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A Facile Oxidation of 1-Naphthols to 1, 4-Naphthaquinones Using Active Manganese Dioxide

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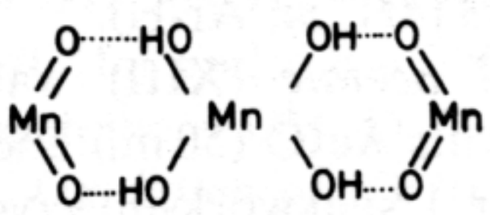
Selective oxidation of 3, 5-disubstituted 1-naphthols to the corresponding *p*-quinones is achieved using active MnO_2. A facile synthesis of juglone(III) by the oxidation of 1, 5-dihydroxynaphthalene by active MnO_2 is also reported. It is observed that very good yields of 1, 4-quinones are obtained when the starting phenols are 3, 5-disubstituted.

The oxidation phenols with active MnO_2(I), is shown to proceed through a radical mechanism resulting in the formation of dimers and polymers[1]. As manganese dioxide is known to contain highly labile hydroxy radicals[1], we investigated the oxidation of 1-naphthols with this oxidant to explore the possibility of the mesomeric naphthoxy radical undergoing initial hydroxylation followed by oxidation to give quinones.

Thus, 1, 5-dihydroxynaphthalene (II) when oxidised with I (prepared by Attenburrow's method[2]) in benzene indeed gave juglone (III, 5-hydroxy-1, 4-naphthaquinone) in 60% yield. In order to understand the possible mechanism and ascertain the generality of this reaction, some substituted 1-naphthols (XIV-XVI, XVIII) were synthesised (Scheme 1) and their reactions with active MnO_2 were investigated. The results of oxidation are presented in Table 1.

It is evident from Table 1 that MnO_2 oxidation gave very good yields of 1, 4-quinones only when the starting naphthols are 3, 5-disubstituted. Extensive polymerisation was observed in the oxidation of 1-naphthol, 5-methoxy-1-naphthol and 3-methyl-1-naphthol (XVI). However, under controlled conditions, 4, 4′- and 4, 2′-binaphthols could be obtained in low yields in the oxidation of 1-naphthol. These results can be explained by the radical mechanism. The unsubstituted naphthoxy radicals can undergo dimerisation and/or polymerisation to give binaph-



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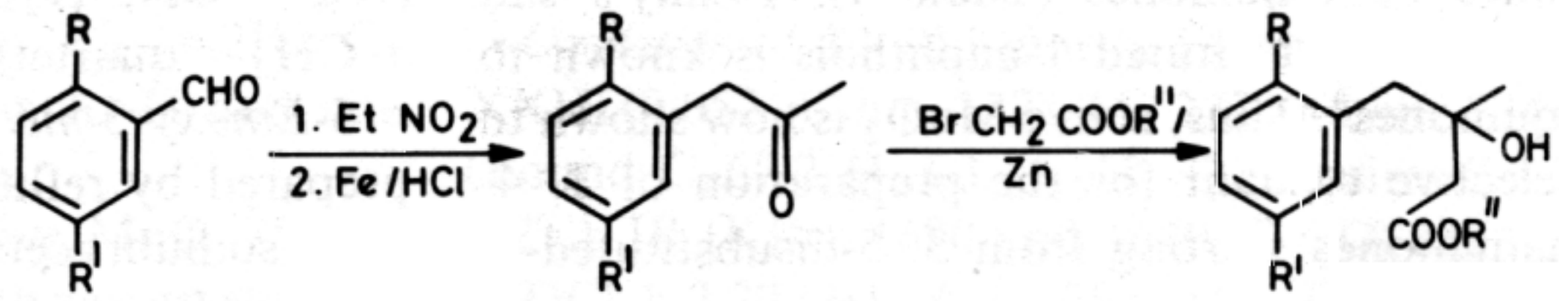
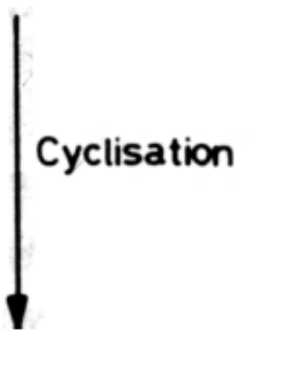
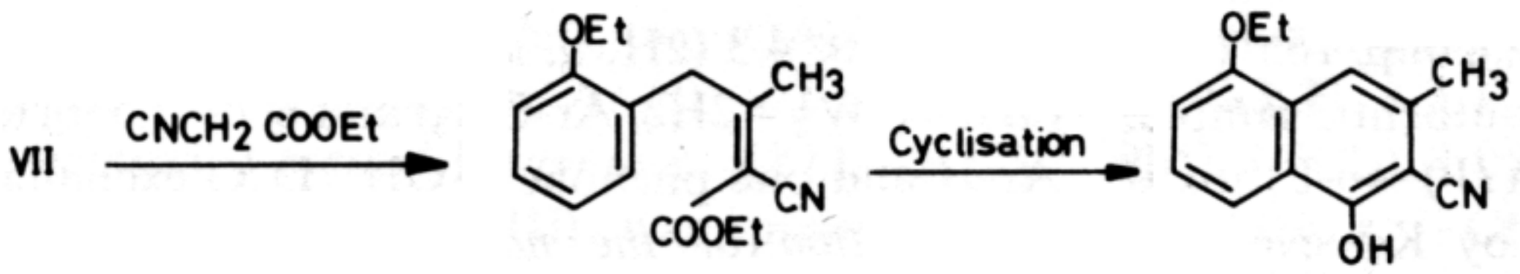


IV, R=OEt, R'=H
V, R=R'=OCH3
VI, R=R'=H

VII, R=OEt, R'=H
VIII, R=R'=OCH3
IX, R=R'=H

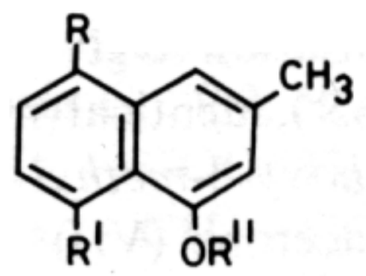
X, R=OEt, R'=H, R''=CH3
XI, R=R'=OCH3, R''=Et
XII, R=R'=H, R''=Et





XVII

XVIII



XIII, R=OEt, R'=H, R''=AC
XIV, R=OEt, R'=R''=H
XV, R=R=OCH3, R''=H
XVI, R=R'=R''=H

Scheme 1

†Paper dedicated to Dr G S Sidhu on his 60th Birthday

Table 1—Oxidation of 1-Naphthols by Active Manganese Dioxide and Fremy's Salt

Substrate	Product of oxidation by MnO_2	Yield %	Product of oxidation by Fremy's salt	Yield* %
II	III	60	III[6]	(49)[6]
			5-Hydroxy-1, 2-naphthaquinone[6]	(51)[6]
XIV	5-Ethoxy-3-methyl-1, 4-naphthaquinone (XIX)	90	5-Ethoxy-3-methyl-1, 2-naphthaquinone (XX)	60
XVIII	2-Cyano-5-ethoxy-3-methyl-1, 4-naphthaquinone (XXI)	91	No Reaction	Nil
XV	5, 8-Dimethoxy-2-methyl-1, 4-naphthaquinone (XXII)	80	5, 8-Dimethoxy-3-methyl-1, 2-naphthaquinone (XXIII)	51
1-Naphthol	4, 2′-Binaphthol	15	1, 4-Naphthaquinone[6]	(91)[6]
	4, 4′-Binaphthol	15		
XVI	Polymerised	Nil		
5-Methoxy-1-naphthol	Polymerised	Nil	5-Methoxy-1, 2-naphthaquinone[3]	(91.6)[3]

* Yields reported within parantheses are from literature.

thols and/or polymeric material. As 3, 5-disubstitution of 1-naphthol increases steric crowding for the dimerisation reaction, the mesomeric radical is, presumably, hydroxylated by the labile hydroxyl released from I. The selective hydroxylation at *para*-position to give 1, 4-naphthaquinones, as end products, can be understood from the stability of the *para* radicals in the naphthalene moiety. Formation of III from II, even in the absence of steric crowding, may be due to the hydrogen bonding of I with the C_5-hydroxyl, followed by hydroxylation at C_4-position.

While MnO_2 oxidation gave selectively *p*-quinones, Fremy's salt oxidation gave either a mixture of *o*- and *p*-quinones or *o*-quinones (Table 1). Fremy's salt oxidation of 5-substituted 1-naphthols is known to give *o*-quinones[3]. Thus, active MnO_2 is now shown to be a selective oxidant for the preparation of 1, 4-naphthaquinones starting from 3, 5-disubstituted-1-naphthols.

Experimental Procedure

All the m.ps are uncorrected, PMR spectra were recorded using TMS as external standard on a Varian A-60/A instrument, IR spectra on a Perkin Elmer-221 spectrophotometer and the mass spectra on a Hitachi RMU 6L. Chemical shifts are given in δ-scale.

Juglone (*III*)—1, 5-Dihydroxynaphthalene (0.16 g) in benzene (10 ml) was stirred with active MnO_2 (0.5 g) for 1 hr. MnO_2 was filtered off, washed with hot benzene and the dark yellow filtrate was evaporated to crystallisation to give III (0.102 g, 60%), m.p. 165° (lit.[4] m.p. 165°), identical (m.m.p) with an authentic sample.

5-*Ethoxy*-3-*methyl*-1-*naphthol* (*XIV*)—*o*-Ethoxyphenylacetone (VII) was prepared by Knoevenagel reaction[5] of *o*-ethoxybenzaldehyde (IV, 68 g) with nitroethane (45 g), in the presence of *n*-butylamine in toluene, followed by reduction with iron (100 g) and HCl (180 ml). The product was passed over a silica gel column in benzene to give VII (30 g); PMR (CCl_4): 1.25 (3H, *t*, $J=7$Hz, $-CH_3$ of $-OEt$), 4.0 (2H, *q*, $J=7$Hz, $-CH_2-$ of $-OEt$), 1.9 (3H, *s*, $-CH_3$), 3.5 (2H, *s*, $-CH_2-$) and 6.6-7.08 (4H, *bm*, Ar-H).

Reformatsky ester (*X*) was prepared by reacting VII (5g) with methyl bromoacetate (5 g) and zinc (2 g). It was purified by chromatography over a silica gel column using benzene as an eluent, yield 7 g (Found: C, 66.5; H, 7.8. $C_{14}H_{20}O_4$ requires C, 66.6; H, 8.0); PMR (CCl_4): 1.2 (3H, *t*, $J=7$ Hz, $-CH_3$ of $-OEt$), 4.0 (2H, *q*, $J=7$Hz, $-CH_2-$ of $-OEt$), 3.6 (3H, *s*, $-COOCH_3$), 1.18 (3H, *s*, tertiary $-CH_3$), 2.98 (2H, *bs*, $-CH_2$-ph), 2.38 (2H, *s*, $-CH_2-COOCH_3$), 4.0 (1H, $-OH$, D_2O exchangeable, merged with the $-CH_2-$ quartet) and 6.76–7.3 (4H, *m*, Ar-H).

5-*Ethoxy*-3-*methyl*-1-*naphthol acetate* (XIII) was prepared by refluxing X (5g) with Ac_2O (50 ml) and fused sodium acetate (5g) for 4 hr. Usual work-up gave a low melting solid which was purified over a silica gel column in benzene and crystallised from methanol (3.4 g), m.p. 92°; PMR (CCl_4): 1.4 (3H, *t*, $J=7$Hz, $-CH_3$ of $-OEt$), 4.1 (2H, *q*, $J=7$Hz, $-CH_2-$ of $-OEt$), 2.3 (3H, *s*, $-OAc$), 2.5 (3H, *bs*, $W_{\frac{1}{2}}=1.5$ Hz, Ar-CH_3), 8.0 (1H, *q*, $J=1.5$ Hz, C_4-H) and 6.8-7.4 (4H, *m*, Ar-H).

Alkaline hydrolysis of XIII (5 g) gave the naphthol (XIV) which was crystallized from pet. ether (3.2g), m.p. 121-22°, M^+202 (Found: C, 77.3; H, 7.0. $C_{13}H_{14}O_2$ requires C, 77.2; H, 7.0%); IR (KBr): 3340 (OH) cm^{-1}; PMR ($CDCl_3$); 1.5 (3H, *t*, $J=7$Hz, $-CH_3$ of $-OEt$), 4.3 (2H, *q*, $J=7$Hz, $-CH_2$-of-OEt), 2.48 (3H, *bs*, $W_{\frac{1}{2}}=2$Hz, Ar-CH_3) and 6.7–7.5 (6H, *m*, five Ar-H and one phenolic $-OH'$, D_2O exchangeable).

Oxidation of the naphthol (*XIV*)—*XIV* (1g) was oxidised with active MnO_2 (5g) by stirring its suspension in benzene (10 ml) for 30 min. MnO_2 was filtered off, washed with hot benzene, the filtrate evaporated to dryness and the residue crystallised from

pet. ether to give the *p*-quinone (XIX, 1.06 g), m.p. 107°, M^+216 (Found: C, 77.2; H, 5.7. $C_{13}H_{12}O_3$ requires C, 77.2; H, 5.6%) IR (KBr); 1650 (C=O) cm^{-1}; PMR ($CDCl_3$): 1.5 (3H, *t*, *J*=7Hz, $-CH_3$ of -OEt), 4.2 (2H, *q*, *J*=7Hz, $-CH_2-$ of-OEt), 2.13 (3H, *d*, *J* =2Hz, C_3-CH_3), 6.76 (1H, *q*, *J*=2Hz, C_2-H) and 7.1-7.7 (3H, *m*, Ar-H). It gave a leucodiacetate, m.p. 124°, M^+ 302 (Found: C, 67.6; H, 6.0. $C_{17}H_{18}O_5$ requires C, 67.5; H, 6.1%); IR (KBr): 1770 and 1760 (C =O) cm^{-1}; PMR ($CDCl_3$): 1.5 (3H, *t*, *J*=8Hz, $-CH_3$ of -OEt), 4.2 (2H, *q*, *J*=8Hz, $-CH_2-$ of -OEt), 2.3, 2.4 and 2.45 (9H, three sharp singlets, two -OAc and one Ar-CH_3) and 7.0-7.05 (4H, *m*, Ar-H).

Oxidation of XIV (0.1 g) with Fremy's salt[6] (1g) gave the *o*-quinone (XX, 0.06g), m.p. 126-27°, M^+ 216 and *m/z* 218 (P+2) (Found: C, 77.3; H, 5.6. $C_{13}H_{12}O_3$ requires C, 77.2; H, 5.6%); IR (KBr): 1690 and 1650 (C =O) cm^{-1}; PMR ($CDCl_3$): 1.51 (3H, *t*, *J*=8Hz, $-CH_3$ of -OEt), 4.25 (2H, *q*, *J*=8Hz, $-CH_2-$ of -OEt), 2.1 (3H, *d*, *J*=2Hz, C_3-CH_3), 7.3 (1H, *q*, *J* =2Hz, C_4-H) and 7.1-7.9 (3H, *m*, Ar-H).

2-*Cyano*-5-*ethoxy*-3-*methyl*-1-*naphthol* (*XVIII*)—Condensation of VII (6g) with ethyl cyanoacetate (10g) in acetic acid (10 ml) and ammonium acetate (0.5g) gave the cyanoester (XVII) which was heated at 220° with acetamide (5g) for 1 hr to give XVIII (1.6g), m.p. 182-84°, M^+ 227 (Found: C, 74.0; H, 5.8; N, 6.2. $C_{14}H_{13}O_2N$ requires C, 74.1; H, 5.8; N, 6.2%); IR (KBr): 3310 (OH) and 2230 (CN) cm^{-1}; PMR ($CDCl_3$): 1.4 (3H, *t*, *J*=8Hz, $-CH_3$ of -OEt), 4.1 (2H, *q*, *J* =8Hz, $-CH_2-$ of -OEt), 2.5 (3H, *bs*, $W_{1/2}$=2Hz, C_3-CH_3) and 6.8−7.79 (5H, *m*, four Ar-H and one phenolic −OH, D_2O exchangeable).

Oxidation of XVIII (1g) with active MnO_2 (5g) in benzene (50 ml) gave XXI (0.9g) which was crystallised from benzene, m.p. 142°, M^+241 (Found: 69.8; H, 4.31; N, 5.8. $C_{13}H_{11}O_3N$ requires C, 69.7; H, 4.6; N, 5.8%); IR (KBr): 2320 (CN), 1670 and 1660 (C=O) cm^{-1}; PMR ($CDCl_3$): 1.8 (3H, *t*, *J*=8Hz, $-CH_3$ of -OEt), 4.3 (2H, *q*, *J*=8Hz, $-CH_2-$ of -OEt), 2.5 (3H, *s*, C_3-CH_3) and 7.6-8.0 (3H, *m*, Ar-H). It gave a leucodiacetate, m.p. 192°, M^+327 (Found: C, 66.1; H, 5.2; N, 4.3. $C_{18}H_{17}O_5N$ requires C, 66.1; H, 5.2; N, 4.3%); IR (KBr): 2230 (CN), 1770 and 1760 (C=O) cm^{-1}; PMR ($CDCl_3$): 1.5 (3H, *t*, *J*=7Hz, $-CH_3$ of -OEt), 4.2 (2H, *q*, *J*=7Hz, $-CH_2-$ of -OEt), 2.47, 2.53 and 2.60 (9H, three sharp singlets, two -OAc and one Ar-CH_3) and 7.07-7.73 (3H, *m*, Ar-H).

5,8-*Dimethoxy*-3-*methyl*-1-*naphthol* (*XV*)—2, 5-Dimethoxyphenylacetone (VIII) was prepared by condensing 2, 5-dimethoxybenzaldehyde[7] (V, 16g) with nitroethane (10g), in the presence of ammonium acetate (0.7g) in toluene (50 ml), followed by reduction with iron (20g) and HCl (36 ml), yield 11g; PMR (CCl_4): 1.75 (3H, *s*, $-CH_3$), 3.3 (2H, *s*, $-CH_2-$), 3.4 (6H, *s*, two -OCH_3) and 6.56-7.06 (3H, *m*, Ar-H).

Reformatsky ester (*XI*)—It was prepared by condensing VIII (5g) with ethyl bromoacetate (5ml) and activated zinc powder (3g) in benzene (50 ml). It was purified by passing over a silica gel column in benzene, yield 4 g (Found: C, 63.8; H, 7.8. $C_{15}H_{22}O_5$ requires C, 63.8; H, 7.9%); PMR (CCl_4): 1.08 (3H, *t*, *J* =7Hz, $-COOCH_2CH_3$), 1.06 (3H, *s*, tertiary $-CH_3$), 2.27 (2H, *s*, $-CH_2$-COOEt), 2.78 (2H, *s*, $-CH_2$-ph), 3.56 (3H, *s*, $-OCH_3$), 3.6 (3H, *s*, $-OCH_3$), 4.03 (2H, *q*, *J*=7Hz, $-COOCH_2CH_3$), 6.6 (2H, *bs*, two Ar-H) and 6.78 (1H, *bs*, Ar-H). The tertiary hydroxyl (D_2O exchangeable) is merged with the quartet at 4.03.

Hydrolysis of Reformatsky ester (XI)—XI (10 g) was hydrolysed with alco alkali and the arylbutyric acid, thus obtained, cyclised with PPA (10 g) at 50° for 2 hr to give XV (2.5 g), m.p. 114° (lit.[8] m.p. 117°), M^+218 (Found: C, 71.6; H, 6.45. Calc. for $C_{13}H_{14}O_3$: C, 71.5; H, 6.5%); IR (KBr): 3340 (OH) cm^{-1}; PMR ($CDCl_3$): 2.55 (3H, *bs*, $W_{1/2}$=1.5Hz, C_3-CH_3), 3.98 (3H, *s*, $-OCH_3$), 4.03 (3H, *s*, $-OCH_3$), 6.78 (2H, *s*, C_6 and C_7Ar-H), 6.9 (1H, *d*, *J*=2Hz, C_2-H), 7.63 (1H, *m*, C_4-H) and 9.45 (1H, *s*, −OH, D_2O exchangeable).

Oxidation of XV (0.1 g) with active MnO_2 (0.5 g) in benzene (10 ml) for 30 min gave XXII (0.09 g), m.p. 146°, M^+232 (Found: C, 67.2; H, 5.21. $C_{13}H_{12}O_4$ requires C, 67.2; H, 5.21%); IR (KBr): 1640 (C=O) cm^{-1}; PMR ($CDCl_3$): 2.16 (3H, *d*, *J*=2Hz, C_2-CH_3), 4.01 (6H, *s*, two $-OCH_3$), 6.78 (1H, *q*, *J*=2Hz, C_3-H) and 7.4 (2H, *s*, C_6 and C_7 Ar-H).

Oxidation of XV (0.1 g) with Fremy's salt[6] (1 g) gave XXIII (0.052 g), m.p. 137°, M^+232 and *m/z* 234 (P+2) (Found: C, 67.2; H, 5.3. $C_{13}H_{12}O_4$ requires C, 67.2; H, 5.2%); IR (KBr): 1690 and 1640 (C=O) cm^{-1}; PMR ($CDCl_3$): 2.20 (3H, *d*, *J*=2Hz, C_3-CH_3), 4.0 (6H, *s*, two $-OCH_3$), 7.15 (1H, *q*, *J*=2Hz, C_4-H) and 7.38 (2H, *s*, C_6 and C_7 Ar-H).

3-*Methyl*-1-*naphthol* (*XVI*)—Phenylacetone (IX) was prepared by condensing benzaldehyde (VI, 10.6 g) with nitroethane (10 g), followed by reduction with iron and HCl, yield 9 g; PMR (CCl_4): 1.82 (3H, *s*, $-CH_3$), 3.54 (2H, *s*, $-CH_2-$) and 6.45-7.03 (5H, *bm*, Ar-H).

Reformatsky ester (*XII*)—It was prepared by reacting phenylacetone (IX, 5 g) with ethyl bromoacetate (4.5 ml) and zinc powder (3 g) in benzene (50 ml). It was purified by chromatography over a silica gel column using benzene as eluent, yield 3.3 g (Found: C, 70.3; H, 8.2. $C_{13}H_{18}O_3$ requires C, 70.2; H, 8.2%); PMR (CCl_4): 1.05 (3H, *t*, *J*=8Hz, $-COOCH_2CH_3$), 1.06 (3H, *s*, $-CH_3$), 2.24 (2H, *s*, $-CH_2-COOEt$), 2.75 (2H, *s*, $-CH_2$-ph), 4.00 (2H, *q*, *J*=8Hz, $-COOCH_2CH_3$), 3.76 (1H, −OH, D_2O exchangeable, merged with quartet at 4.00) and 6.5-7.06 (5H, *bm*, Ar-H).

Hydrolysis of XII—XII (10g) was hydrolysed with alc. alkali and the phenylbutyric acid, thus obtained, was cyclised with PPA (7g) at 50° for 2 hr to give XVI (3g), m.p. 90° (lit.[9] m.p. 90-91°), M^+158 (Found: C, 83.6; H, 6.3. Calc. for $C_{11}H_{10}O$; C, 83.51; H, 7%); PMR ($CDCl_3$): 2.53 (3H, *bs*, $W_{1/2}$ = 1.3 Hz, $-CH_3$) and 6.53 −7.4 (7H, *bm*, Ar-H and phenolic −OH, D_2O exchangeable).

Oxidation of 1-*naphthol with active* MnO_2—1-Naphthol (8.1 g) dissolved in benzene (10 ml) was shaken for 5 min with active MnO_2 (0.5g). TLC of the reaction mixture showed the formation of two new phenolic compounds (A and B) which were separated by column chromatography on silica gel using $CHCl_3$—EtOAc (99:1) as eluent. Compound-A (0.015 g) was crystallised from hexane, m.p. 250°, M^+286 and shown to be 4, 2′-binaphthol. Its structure was confirmed by the PMR spectrum[10] of its diacetate, m.p. 147°, M^+370; PMR ($CDCl_3$): 1.88 (3H, *s*, C_1-OAc), 2.47 (3H, *s*, $C_{1'}$-OAc) and 7.3 − 8.0 (12H, *m*, Ar-H).

Compound-B (0.014g) was crystallised from benzene, m.p. 342°, M^+286 and shown to be 4, 4′-binaphthol. Its structure was confirmed by the PMR spectrum[10] of its diacetate, m.p. 225°, M^+370; PMR ($CDCl_3$): 2.53 (6H, *s*, C_1- and $C_{1'}$-OAc) and 7.4 − 8.0 (12H, *m*, Ar-H).

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