A Convenient Preparation of Indenone

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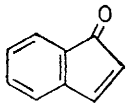
Indenone is made in two steps from indane-1,3-dione, and a by-product is characterised by conversion to *s*-dibenzofulvalene. Indenone undergoes acid-catalysed addition reactions, and all its six protons have magnetic resonance at higher field than expected.

INDENONE (I) polymerises readily.[1] It has been prepared from indene by condensation with *p*-nitrosodimethylaniline followed by hydrolysis,[2] from indene hydroperoxide by treatment with lead tetra-acetate,[3] and from indanone either by radical bromination in the 3-position and dehydrobromination, or by acetoxylation in the 2-position with lead tetra-acetate followed by ester pyrolysis.[1] We find that 3-acetoxyindanone (II), made by reductive acetylation of indane-1,3-dione, affords indenone smoothly with sodium hydrogen carbonate solution.

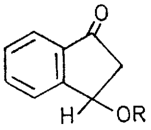
Indane-1,3-dione is rapidly reduced by zinc and acetic acid in the presence of acetic anhydride and sodium acetate to 3-acetoxyindan-1-one; and a little of the pinacol (VI) can be isolated. Zinc and acetic acid does not typically reduce ketones,[4] so there is enhanced reactivity of one of the carbonyl groups of indane-1,3-dione.

If water is used in the isolation procedure, the hydroxy-ketone (III) is formed, but treatment of the acetoxy-ketone (II) with aqueous alkali gives indenone (I) and not the hydroxy-ketone. If this elimination is enolisation-dependent, then it should occur with milder bases, and sodium hydrogen carbonate is found to be effective, being superior to sodium hydroxide in that it does not destroy the indenone if present in excess of one equivalent.

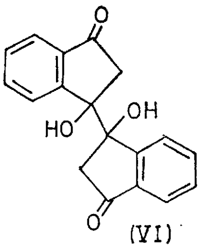
The status of indenone as an aromatic or an anti-aromatic substance is of interest: apart from its easy polymerisation we find that it shows enhanced reactivity to nucleophiles, spontaneously adding acetic acid, water or ethanol, giving ketones (II), (III), and (V) respectively, in acid-catalysed reactions at room temperature. This is in marked contrast to cyclopent-2-enone which shows negligible addition of methanol even in the presence of one equivalent of sodium methoxide.[5]



(I)



(II) R = Ac
(III) R = H
(IV) R = $CO{\cdot}CF_3$
(V) R = Et



(VI)

Even the weakly nucleophilic trifluoroacetic acid adds spontaneously to indenone giving 3-trifluoroacetoxyindan-1-one (IV) whereas there is no such reaction in the cases of cyclopent-2-enone, 3-phenylcyclopent-2-enone or chalcone; so it appears that conjugation in the five-membered ring of indenone actually destabilises the molecule.

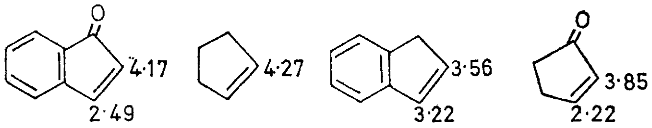
The proton magnetic resonances of indanone and indenone in deuteriochloroform reveal paramagnetic shifts ($\Delta\tau$) for the protons on the six-membered ring (positions 4—7) of indenone.

Chemical shifts (τ) of vinylic protons

Position:	2	3	4	5, 6	7
Indanone			2·67 [a]	2·54 [b]	2·30 [a]
Indenone [c]	4·17 [d]	2·49 [d,e]	3·00 [a]	2·77 [b]	2·61 [a]
$\Delta\tau$			+0·33	+0·23	+0·31

[a] Double doublet (7, 1·5 Hz). [b] 2H Multiplet. [c] These values accord with those reported for indenone in carbon tetrachloride, ref. 6 [d] Doublet (6 Hz). [e] Collapses to a singlet on irradiation at 4·17.

The α- and β-vinylic proton resonances of 2,4-di-t-butylcyclopentadienone (in carbon tetrachloride) occur up-field from estimated values by +1·72 and +1·54 p.p.m., respectively.[7] An analogous comparison for the α- and β-vinylic proton resonances of indenone (in deuteriochloroform) shows that they also occur up-field from values estimated by the same procedure.



Chemical shifts (τ) of vinylic protons (in $CDCl_3$)

$$\Delta\tau\ (\alpha) = 4{\cdot}17 - [3{\cdot}85 - (4{\cdot}27 - 3{\cdot}56)] = +1{\cdot}03 \text{ p.p.m.}$$
$$\Delta\tau\ (\beta) = 2{\cdot}49 - [2{\cdot}22 - (4{\cdot}27 - 3{\cdot}22)] = +1{\cdot}32 \text{ p.p.m.}$$

Whether these shifts reflect an unusual distribution of electron density in indenone, or a paramagnetic ring current on the five-membered ring remains to be determined.

The pinacol (VI) when boiled with acetic anhydride, instead of being dehydrated, gave the orange diacetate (VII) at a lower level of oxidation, together with more polar material that was not characterised. However, briefer treatment with acetic anhydride gave a compound

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[1] C. S. Marvel and C. W. Hinman, *J. Amer. Chem. Soc.*, 1954, **76**, 5435.

[2] R. Stoermer and E. Asbrand, *Ber.*, 1931, **64**, 2796.

[3] H. Hock and F. Ernst, *Chem. Ber.*, 1959, **92**, 2723.

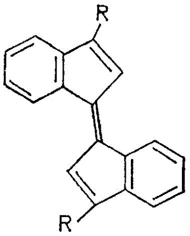
[4] O. H. Wheeler in 'The Chemistry of Carbonyl Compounds,' ed. S. Patai, Interscience, 1966, p. 515.

[5] P. Chamberlain and G. H. Whitham, *J. Chem. Soc. (B)*, 1969, 1131.

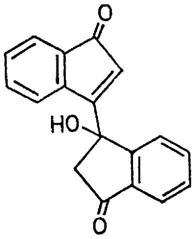
[6] R. F. C. Brown and M. Butcher, *Austral. J. Chem.*, 1969, **22**, 1457.

[7] E. W. Garbisch and R. F. Sprecher, *J. Amer. Chem. Soc.*, 1969, **91**, 6785.

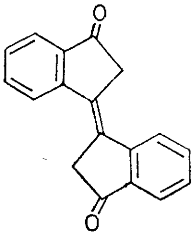
which appears to be the product (IX) of partial dehydration, since its u.v. spectrum corresponds to summation of the chromophores of indanone and indenone; it has one hydroxy-group ($\nu_{max.}$ 3570 cm.$^{-1}$, τ 6·60 in $CHCl_3$ and $CDCl_3$ respectively), one indenone α-proton (τ 4·14, a singlet and therefore lacking a β-proton), and one methylene group (τ 6·8, 6·9, 23 Hz). It also has the expected mass spectrum. The diacetoxy-compound (VII) was methanolysed to a diketone (X), which was reduced with borohydride to the corresponding diol, then dehydrated in low yield with boiling acetic anhydride to *s*-dibenzofulvalene (VIII), a known compound,[8] whose ultraviolet spectrum clearly distinguishes it from its isomers chrysene and naphthacene.



(VII) R=OAc
(VIII) R=H



(IX)



(X)

EXPERIMENTAL

Reductive Acetylation of Indane-1,3-*dione*.—(*a*) Indane-1,3-dione (1·05 g.), acetic acid (50 ml.), acetic anhydride (50 ml.), and anhydrous sodium acetate (5 g.; purple colour on the surface of the solid) was stirred and treated with zinc powder (10 g.) during 15 min.; the mixture was stirred for a further 2 hr. and was then filtered. The solids were rinsed with acetic acid and the combined filtrate and washings were concentrated under reduced pressure to give a sticky solid; this was dissolved in a mixture of saturated sodium chloride solution (50 ml.) and ethyl acetate (50 ml.). The organic layer was washed successively with sodium chloride solution and then twice with aqueous sodium hydrogen carbonate; it was then dried (Na_2SO_4) and concentrated under reduced pressure to give an orange oil (1·07 g.), which was chromatographed on silica. Elution by benzene–ethyl acetate (4 : 1) gave first indenone (0·14 g.), then 3-*acetoxyindan*-1-*one* (0·81 g.) as an oil, b.p. 110° (bath temp.)/15 mm. [Found (on distilled material containing indenone): C, 69·5; H, 5·2. $C_{11}H_{10}O_3$ requires C, 68·8; H, 5·3%]; $\nu_{max.}$ ($CHCl_3$) 1725br cm.$^{-1}$; $\lambda_{max.}$ (MeOH) 242, 280, and 287 nm. (4·06, 3·14, 3·13); $\lambda_{sh.}$ 272 nm. (3·04); n.m.r. (CCl_4) τ 2·3—2·6 (4H, m), 3·78 (1H, dd; *J* 7 and *J* 3 Hz), 6·98 (1H, dd, *J* 19 and *J* 7 Hz), 7·52 (1H, dd, *J* 19 Hz and *J* 3 Hz), 7·97 (3H, s); *m*/*e* 190 (M^+ 12%), 148 (45%, loss of C_2H_2O by metastable at 115·5), 131 (22%), 130 (22%), 102 (52%), 91 (22%), 77 (52%), 43 (100%).

If the total oily reduction product was kept for some hours before chromatography, it deposited crystals. These were washed with ether and recrystallised from acetone giving 1,1′-*dihydroxy*-3,3′-*dioxo*-1,1′-*bi-indanyl* (196 mg.), m.p. 206—208° (Found: C, 73·2; H, 4·9. $C_{18}H_{14}O_4$ requires C, 73·4; H, 4·8%); $\nu_{max.}$ (Nujol) 3390, 3290, 1715w, 1695 cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 243, 285, 290 nm. (4·35, 3·57, 3·57); n.m.r. [$(CD_3)_2SO$], τ 2·3—2·8 (8H, m), 3·96 (2H, s, exchangeable), 6·92 and 7·38 (both 2H, d, *J* 19 Hz); *m*/*e* 276 (2%, M^+ − 18), 260 (2%), 148 (100%), 130 (21%), 129 (27%).

(b) Indane-1,3-dione (103 mg.) was reduced as above on a 1/10th scale, but the reaction mixture after being stirred for 2 hr., was diluted with water (20 ml.) and stirred for 1 hr.; it was then neutralised with sodium hydrogen carbonate solution and extracted with ether (3 × 50 ml.). The extract was washed with sodium chloride solution, dried (Na_2SO_4), and concentrated to an oil (118 mg.); preparative t.l.c. with ethyl acetate–benzene (1 : 4) for development gave indenone R_F 0·60 (3 mg.), 3-acetoxyindan-1-one R_F 0·48 (9 mg.), and 3-*hydroxyindan*-1-*one* R_F 0·28 (73 mg.) as an oil [Found (on undistilled material containing solvent ethyl acetate): C, 70·9; H, 5·2. $C_9H_8O_2$ requires C, 73·0; H, 5·9%]; $\nu_{max.}$ ($CHCl_3$) 3590, 1717 cm.$^{-1}$; $\lambda_{max.}$ (MeOH) 244, 282, and 288 nm. (4·02, 3·13, 3·14); n.m.r. ($CDCl_3$) τ 2·1—2·7 (4H, m), 4·70 (1H, dd, *J* 7 and *J* 3 Hz), 5·98br (1H, s, exchangeable), 7·02 (1H, dd, *J* 19 and *J* 7 Hz), 7·52 (1H, dd, *J* 19 and *J* 3 Hz); *m*/*e* 148 (M^+, 100%), 131 (21%), 130 (19%), 119 (46%), 102 (43%), 91 (13%), 77 (65%).

Indenone.—3-Acetoxyindan-1-one (112 mg.), methanol (1 ml.), and saturated aqueous sodium hydrogen carbonate (5 ml.) were stirred for 10 min. in subdued light; the mixture was then diluted with water and extracted with ether. The extract, after being dried (Na_2SO_4), was concentrated to a bright yellow oil consisting of indenone and a trace of starting material which could be removed by filtration through a short column of silica in benzene–ethyl acetate (9 : 1). Distillation at 100° (bath temp.)/15 mm. gave indenone (52 mg.) (Found: C, 83·5; H, 4·6. Calc. for C_9H_6O: C, 83·1; H, 4·6%), $\nu_{max.}$ ($CHCl_3$) 1737w, 1713 cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 233, 238, 318, and 380 nm. (4·30, 4·31, 3·08, 2·44).

Acid-catalysed Additions to Indenone.—These reactions were followed by u.v. spectroscopy, in each case the characteristic pattern of indenone changing with two isobestic points to that of a 3-substituted indanone. The approximate half-lives of indenone at room temperature (min.) were as follows: in 5% sulphuric acid in ethanol (0·2); in 5% sulphuric acid in acetic acid (1); in trifluoroacetic acid (75); in 5% sulphuric acid in (1 : 1) tetrahydrofuran-water (700).

3-Acetoxyindan-1-one and 3-hydroxyindan-1-one were identified by their R_F values and i.r. and n.m.r. spectra. The reaction of indenone with trifluoroacetic acid was followed additionally by n.m.r. spectroscopy: the resulting solution of 3-trifluoroacetoxyindan-1-one showed τ 2·0—2·5 (4H, m), 3·35 (1H, dd, *J* 7 and *J* 3 Hz), 6·46 (1H, dd, *J* 19 and *J* 7 Hz), 6·96 (1H, dd, *J* 19 and *J* 3 Hz). Finally, the trifluoroacetic acid was removed under reduced pressure, leaving an oil having $\nu_{max.}$ ($CHCl_3$) 1785 and 1720 cm.$^{-1}$. After the ethanol addition, the reaction mixture was diluted with water and extracted with ether. The extract was washed with aqueous sodium chloride, dried (Na_2SO_4), and concentrated to an oil (21 mg.) which appeared homogeneous by t.l.c., and was distilled at 140—145° (bath temp.)/15 mm., giving 3-*ethoxyindan*-1-*one* (17 mg.) (Found: C, 74·7; H, 7·0. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%);

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[8] A. G. Anastassiou, F. L. Setliffe, and G. W. Griffin, *J. Org. Chem.*, 1966, **31**, 2705.

$\nu_{max.}$ ($CHCl_3$) 1712 cm.$^{-1}$; $\lambda_{max.}$ (MeOH) 243, 282, and 288 nm. (4·00, 3·17, 3·17); n.m.r. ($CDCl_3$) τ 2·2—2·6 (4H, m), 4·94 (1H, dd, *J* 7 and *J* 3 Hz), 6·34 (2H, q, *J* 7 Hz), 7·02 (1H, dd, *J* 19 and *J* 7 Hz), 7·38 (1H, dd, *J* 19 and *J* 3 Hz), 8·74 (3H, t, *J* 7 Hz); *m/e* 176 (M^+, 92%), 162 (11%), 147 (53%), 131 (100%), 119 (44%), 105 (51%), 103 (80%), 91 (49%), 77 (97%).

Dehydration of the Pinacol (VI).—(*a*) This compound (70 mg.) was boiled with acetic anhydride under nitrogen for 14 hr.; the mixture was then concentrated under reduced pressure, taken up in ether, washed successively with sodium chloride solution and sodium hydrogen carbonate solution, and then dried (Na_2SO_4) and concentrated to a gum. This was chromatographed on a short column of silica; benzene eluted 3,3′-*diacetoxy*-s-*dibenzofulvalene* (VII) (20 mg.) as bright orange crystals, m.p. 224—226°, $\nu_{max.}$ ($CHCl_3$) 1773, 1550, 1450, 1366; $\lambda_{max.}$ (MeOH) 240, 291, 348, 370, 389 nm. (4·03, 3·91, 3·88, 4·02, 3·97); $\lambda_{sh.}$ 450 nm. (3·35); n.m.r. ($CDCl_3$) τ 2·10 (2H, dd, *J* 7 and *J* 3 Hz), 2·55 (2H, s), 2·65—2·80 (6H, m), 7·62 (6H, s); *m/e* 344 (M^+, 6%), 302 (8%, loss of C_2H_2O indicated by metastable at 265), 260 (89%, loss of C_2H_2O from 302 indicated by metastable at 224), 232 (7%, loss of CO from 260 indicated by metastable at 206), 231 (18%), 215 (6%), 213 (5%), 204 (5%, loss of CO from 232 indicated by metastable at 178), 203 (24%), 202 (70%), 201 (19%), 200 (23%), 43 (100%); accurate mass 344·103389, $C_{22}H_{16}O_4$ requires 344·104851.

(*b*) Pinacol (VI) (60 mg.) was boiled with acetic anhydride under nitrogen for 1 hr., and then worked up as in (*a*). Chromatography on a short column of silica gave on elution with ethyl acetate–benzene (1 : 4), a pale yellow solid (20 mg.), assigned structure (IX) on the basis of the following data: $\nu_{max.}$ ($CHCl_3$) 3570, 1715, 1710 cm.$^{-1}$; $\lambda_{max.}$ (MeOH) 239, 280, 290, 312 nm. (4·44, 3·33, 3·32, 3·10), $\lambda_{sh.}$ 360 nm. (2·60); n.m.r. ($CDCl_3$) τ 2·1—2·9 (7H, m), 3·38 (1H, dd, *J* 5 and *J* 3 Hz), 4·14 (1H, s), 6·60br (1H, s, exchangeable), 6·80, 6·90 (1H, both d, *J* 23 Hz); *m/e* 276 (M^+, 73%), 248 (19%, loss of CO from 276 indicated by metastable at 223), 247 (33%, loss of CHO from 276 indicated by metastable at 221), 234 (100%, loss of C_2H_2O from 276 indicated by metastable at 198·5), 231 (43%), 220 (20%), 219 (17%), 206 (15%, loss of CO from 234 indicated by metastable at 181·5), 205 (12%), 204 (7%), 203 (24%), 202 (42%); accurate mass 276·078237, $C_{18}H_{12}O_3$ requires 276·078638.

3,3′-*Dioxobi-indanylidene* (X).—3,3′-Diacetoxy-*s*-dibenzofulvalene (20 mg.) was boiled with methanol for 3 hr. and then concentrated to a pale yellow solid which was chromatographed on a short column of silica. Ethyl acetate–benzene (1 : 4) eluted the pale yellow dione (X) (18 mg.), m.p. 248—250°; $\nu_{max.}$ ($CHCl_3$) 1712 cm.$^{-1}$; $\lambda_{max.}$ (MeOH) 240, 297, 309, 343 nm. (4·05, 3·99, 4·00, 3·85); $\lambda_{sh.}$ 255, 285, 332, 368 (3·92, 3·81, 3·81, 3·54); too insoluble for n.m.r. spectroscopy; *m/e* 260 (molecular ion, 100%), 231 (66%, loss of CHO from 260 indicated by metastable at 205), 215 (18%), 203 (58%), 202 (96%, loss of CHO from 231 indicated by metastable at 178·5); accurate mass 260·083762, $C_{18}H_{12}O_2$ requires 260·083724.

Conversion of the Dione (X) *to* s-*Benzofulvalene* (VIII).—This compound (15 mg.) in ethanol (10 ml.) was treated with aqueous sodium borohydride until the reduction, as monitored by u.v. absorption, was complete (2 hr.). The solution was diluted with water and extracted by ethyl acetate. The organic layer was dried (Na_2SO_4) and concentrated to a pale yellow solid, not melting below 320°, and appearing homogeneous by t.l.c. The following data is consistent with it being 3,3′-dihydroxy-1,1′-bi-indanylidene of unknown stereochemistry: $\lambda_{max.}$ (EtOH) 230, 236, 243, 300, 314, 329 nm. (3·89, 3·92, 3·80, 4·16, 4·28, 4·26); λ_{sh} 287 nm. (4·03); n.m.r. (C_5D_5N) τ 2·18—2·80 (8H, m), 4·40 (2H, m), 5·10br (2H, s, exchangeable), 6·32br, 6·75br (both 2H, d, *J* 15 Hz); *m/e* 264 (M^+, 31%), 246 (42%, loss of H_2O from 264 indicated by metastable at 229), 231 (100%), 228 (11%), 217 (18%), 215 (20%), 203 (28%, loss of CO from 231 indicated by metastable at 178·5), 202 (34%, loss of CHO from 231 indicated by metastable at 177). This product (10 mg.) was boiled with acetic anhydride under nitrogen for 20 hr.; the mixture was then concentrated under reduced pressure to a gum which, dissolved in ethyl acetate, was washed with aqueous sodium chloride, dried (Na_2SO_4), and concentrated. Preparative t.l.c. with benzene for development gave three fractions, R_F 0·17 (starting material), R_F 0·32, and R_F 0·65. The last-mentioned component was eluted as an orange solid (2 mg.), identified as somewhat impure *s*-dibenzofulvalene (VIII) on the basis of the following: $\lambda_{max.}$ (MeOH) 245, 282, 376, 397 nm. (4·44, 4·30, 4·15, 4·16); $\lambda_{sh.}$ 289, 357 nm. (4·18, 4·02); [*cf.* ref. 8, $\lambda_{max.}$ (hexane) 248, 285, 380, 401 nm. (4·29, 4·35, 4·43, 4·48); $\lambda_{sh.}$ 291, 360 nm. (4·32, 4·26)]; *m/e* 228 (M^+, 15%), 227 (8%), 226 (7%), 149 (28%), 129 (24%), 111 (24%), 97 (43%), 85 (42%), 83 (48%), 73 (55%), 71 (62%), 69 (69%), 57 (100%); accurate mass 228·093013, $C_{18}H_{12}$ requires 228·093900.

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