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DEHYDROGENATION STUDIES WITH TETRACHLORO-*o*-BENZOQUINONE

STRUCTURE OF A NOVEL DEHYDROGENATION-ADDITION PRODUCT OF ABIETIC ACID*

T. R. Kasturi, E. Raghavan, Sukh Dev† and D. K. Banerjee
Department of Organic Chemistry, Indian Institute of Science Bangalore, India

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Abstract—The structure of the solid adduct, obtained by treatment of methyl abietate with tetrachloro-*o*-benzoquinone in xylene has been shown to be 2-[2′,2′-(5′,6′,7′,8′-tetrachloro-benzo-1′,4′-dioxano)]-ethyl-3,4,4a(α),4b,5,6,7,8,8a(α),9-decahydro-4b(β),8(β)-dimethyl-8(α)-carbomethoxyphenanthrene (Ia).

Several methods are reported in literature for the conversion of abietic acid to dehydroabietic acid.[1–4] The recently developed methods utilize either chloranil[5] or N-lithioethylenediamine[6] as the dehydrogenating agent. As we failed to realize the reported yield and purity of dehydroabietic acid by the chloranil method,[5] the use of tetrachloro-*o*-benzoquinone, which is known to react very much faster than chloranil,[7] as a dehydrogenating agent for abietic acid has been studied.

Methyl abietate[8] (1 mole) on treatment with tetrachloro-*o*-benzoquinone (1 mole) in xylene gave a solid ester (Ia) in 41% yield, which on hydrolysis with 10% butanolic potassium hydroxide gave the corresponding acid (Ib). Diazomethane esterification of Ib gave back the original ester. The physical and spectral characteristics of Ia and Ib are given in Table 1.

The presence of chlorine and the UV band at 236 mμ, characteristic of abieta-diene system,[9] in Ia and Ib indicated that this could be an adduct; this view was confirmed by the mol. wt. of Ib. The absence of the isopropyl doublet[10] at 1380 and 1370 cm^{-1} in the IR spectra of Ia and Ib indicated modification of the isopropyl group.

Hydrogenation of Ia and Ib in presence of PtO_2 in acetic acid gave crystalline

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† Present address: National Chemical Laboratory, Poona-8, India.

[1] L. F. Fieser and W. P. Campbell, *J. Amer. Chem. Soc.* **60**, 2633 (1938).

[2] O. Jeger, O. Durst and O. Buchi, *Helv. Chim. Acta* **30**, 1853 (1947).

[3] G. Dupont, R. Dulou and U. Leon, *Bull. Soc. Chim. Fr.* **11**, 61 (1951).

[4] G. Dupont, R. Dulou, G. Ourisson and C. Thibault, *Bull. Soc. Chim. Fr.* **15**, 708 (1955).

[5] H. Kanno, *Nippon Kagaku* **81**, 1858 (1960); cf. *Chem. Abstr.* **56**, 7366 (1962).

[6] B. N. Joshi, R. Seshadri, K. K. Chakravarthi and S. C. Bhattacharya, *Tetrahedron* **20**, 2911 (1964). This publication appeared after the completion of our work.

[7] R. A. Raphael, E. C. Taylor and H. Wynberg, *Advances in Organic Chemistry Methods and Results* Vol. 2, p. 329. Interscience, N.Y. (1960).

[8] S. Palkin and T. H. Harris, *J. Amer. Chem. Soc.* **56**, 1936 (1964).

[9] C.N.R. Rao, *Chemical Applications of Ultraviolet and Visible Spectroscopy* p. 26. Butterworths, London (1961).

[10] C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy* p. 139. Academic Press, N.Y. (1963).

TABLE 1. PHYSICAL AND SPECTRAL CHARACTERISTICS OF THE ADDUCT

Ester (Ia)		Acid (Ib)
132–136°	m.p.	245°
C,H,O and Cl	elements	C,H,O and Cl
—	mol. wt.	m/e 544 (Cl^{35})
236 mμ (ε 35,810)	EtOH	236 mμ (ε 39,630)
302 mμ (ε 2,877)	λ_{max}	302 mμ (ε 3,255)
	IR (Nujol)	
1718 (s) ester carbonyl		1698 (s) acid carbonyl
1640 (w)	conjugated	1640 (w)
1600 (w)	double-bond	1600 (w)
1550 (M)	aromatic double-bond	1548 (m)
1420 (s)	assignment in sequel	1420 (s)
1048 (v.s.)	vinyl ether of the type =C—O—C	1050 (v.s.)
805 (s)	tri-substituted double-bond	806 (s)

tetrahydro derivatives, IIa and IIb, respectively. Mol. wt. of IIb by mass spectral analysis (m/c at 548 based on Cl^{35}) corresponded to $C_{28}H_{32}O_4Cl_4$.

The NMR spectra of Ia and Ib (Fig. 1) show the absence of an isopropyl group but three distinct three proton singlets of nearly equal half-width indicating the presence of three methyl groups in different environments. The signal at 48·5 c/s is attributed to the C_{4b} angular methyl protons and the one at 74 c/s to the C_8 axial methyl protons; the signal at 87·5 c/s could be due to a methyl group attached either to an olefinic carbon[11] or to a carbon carrying an electronegative oxygen. More

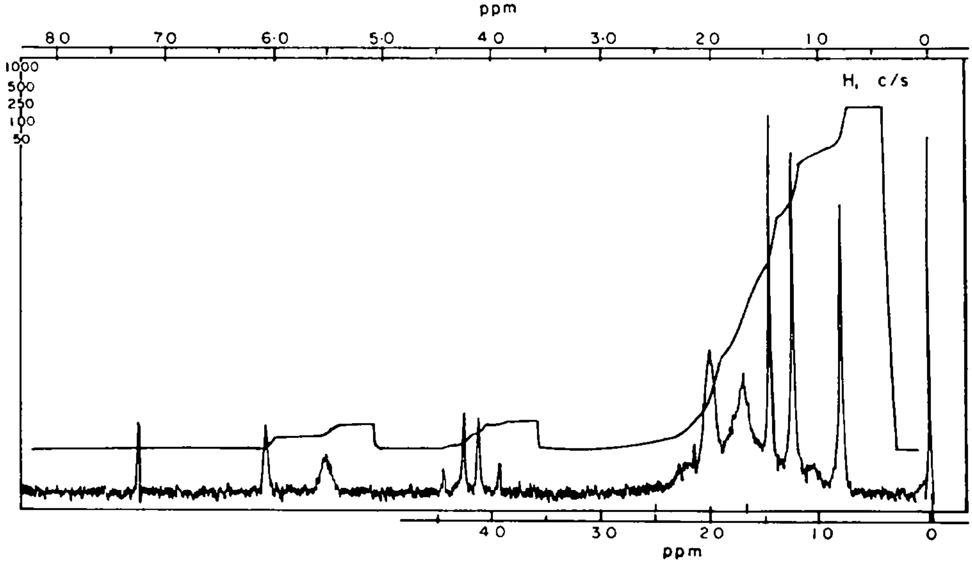

FIG. 1. NMR spectrum of Ib.

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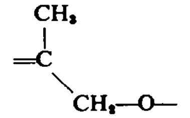
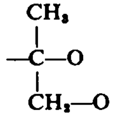
[11] Even though this value is somewhat lower than the normal value for such methyl resonances, cases are known of similar assignments. cf. R. L. Rowland, A. Rodgman, J. N. Schumacker, D. L. Roberts, L. C. Cook and W. E. Walker, *J. Org. Chem.* **29**, 16 (1964).

interesting is the appearance of an AB quartet centred at 259 c/s (J_{AB} = 11·5 c/s) which is indicative of an oxymethylene moiety of the type *a* or *b*. However, a closer



a



b

examination of the NMR spectrum revealed that all methyl signals are equally narrow. The vinylic methyl group in the moiety *a* should give rise to a broader resonance.[12,13]

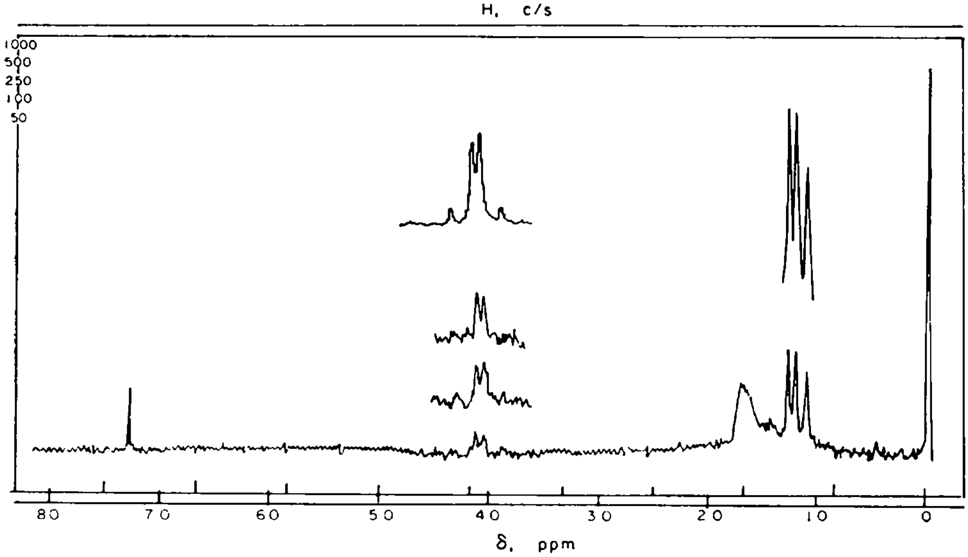


FIG. 2. NMR spectrum of IIb.

Further, the appearance of a well resolved quartet for the magnetically non-equivalent methylene protons leaves little doubt that the methylene group is attached to an asymmetric centre[14] as in the moiety *b*. Hence, the presence of moiety *a* was ruled out. There are two signals in the vinyl proton region, a broad multiplet at 332·5 c/s (IH; W_H = 6·2 c/s) and a singlet at 365 c/s (IH; W_H = 3–3·2 c/s). It is well known[15] that hydrogen bonding causes a large paramagnetic shift of phenolic proton resonance. As the monomethyl ether of tetrachlorocatechol showed a phenolic proton resonance at 365·6 c/s, the possibility of the signal at 365 c/s in Ib arising from a similar proton could not be ruled out. However, the persistence of these two signals in Ib even after exchange with D_2O and their disappearance in the tetrahydro derivative (IIb; Fig. 2) disproved the presence of a phenolic proton. The absence of the UV max at 236 mμ in the tetrahydro derivatives and the fact that the UV max at 302 mμ in Ia

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[12] S. Sternhell and J. T. Pinhey, *Tetrahedron Letters* 275 (1963).

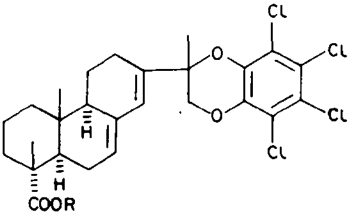
[13] S. Sternhell, *Rev. Pure and Appl. Chem.* **14**, 15 (1964).

[14] E. J. Snyder, *J. Amer. Chem. Soc.* **85**, 2624 (1963).

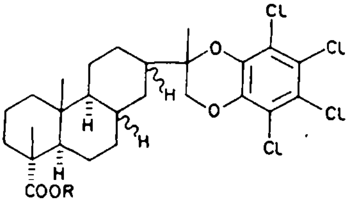
[15] L. M. Jackman, *Applications of NMR Spectroscopy in Organic Chemistry* p. 66. Pergamon Press, London (1959).

does not show any bathochromic shift in alkaline solution characteristic of phenols also corroborated this view. Hence, the two signals must arise from vinyl protons only.

Treatment of Ia or IIa with reagents like HCl–HoAc, LAH in presence of $NiCl_2$ or $AlCl_3$ in xylene, resulted in the formation of tetrachlorocatechol and neutral products[16] in each case. The proposed structure I and II for the adduct and its tetrahydro derivative[17] respectively explain all the UV, IR, NMR and mass spectral characteristics. The UV max at 302 $m\mu$ in Ia, Ib, IIa and IIb may be assigned to the benzo-1,4-dioxan system.[18] The strong band at 1420 cm^{-1} in the IR spectra of all these compounds is obviously due to the C—O stretching of the benzo-1,4-dioxan system.[19] The narrow vinylic proton signal at 365 c/s ($\omega_H = 3$–$3{\cdot}2$ c/s) may be assigned to that on C_1 which would experience only allylic coupling.



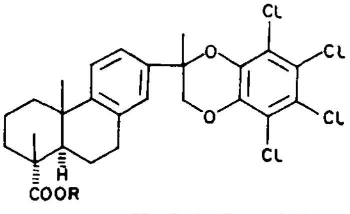
Ia, R = CH_3
Ib, R = H



IIa, R = CH_3
IIb, R = H

The NMR spectrum of the tetrahydro acid (IIb; Fig. 2) which shows signals at 67·5 (3H, singlet), 73·5 (3H, singlet), 77·5 (3H, singlet) and 245 c/s (2H, quartet $J_{AB} = 12$ c/s) also confirms the above structures. The down field shift of the C_{4b} angular methyl signal on hydrogenation is probably due to the removal of long range shielding by the Δ^{10}-double bond, conforming to the observations of Schoolery and Rogers[20] that the C_{10} methyl protons in Δ^7-steroids exhibit a diamagnetic shift of 0·1 ppm. The up field shift of the signal from the methyl protons on the benzo-1,4-dioxan moiety in IIb may likely be due to some deshielding factors in Ib being removed on hydrogenation.

The structure Ia was further proved by its conversion to a dehydroabietic acid derivative (IIIa) with chloranil in xylene followed by hydrolysis of the resulting product with butanolic potassium hydroxide. The NMR spectrum of IIIb showed aromatic proton centred at 428 c/s.



IIIa, R = H; IIIb, R = CH_3

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[16] The identification of the neutral products in each case is in progress.

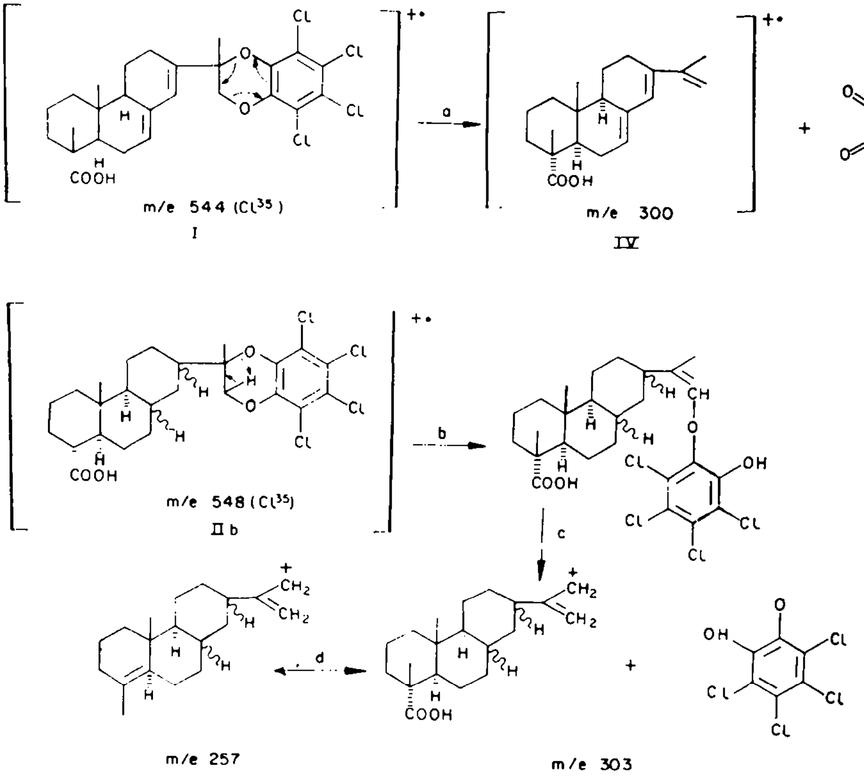
[17] We are grateful to Dr. J. S. Shannon, Division of Coal Research, Council of Scientific & Industrial Research Organization, Chatswood, Australia, in helping us to arrive at this structure by studying the mass spectra of Ib and IIb.

[18] L. Horner and M. Merz, *Liebigs Ann.* **570**, 89 (1950).

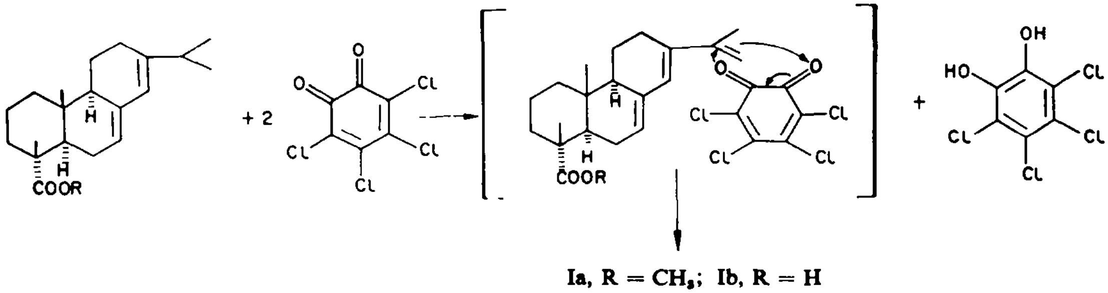
[19] (The late) E. A. Braude, L. M. Jackman, R. P. Linstead and G. Lowe, *J. Chem. Soc.* 3123 (1960).

[20] J. N. Schoolery and M. T. Rogers, *J. Amer. Chem. Soc.* **80**, 5121 (1958).

The mass spectral data[17] for Ib and IIb lend additional support to the above structures. The possible ion reactions[17] are indicated in Chart I. Reaction *c* is accompanied by hydrogen atom transfer. It is not very clear why reaction *d* should occur in IIb and not in Ib. The difference between reactions *a* and *b* may be due to the formation of the stable conjugated triene radical ion (IV) from Ib which is not possible from IIb.



The formation of I from abietic acid and tetrachloro-*o*-benzoquinone can be rationalized by a dehydrogenation-addition sequence. When two moles of tetrachloro-*o*-benzoquinone were used for one mole of methyl abietate, as expected,[21] the yield of the adduct was almost doubled (79·5%).



Ia, R = CH_3; Ib, R = H

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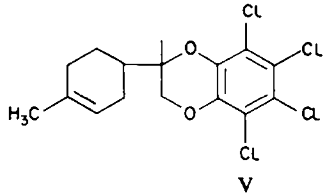
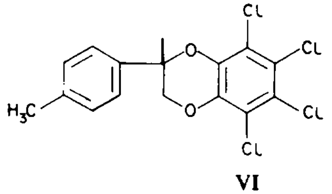
[21] We are thankful to Dr. S. K. Balasubramanian of our department for helpful discussions.

With a view to studying the addition of *o*-quinone to an isopropenyl group, the above reaction was studied with limonene, when a crystalline solid showing a UV max at 301 mμ and a strong IR band at 1420 cm^{-1} was obtained. The NMR spectrum of this compound showed no vinyl proton signal as expected for structure V, but an A_2B_2 pattern of aromatic protons centred at 435 c/s. A quartet appears at 260 c/s (J_{AB} = 12 c/s) for the oxymethylene group. There are two 3-proton signals, one at 140 c/s (aromatic CH_3) and the other at 99 c/s [—$C(CH_3)$—O]. Hence this adduct has been assigned the structure VI. *p*-Cymene on treatment with tetrachloro-*o*-benzoquinone gave the same adduct confirming its structure. Some α,*p*-dimethylstyrene was also obtained in both the reactions.


V


VI

EXPERIMENTAL[22]

Treatment of methyl abietate with tetrachloro-o-benzoquinone

(a) *Using equimolar quantities of quinone and methyl abietate.* A solution of methyl abietate[8] (10·8 g) in dry xylene (75 ml) was refluxed with tetrachloro-*o*-benzoquinone (8·51 g) for 2 hr. Xylene was removed *in vacuo*, the residue in ether (400 ml) was extracted with 50 ml portions of 1% NaOHaq (300 ml). The ether layer was washed with water and the solvent evaporated to give a residue (16·56 g), which was chromatographed on alumina (100 g). Elution with 1:1 pet. ether–benzene (200 ml) gave a lemon-yellow residue (14·1 g) which was repeatedly crystallized from acetone–MeOH to give Ia (7·9 g; 41%), m.p. 132–136° (Found: C, 58·30; H, 5·37. $C_{27}H_{30}O_4Cl_4$ requires: C, 57·86; H, 5·36%.) The NMR spectrum (CCl_4) showed signals at 49 (3H), 73 (3H), 88 (3H), 216·5 (3H), 248 (2H), 331 (1H) and 362 c/s (1H).

Acidification of the alkali extract followed by ether extraction gave a residue (4·53 g) which was crystallized from aqueous alcohol to give tetrachlorocatechol, m.p. 193–194° (Lit.[7] m.p. 194°).

(b) *Using 2 moles of quinone for 1 mole of methyl abietate.* The above experiment was repeated with methyl abietate (3·3 g) and tetrachloro-*o*-benzoquinone (5·2 g) when the adduct Ia (4·5 g, 79·5%), m.p. 132–136°, and tetrachlorocatechol (2·72 g) were obtained.

Hydrolysis of the adduct (Ia)

A mixture of Ia (2·5 g) and 10% butanolic KOH[23] (25 ml) was refluxed for 5 hr at 130–135° (bath temp). Butanol was removed *in vacuo*, the residue dissolved in water and acidified with conc. HCl. The liberated acid was extracted with ether and the ether solution washed several times with 1% NaOHaq (150 ml). The alkali extract was acidified with ice-cold HCl (1:1) and extracted with ether. Removal of the solvent and crystallization of the residue from acetone–MeOH yielded Ib (1·5 g, 61·5%), m.p. 245°. (Found: C, 56·85; H, 5·15. $C_{26}H_{28}O_4Cl_4$ requires: C, 57·14; H, 5·13%.)

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[22] All m.ps are uncorrected. UV spectra were determined in 95% EtOH using a Beckmann DU Model spectrophotometer. IR spectra were taken with a Perkin–Elmer Infracord, Model 137B. All NMR spectra were measured in $CDCl_3$ solutions (unless otherwise stated) on Varian A-60 instrument. The signals are recorded in c/s from tetramethylselane as zero (internal standard). Pet. ether, b.p. 40–60°, has only been used. Alumina refers to activated Brockman variety. Microanalyses were acrried out by Mr. B. R. Seetharamia of this department and the Ciba Research, India.

[23] U. R. Ghatak, D. K. Datta and S. Ray, *J. Amer. Chem. Soc.* **82**, 1731 (1960).

Hydrogenation of Ia *and* Ib

A solution of Ib (1·02 g) in acetic acid (AR 75 ml) was stirred with pre-reduced PtO_2 catalyst[24] (100 mg) till H_2 (2 moles) uptake was complete. The catalyst was filtered and the solvent removed from the filtrate to give a crystalline material (1·05 g) which was repeatedly crystallized from aqueous MeOH to give IIb, m.p. 145–155°. (Found: C, 56·27; H, 5·89. $C_{26}H_{32}O_4Cl_4$ requires: C, 56·72; H, 5·82%.) UV λ_{max} 302 mμ (ϵ, 2240). IR (Nujol) Peaks at 3580 (broad), 1695, 1558, 1420 and 1053 cm^{-1}.

Similarly Ia (0·2 g) was hydrogenated using PtO_2 catalyst (25 mg) in acetic acid (AR 30 ml) to give IIa, m.p. 75–85°*. (Found: C, 57·22; H, 5·83. $C_{27}H_{34}O_4Cl_4$ requires: C, 57·4; H, 5·92%.) UV λ_{max} 302 mμ (ϵ, 2487). IR (Nujol) peaks at 1740, 1560 and 1420 and 1042 cm^{-1}.

*Cleavage of the tetrachlorobenzo-*1,4*-dioxan moiety in* Ia

a. A mixture of Ia (2 g), acetic acid (65 ml) and conc. HCl (30 ml) was refluxed for 10 hr at 120–130° (bath temp). Most of the acetic acid was removed *in vacuo*, the residue dissolved in ether, washed several times with water to remove the last traces of acetic acid present and then extracted with 5% NaOHaq (100 ml). The ether solution was washed with water and the solvent evaporated to give a gummy residue (1·11 g).

The alkali solution was acidified and extracted with ether. The residue, obtained after removal of the solvent, was purified by short path distillation at 140–150° (2 mm), followed by repeated crystallizations from aqueous EtOH to give tetrachlorocatechol, m.p. 193–194°. The m.p. remained undepressed on admixture with an authentic sample of the same and the IR spectra of the two were superimposable.

b. To a mixture of Ia (1·12 g) and $NiCl_2$ (0·04 g) in absolute tetrahydrofuran (10 ml) was added with stirring a solution of LAH (0·23 g) in tetrahydrofuran (10 ml) at the reflux temp.[25] The reaction mixture was refluxed for 24 hr, the excess LAH was decomposed with moist ether and acidified with 10% HCl (10 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined ether extract was worked up as before to yield a neutral product (0·93 g) and tetrachlorocatechol (0·2 g).

c. A mixture of Ia (1·12 g) in xylene (30 ml) and anhydrous $AlCl_3$ (0·34 g) was refluxed for 5 hr at 145–150° (bath temp). Xylene was removed *in vacuo*, the residue decomposed with conc. HCl and extracted with ether. The ether extract yielded a neutral material (0·85 g) and tetrachlorocatechol (0·56 g).

Dehydrogenation of Ia *with chloranil*

A solution of Ia (1·12 g) in xylene (25 ml) was refluxed with chloranil (0·54 g) for 32 hr. The xylene was removed *in vacuo* and the residue was dissolved in ether and washed with 2% NaOHaq (100 ml) followed by water. The solvent was removed to give a gummy material (1·28 g) which was chromatographed over alumina (50 g). Elution with 1:1 pet. ether–benzene (250 ml) gave a crystalline solid (1·05 g) which was hydrolysed by refluxing with 10% butanolic KOH (10 ml) for 5 hr to give IIIa, which could be crystallized from acetone–MeOH (0·51 g, 50%), m.p. 249–250°. (Found: C, 57·52; H, 4·99. $C_{26}H_{26}O_4Cl_4$ requires: C, 57·36; H, 4·78%.) UV λ_{max} 291 mμ (ϵ 4301), 301 mμ (ϵ 4871); IR (Nujol): Peaks at 1695 (acid carbonyl) 1558, 1425, and 1044 cm^{-1}.

Esterification of IIIa with diazomethane in ether solution gave IIIb, which was purified by crystallization from acetone–pet. ether, m.p. 130–134°. (Found: C, 58·35; H, 5·00. $C_{27}H_{28}O_4Cl_4$ requires: C, 58·06; H, 5·02%.) UV λ_{max} 291 mμ (ϵ 4167); 301 mμ (ϵ 4547); IR (Nujol): Peak at 1721 (ester carbonyl) 1558 (aromatic C=C) 1425 and 1044 cm^{-1}.

Monomethylation of tetrachlorocatechol

A solution of KOH (0·8 g) in water (2 ml) was added to a mixture of tetrachlorocatechol (4·96 g) and $(CH_3)_2SO_4$ (2·4 ml) with occasional swirling. An equal quantity of KOH solution was gradually introduced after 1 hr and the mixture then heated on the steam bath for 4 hr. The cooled mixture was acidified and extracted with benzene. The benzene extract was washed with water and extracted

* Mixture of isomers.

[24] *Organic Synthesis*, Coll. Vol. I, p. 463. J. Wiley, N.Y. (1941).

[25] V. L. Tweedie and M. Cuscurida, *J. Amer. Chem. Soc.* **79**, 5463 (1957).

thrice with 2% NaOHaq. The alkaline solution was acidified, extracted with benzene and the benzene extract washed with water. The solvent was removed and the residue crystallized from aqueous EtOH to give the monomethyl ether of tetrachlorocatechol,[16] m.p. 123–125°, the homogeneity of which was confirmed by TLC. (Found: C, 32·58; H, 1·59. Calc. for $C_7H_4O_2Cl_4$: C, 32·21; H, 1·52%.) UV λ_{max} 299 mμ (ε 2001); $\lambda_{max}^{EtOH(alkaline)}$ 316 mμ (ε 5790); IR (Nujol) peaks at 3500 (OH), 1550 (aromatic C=C) and 1020 cm^{-1} (=C—O—C); NMR signals at 238·7 (3H) and 365·6 c/s (1 H).

Treatment of limonene with tetrachloro-o-benzoquinone

A solution of freshly distilled limonene (2·85 g) in dry xylene (30 ml) was refluxed with tetrachloro-*o*-benzoquinone (5·22 g) for 7 hr and worked up as before (preparation of Ia) to give a neutral product (2·92 g) which was chromatographed over alumina (70 g). Elution with pet. ether (200 ml) gave an oil (0·7 g) which was shown to be α,*p*-dimethylstyrene[17] by UV λ_{max} 248 mμ (ε 8,710), and IR (smear) 1639, 1623 (doublet $>C=CH_2$), 1506 (aromatic C=C), 885 (out of plane bend $=CH_2$) and 823 cm^{-1} (out of plane bend of aromatic protons). Further elution with 4:1 pet. ether–benzene (500 ml) gave a viscous gum (0·66 g), which on crystallization from MeOH–ethyl acetate gave VI, m.p. 136–138°. (Found: C, 51·00; H, 3·18. $C_{16}H_{12}O_2Cl_4$ requires: C, 50·79; H, 3·16%.) UV λ_{max} 301 mμ (ε 2512); IR (Nujol) 1550, 1515, 1425 and 1053 cm^{-1}.

Dehydrogenation of p-*cymene using tetrachloro-o-benzoquinone*

A solution of *p*-cymene (2·01 g) in xylene (30 ml) was refluxed with tetrachloro-*o*-benzoquinone (4·42 g) for 2 hr yielding a neutral product (3·48 g). Chromatography of this product over alumina (75 g) and elution with pet. ether (50 ml) gave an oil (0·49 g) consisting mostly *p*-cymene. Further elution with pet. ether (50 ml) gave α,*p*-dimethylstyrene (1·22 g) containing traces of *p*-cymene (from VPC and refractive index measurements). Elution with 4:1 pet. ether–benzene (200 ml) gave a viscous gum (0·53 g), which was crystallized from MeOH–ethyl acetate to give VI, m.p. 136–138°. A mixture m.p. of this with the compound obtained from limonene dehydrogenation was the same.

Acknowledgments—We are grateful to Dr. T. R. Govindachari, Ciba Research, India, Dr. S. Sternhell, University of Sydney, Sydney, Australia, Dr. M. Nagabhushanam, Oklahoma State University, Stillwater and Mr. B. L. Mylari, Indiana University, Bloomington, for their help in taking the NMR spectra reported here. We are particularly thankful to Dr. S. Sternhell for valuable discussions on some of the NMR spectra.

One of us [E. R.] thanks the Council of Scientific & Industrial Research, India, for the award of a Junior Research Fellowship.

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[16] Bruggeman, *J. Prakt. Chem.* **53**, 251 (1896) records a m.p. 185–186° for the same compound prepared by an alternate method. This could be a polymorph of the same.

[17] J. J. Loovi and A. R. Cover, *J. Food and Sci.* **29**, 576 (1964).