when a reaction was carried out with limited amount (0.5 equivalent) of ethyl chloroformate better yield of carbinol Va⁷ was obtained. The reaction of I with aryl aldehydes has also been studied and good yields of benzhydrols have been obtained. Using *o*-methoxybenzaldehyde, 2,2'-dimethoxybenzhydrol (IIIc)¹⁰ was prepared.

Lithiation of 1,3-dimethoxybenzene under ultrasonic irradiation was complete in 15 min. Reaction of II with 0.5 equivalent of ethyl chloroformate gave ethyl 2,6-dimethoxybenzoate (VI)¹¹ as the sole product. Thus, unlike with I, in the case of II the reaction does not proceed beyond the ester stage. Advantage has been taken of this for the synthesis of benzophenones. Good yields of benzophenones (IVc¹² and IVd¹³) were obtained when II was quenched with methyl 2-methoxybenzoate and benzoyl chloride. Absence of the formation of triarylcarbinol could be explained by the fact that in II the reactive centre is crowded by two adjacent methoxyl groups, which offer steric hindrance to subsequent reaction. 2,2'-Dialkoxybenzophenones are important intermediates because of their ready

conversion to xanthenes¹³. Benzhydrol (IIIc), which was obtained in excellent yield, could be oxidized to IVa by PCC¹⁴. Benzophenones (IVa and IVc) were converted into xanthenes (VII¹⁵ and VIII¹⁶) by heating with pyridine hydrochloride¹⁷. Thus this constitutes a convenient synthesis of xanthenes.

Table 1 gives a summary of the results of the use of lithiated compounds in synthesis.

Synthesis of 2,2'-dimethoxybenzophenone (IVa) and tris(o-methoxyphenyl) carbinol (Va); Typical procedure:

A mixture of anisole (0.54 g, 5 mmol), lithium (70 mg, 10 mg-atom) and *n*-butyl chloride (0.47 g, 5 mmol) in THP (10 ml) was sonicated in an ultrasonic cleaning bath (40 kHz) at 20°C under dry and inert atmosphere. When lithium had reacted as evidenced by the disappearance of lithium pieces, the flask was cooled to -78°C and methyl *o*-methoxybenzoate (0.83 g, 5 mmol) in 10 ml of THF was added slowly.

After completion of the reaction (30 min, monitored by TLC) the reaction mixture was diluted with ether, acidified with 1:1 HCl, extracted with ether and dried (Na_2SO_4). Removal of solvent gave a mixture of IVa and Va, which were separated by column chromatography (SiO_2). On successive elution of the column with petroleum ether-ethyl acetate mixtures (95:5 and 9:1) two fractions A and B were obtained. Colourless crystals (hexane) of IVa were isolated from fraction A; 300 mg, m.p. 103°C (lit. m.p. 104°C)⁶; DNP (+); IR (KBr): 1640, 1600, 1490 cm^{-1} ; 60 MHz

Table 1 Synthetic application of sonochemical lithiation

Compound lithiated	Conditions	Substrates	Product §	Yield (%)	Ref.	
Anisole	Li/ <i>n</i> -BuCl/THP 20°C , Sono, 0.5 h	Acetone	(IIIa)	(75)	4	
	"	Acetophenone	(IIIb)	(84)	5	
	"	Methyl <i>o</i> -methoxy benzoate	(IVa)+(Va)	(25) (37)	6 7	
	"	Benzoyl chloride	(IVb)+(Vb)	(33) (38)	8 9	
	"	1/2 ClCO_2 Et	(IVa)+(Va)	(19) (68)	6 7	
	"	"	<i>o</i> -Methoxy benzaldehyde	(IIIc)	(75)	10
	1,3-Dimethoxybenzene	Li/ <i>n</i> -BuCl/THP 20°C , Sono, 0.25 h	1/2 ClCO_2 Et	(VI)	(79)*	11
"		Methyl <i>o</i> -methoxy benzoate	(IVc)	(51)	12	
"		Benzoyl chloride	(IVd)	(55)	13	

§ Physical and chemical data of compounds were in complete agreement with those reported in the literature;

*Based on the substrate.

PMR (CCl_4): δ 3.63 (s, 6H, 2x-OMe), 6.73–7.57 (m, 8H, Ar-H). Similarly, Va was obtained as colourless crystals (hexane) from fraction B; 320 mg, m.p. 180°C (lit. m.p. 181°C)⁷; IR (KBr): 3500, 1600, 1580 cm^{-1} ; 60 MHz PMR (CDCl_3): δ 3.5 (s, 9H, 3x-OMe), 6.8–7.43 (m, 12H, Ar-H).

Cyclization of 2,2'-dimethoxybenzophenone (IVa) to xanthone (VII)

A mixture of IVa (50 mg) and pyridine hydrochloride in 1:5 proportion was heated in a dry flask in an oven at 180°C for 36 h. After cooling, water was added and the mixture extracted with ether and dried. Removal of ether gave crude product which on purification (prep. TLC) and crystallization from ethanol furnished colourless crystals of VII; 35 mg, m.p. 174°C (lit. m.p. 174°C)¹⁵. NMR and IR data are in agreement with those of xanthone.

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INDUCED SHY MUTANT OF LENTIL (*LENS CULINARIS* MED.)

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DURING induced mutation studies in lentil, various types of mutants with altered morphological characteristics were isolated. In the present communication a morphological mutant with changed leaflet shape and size and shy in flowering and pod bearing is reported.

Dry seeds of a lentil variety Sehore 74–7 were irradiated with 5, 10, 15 and 20 krad of γ -ray at the Gamma Cell Laboratory of Indian Agricultural Research Institute, New Delhi. The M_1 and later generations were grown at the College Farm, Dholi of the Rajendra Agricultural University. In M_2 generation from 10 krad treated population one dwarf mutant with narrow leaflets and slight longitudinal bending was isolated. This had less flowers and fruits. The mutant was therefore named 'shy mutant'. In M_3 it did not segregate indicating recessiveness of the character induced. Some M_3 mutant plants were crossed with the parent variety. F_1 was like parent and F_2 segregated in the ratio of 3 tall-like parent:1 dwarf-like mutant. The ratio confirmed that shyness is a monogenically controlled recessive character. M_3 mutant was separately evaluated for other characteristics.

Though the mutant plants were dwarf there were no significant differences in flowering and maturity days (table 1). Mutant plants were erect and non-bushy whereas the parent was semispreading and bushy. Rachis length, leaflets/leaf, leaflet length, leaflet breadth and stipule length of mutant plants were significantly lower than that of parent plants. Pod-bearing was significantly lower in the mutant compared to the parent. Seed weight and seed colour were almost the same as in the parent.