Synthesis of Some Indan-1-ones

By **Jaysukhlal R. Merchant,* Meera S. Kamath, and Suneel Y. Dike,** Department of Organic Chemistry, Institute of Science, Bombay-400 032, India

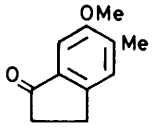
The reactions of acrylic and substituted acrylic acids with dimethylphenol ethers in the presence of polyphosphoric acid give indan-1-ones in moderate yields. Evidence as to whether the reaction is a Friedel–Crafts acylation or alkylation is discussed

INDAN-1-ONES are useful intermediates in the preparation of steroids and alkaloids. Several 13-ethyl-steroids have enhanced biological activity [1] and certain B-nor-steroids are useful for the treatment of atherosclerosis. Growing interest in the biological properties of steroid hormones in which the basic ring skeleton is modified has resulted in the synthesis of hormone analogues possessing the C-nor-D-homo-steroid system from natural precursors.[2-6]

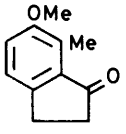
Several methods have been reported for the synthesis of the above compounds; that developed by Bhattacharya *et al.*[7] utilises indan-1-one derivatives as starting materials. Very recently, Birch *et al.*[8] have synthesised (±)-18-methyl-B-noroestrone and (±)-18-methyl-8-*epi*-B-noroestrone *via* indan-1-ones.

A common method for the synthesis of indan-1-ones involves nuclear cyanoethylation of a phenol ether with acrylonitrile (Michael addition) followed by hydrolysis of the resulting propiononitrile to the corresponding propionic acid and cyclisation of the product with reagents such as polyphosphoric acid (PPA) or aluminium chloride. This method, apart from being elaborate, is not suitable for indan-1-ones having alkyl or phenyl substituents in the cyclopentene ring, since the corresponding substituted propiononitriles are not easily available. A shorter and more convenient synthesis, reported here, consists of heating the phenol ether with a substituted αβ-unsaturated acid in the presence of PPA; indan-1-ones are obtained in 30—35% yield in most cases.

Chatterjee *et al.*[9] have reported that treatment of *o*-cresol methyl ether with acrylonitrile followed by hydrolysis and cyclisation of the resulting propionic acid affords both the indan-1-ones (1) and (2).[10] On



(1)

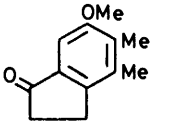


(2)

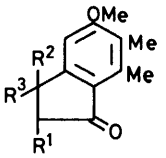
heating the same methyl ether directly with acrylic acid in the presence of PPA we isolated only compound (1) (single spot on t.l.c.; mixed m.p.[10]), in 5% yield, along with a lot of tarry material. The u.v. spectrum [$\lambda_{max.}$ 255 and 320 nm (in methanol)] establishes the position of the carbonyl group (*cf.* $\lambda_{max.}$ 249 nm for an *m*-methoxyacetophenone [11]). The n.m.r. signals for two aromatic protons at δ 6.85 and 7.55 are also consistent with structure (1).

The above reaction can be envisaged as proceeding in either of two ways: (i) by Friedel–Crafts alkylation *para* to the methoxy-group followed by cyclization, and (ii) by Friedel–Crafts acylation *meta* to the methoxy-group followed by ring closure. However, the latter possibility is remote, since intramolecular acylation *meta* to a methoxy-group is difficult.[12]

In order to confirm the above findings, the methyl ethers of various dimethylphenols were treated with αβ-unsaturated acids in the presence of PPA to obtain the



(3)



(4) R^1 = Me, R^2 = R^3 = H
(5) R^1 = H, R^2 = Me, R^3 = H
(6) R^1 = H, R^2 = R^3 = Me
(7) R^1 = H, R^2 = Ph, R^3 = H
(8) R^1 = R^2 = H, R^3 = C_5H_4N

corresponding indan-1-ones. These particular ethers were selected since the u.v. and in some cases the n.m.r. spectra of the resultant indan-1-ones were expected to furnish valuable information on the course of the reaction.

On treating the methyl ether of 2,3-dimethylphenol with acrylic acid in the presence of PPA we obtained only one compound [13] (3) (single spot on t.l.c.) after chromatography over alumina. The same ketone was also obtained by nuclear cyanoethylation of the above phenol ether with acrylonitrile followed by hydrolysis and cyclisation of the resulting propionic acid with PPA. Its n.m.r. spectrum ($CDCl_3$) showed a singlet for two aromatic methyl groups at δ 2.25 and the aromatic proton absorption at δ 7.05. The u.v. spectrum showed $\lambda_{max.}$ (MeOH) 255 and 320 nm.

Similarly, on treating 2,3-dimethylphenol methyl

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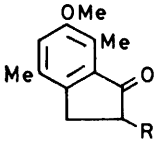
[13] J. R. Merchant, S. M. Thakkar, and M. S. Kamath, *Indian J. Chem.*, 1975, **13**, 862.

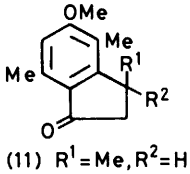
ether with α-methylacrylic acid in the presence of PPA we isolated only compound (4) after chromatography over alumina. The n.m.r. spectrum ($CDCl_3$) showed two different signals for the two aromatic methyl groups at δ 2.15 and 2.63. If this reaction had proceeded by Friedel–Crafts alkylation *para* to the methoxy-group, the n.m.r. spectrum of the product would have shown coincident aromatic methyl signals; thus Friedel–Crafts acylation must have occurred at the *para*-position, followed by ring closure. Also, in the former case, the aromatic proton would have given a signal at δ *ca.* 7.1 (due to deshielding by C=O), whereas the signal in fact occurs at δ 6.75. Further, the u.v. spectrum (MeOH) showed maxima at 275 and 345 nm, in agreement with those for *para*-alkoxyacetophenones. The u.v. spectra of compounds of (1), (3), and (4) show that the first two can be considered as *m*-methoxy-ketones ($\lambda_{max.}$ 255) and the last as a *p*-methoxyacetophenone ($\lambda_{max.}$ 276 nm).

Treatment of the same phenol methyl ether with crotonic and ββ-dimethylacrylic acids in the presence of PPA yielded compounds (5) and (6), respectively. In the n.m.r. spectra of both products, two distinct signals are observed for the aromatic methyl protons, at δ 2.15 and 2.6, and the aromatic proton signal appears at δ 6.7, indicating that the reaction has followed the Friedel–Crafts acylation route. In the case of cinnamic acid the same observation was made; only compound (7) was obtained. The reaction between β-3-pyridylacrylic acid and 2,3-dimethylphenol methyl ether in the presence of PPA was then studied. After the usual work-up and chromatography over alumina, a single compound was isolated. The n.m.r. spectrum ($CDCl_3$) showed different signals for the two methyl groups, at δ 2.15 and 2.65, and the aromatic proton signal at δ 6.5. In all these cases, the u.v. spectrum showed maxima at 275—280 nm.

Treatment of the methyl ether of 2,5-dimethylphenol with acrylic acid in the presence of PPA afforded only one compound, identical with that obtained *via* cyanoethylation, hydrolysis, and cyclisation. Its u.v. spectrum (MeOH) showed absorptions at 255 and 330 nm, indicating the structure (9). The same observation



(9) R = H
(10) R = Me



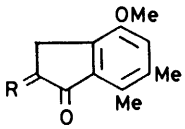
(11) R^1 = Me, R^2 = H
(12) R^1 = R^2 = Me
(13) R^1 = Ph, R^2 = H

was made in the case of α-methylacrylic acid: compound (10) (single spot on t.l.c.) was isolated, identical with the product obtained *via* the cyanoethylation route with methylacrylonitrile. Its u.v. spectrum (MeOH) showed maxima at 255 and 330 nm.

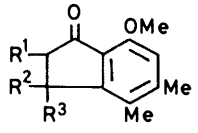
However, when the same methyl ether was heated with crotonic, ββ-dimethylacrylic, or cinnamic acid the products had different structures. Their u.v. spectra (MeOH) showed maxima at 285 and 320 nm, indicating structures (11)—(13). In the n.m.r. spectrum of (13) the methyl protons, shielded by the phenyl ring, give rise to a singlet at δ 1.85.

The methyl ether of 3,4-dimethyl phenol, when heated with αβ-unsaturated acids in the presence of PPA, gave two types of product. With acrylic acid the product was (14) [$\lambda_{max.}$ (MeOH) 255 and 320 nm]. Its n.m.r. spectrum confirmed the structure, showing two distinct signals for the aromatic methyl groups. Compound (14) was identical with that obtained by the cyanoethylation route.

However, when α-methylacrylic, crotonic, and ββ-dimethyl acrylic, and cinnamic acids reacted with 3,4-dimethylphenol methyl ether, the products had the alternative structures (16)—(19) [$\lambda_{max.}$ (MeOH) 260 and



(14) R = H
(15) R = Me



(16) R^1 = Me, R^2 = R^3 = H
(17) R^1 = R^2 = H, R^3 = Me
(18) R^1 = H, R^2 = R^3 = Me
(19) R^1 = R^2 = H, R^3 = Ph

320 nm]. In all the cases the aromatic methyl signals appeared as a six-proton singlet.

The indanone (15) (m.p. 80—81°), obtained by the reaction of α-methylacrylonitrile with 3,4-dimethylphenol methyl ether followed by hydrolysis and subsequent cyclisation, was different from that, (16), obtained by the reaction of the same methyl ether with α-methylacrylic acid in the presence of PPA (m.p. 84—86°). The 2,4-dinitrophenylhydrazones of the indanones (15) and (16) were also different.

EXPERIMENTAL

M.p.s were determined by heating in a sulphuric acid bath. I.r. spectra were recorded with a Perkin-Elmer spectrophotometer for solutions in methylene chloride or potassium bromide discs. ^1H N.m.r. spectra were recorded with a Varian A-60 instrument for solutions in deuteriochloroform or trifluoroacetic acid (Me_4Si as internal standard). T.l.c. was carried out on plates of silica gel G; spots were developed with iodine vapour. Column chromatography was performed on neutral alumina (B.D.H.). Analyses were performed in the microanalytical laboratory of the Institute of Science.

Cyanoethylation of Methyl Ethers of Dimethylphenols with Acrylonitrile and α-Methylacrylonitrile.—Finely powdered anhydrous aluminium chloride (1 mol. equiv.) was added slowly to a stirred solution of the methyl ether (1 mol. equiv.) and acrylonitrile or (methacrylonitrile) (5 mol. equiv.) in a dry system containing tetrachloroethane (1 mol. equiv.). Dry hydrogen chloride was passed through the mixture maintained at 10—15 °C for 1.5 h. The homogeneous product was then heated on a steam-bath at 90—95 °C for 1.5 h. The mixture was stirred continuously by

the passage of dry hydrogen chloride. The product was decomposed with ice and extracted with ether. The extract was washed with water and dried. Removal of ether left a liquid, which was distilled.

Hydrolysis of the Propiononitriles.—The nitrile (300 mg) was refluxed with concentrated hydrochloric acid (50 ml) for 3 h. The solution was then cooled and extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution. The washings were acidified and extracted with chloroform; this extract was washed with water, dried (Na_2SO_4), and evaporated to leave the corresponding propionic acids.

Cyclisation of the Propionic Acids.—The acid (300 mg) was added to a mixture of phosphorus pentaoxide (10 g) and phosphoric acid (4 ml) preheated at 100 °C for 0.5 h. Heating was continued for 3 h more. The mixture was cooled, decomposed with ice, and extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution and water, dried, and evaporated to leave the indanone, which was recrystallised. The 2,4-dinitrophenylhydrazone was crystallised from acetic acid.

Reactions of Phenol Ethers with αβ-Unsaturated Acids in the Presence of PPA.—To a mixture of phosphorus pentaoxide (50 g) and phosphoric acid (25 ml) preheated at 100 °C for 0.5 h were added the methyl ether of the dimethylphenol (0.1 mol) and the αβ-unsaturated acid (0.1 mol). Heating was continued for 4.5 h more at 100 °C with occasional shaking. The mixture was poured into ice–water (500 ml), then extracted with chloroform. The extracts were washed with sodium hydrogen carbonate solution and water, and dried (Na_2SO_4). Removal of the solvent left a dark semi-solid, which was chromatographed over alumina. The yields of the indanones in most cases ranged between 30 and 35%. They readily formed crystalline 2,4-dinitrophenylhydrazones.

6-Methoxy-5-methylindan-1-one (1) had m.p. 108° [from light petroleum (b.p. 40—60 °C)], yellow needles, $\nu_{max.}$ (CH_2Cl_2) 1 700 cm^{-1} (cyclopentenone); δ ($CDCl_3$) 2.2 (3 H, s, CH_3), 2.65 (2 H, t, CH_2), 3.1 (2 H, t, CH_2), 3.9 (3 H, s, OCH_3), 6.85 (1 H, s, ArH), and 7.55 (1 H, s, ArH) (Found: C, 74.9; H, 7.0. Calc. for $C_{11}H_{12}O_2$: C, 75.0; H, 6.8%); 2,4-dinitrophenylhydrazone, m.p. 281° (Found: N, 15.6. Calc. for $C_{17}H_{16}N_4O_5$: N, 15.7%).

6-Methoxy-4,5-dimethylindan-1-one (3),[12] eluted with light petroleum (b.p. 40—60 °C), had m.p. 142—144° [yellow needles from light petroleum (b.p. 40—60 °C)], $\nu_{max.}$ (Nujol) 1 692 cm^{-1} (cyclopentenone), δ (CCl_4) 2.25 (6 H, s, 2 CH_3), 2.7 (2 H, m, CH_2), 2.8 (2 H, t, CH_2), 3.85 (3 H, s, OCH_3), and 7.05 (1 H, s, ArH) (Found: C, 75.5; H, 7.8. Calc. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.6%); 2,4-dinitrophenylhydrazone, m.p. >333° (Found: N, 14.9. Calc. for $C_{18}H_{18}N_4O_5$: N, 15.0%).

5-*Methoxy*-2,6,7-*trimethylindan*-1-*one* (4), eluted with light petroleum (b.p. 40—60 °C) as yellow needles, had m.p. 92—94° [from light petroleum (b.p. 40—60 °C)], $\nu_{max.}$ (CH_2Cl_2) 1 700 cm^{-1} (cyclopentenone), δ ($CDCl_3$) 1.4 (3 H, d, 2-CH_3), 2.15 (3 H, s, CH_3), 2.63 (3 H, s, CH_3), 2.75 (2 H, d, CH_2, *J* 8 Hz), 3.2—3.4 (1 H, m, CH), 3.9 (3 H, s, OCH_3), and 6.75 (1 H, s, ArH) (Found: C, 76.9; H, 7.9. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.8%); 2,4-*dinitrophenylhydrazone*, m.p. 241—242° (Found: N, 15.0. $C_{19}H_{20}N_4O_5$ requires N, 14.6%).

5-*Methoxy*-4,6,7-*trimethylindan*-1-*one* (5), eluted with light petroleum (b.p. 40—60 °C), gave yellow needles, m.p. 80—82° [from light petroleum (b.p. 40—60 °C)], $\nu_{max.}$ (KBr) 1 700 cm^{-1} (cyclopentenone), δ ($CDCl_3$) 1.3 (3 H, d, 3-CH_3), 2.19 (3 H, s, CH_3), 2.65 (3 H, s, CH_3), 2.8 (2 H, d, CH_2, *J* 5 Hz), 3.2—3.4 (1 H, m, CH), 3.9 (3 H, s, OCH_3), and 6.75 (1 H, s, ArH) (Found: C, 76.9; H, 7.7. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.8%), 2,4-*dinitrophenylhydrazone*, m.p. 262—264° (Found: N, 14.9. $C_{19}H_{20}N_4O_5$ requires N, 14.6%).

5-*Methoxy*-3,3,6,7-*tetramethylindan*-1-*one* (6), eluted with light petroleum (b.p. 40—60 °C), was a yellow oil, b.p. 155—158° at 3.3 mmHg, $\nu_{max.}$ (CH_2Cl_2) 1 720 cm^{-1} (cyclopentenone), δ (CCl_4) 1.39 (6 H, s, gem Me_2), 2.15 (3 H, s, CH_3), 2.4 (2 H, s, CH_2), 2.6 (3 H, s, CH_3), 3.95 (3 H, s, OCH_3), and 6.7 (1 H, s, ArH) (Found: C, 77.1; H, 8.3. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.2%); 2,4-*dinitrophenylhydrazone*, m.p. 257—259° (Found: N, 13.9. $C_{20}H_{22}N_4O_5$ requires N, 14.0%).

5-*Methoxy*-6,7-*dimethyl*-3-*phenylindan*-1-*one* (7), eluted with light petroleum (b.p. 40—60 °C)–benzene (1 : 9), gave yellow needles, m.p. 112—113° [from light petroleum (b.p. 40—60 °C)], $\nu_{max.}$ (KBr) 1 700 cm^{-1} (cyclopentenone), δ ($CDCl_3$) 2.05 (3 H, s, CH_3), 2.65 (3 H, s, CH_3), 3.0 (2 H, d, CH_2), 3.7 (3 H, s, OCH_3), 4.4 (1 H, m, CH), 6.45 (1 H, s, ArH), and 7.1 (5 H, m, Ph) (Found: C, 80.8; H, 6.9. $C_{18}H_{18}O_2$ requires C, 81.2; H, 6.8%); 2,4-*dinitrophenylhydrazone*, m.p. 248—249° (Found: N, 12.7; $C_{24}H_{22}N_4O_5$ requires N, 12.6%).

5-*Methoxy*-6,7-*dimethyl*-3-(3-*pyridyl*)*indan*-1-*one* (8), eluted with light petroleum (b.p. 40—60 °C), gave needles, m.p. 121—123° [from light petroleum (b.p. 100—120 °C)], $\nu_{max.}$ (CH_2Cl_2) 1 700 cm^{-1} (cyclopentenone), δ ($CDCl_3$) 2.15 (3 H, s, CH_3), 2.65 (3 H, s, CH_3), 3.1 (2 H, d, CH_2, *J* 8 Hz), 3.75 (3 H, s, OCH_3), 4.35—4.55 (1 H, m, CH), 6.48 (1 H, s, ArH), 7.35br (2 H, s, β- and γ-pyridine protons), and 8.4br (2 H, s, pyridine α-protons) (Found: C, 76.0; H, 6.7; $C_{17}H_{17}NO_2$ requires: C, 76.4; H, 6.4%); 2,4-*dinitrophenylhydrazone*, m.p. 237—240° (Found: N, 15.6. $C_{23}H_{21}N_5O_5$ requires N, 15.6%).

6-Methoxy-4,7-dimethylindan-1-one (9),[13] eluted with benzene, gave yellow needles, m.p. 162—164° [from benzene–light petroleum (b.p. 40—60 °C)], $\nu_{max.}$ (Nujol) 1 692 cm^{-1} (cyclopentenone), δ ($CDCl_3$) 2.25 (3 H, s, CH_3), 2.5 (3 H, s, CH_3), 2.65 (2 H, t, CH_2), 2.7 (2 H, t, CH_2), 3.9 (3 H, s, OCH_3), and 6.95 (1 H, s, ArH) (Found: C, 76.1; H, 7.4. Calc. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.6%), 2,4-dinitrophenylhydrazone, m.p. 286—288° (Found: N, 15.2. Calc. for $C_{18}H_{18}N_4O_5$: N, 15.0%).

6-*Methoxy*-2,4,7-*trimethylindan*-1-*one* (10), eluted with light petroleum (b.p. 40—60 °C), gave yellow needles, m.p. 69—71° [from light petroleum (b.p. 40—60 °C)], $\nu_{max.}$ (KBr) 1 700 cm^{-1} (cyclopentenone), δ ($CDCl_3$) 1.3 (3 H, d, 2-CH_3), 2.3 (3 H, s, CH_3), 2.6 (3 H, s, CH_3), 2.75 (2 H, d, CH_2), 3.2—3.4 (1 H, m, CH), 3.8 (3 H, s, OCH_3), and 6.9 (1 H, s, ArH) (Found: C, 76.5; H, 7.7. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.8%); 2,4-*dinitrophenylhydrazone*, m.p. 218—219° (Found: N, 14.2. $C_{19}H_{20}N_4O_5$ requires N, 14.6%).

5-*Methoxy*-3,4,7-*trimethylindan*-1-*one* (11), eluted with benzene, gave yellow needles, m.p. 63—65° [from light petroleum (b.p. 40—60°)], $\nu_{max.}$ (CH_2Cl_2) 1 700 cm^{-1} (cyclopentenone), δ ($CDCl_3$) 1.4 (3 H, d, 3-CH_3), 2.2 (3 H, s, CH_3), 2.65 (3 H, s, CH_3), 2.75 (2 H, d, CH_2), 3.2—3.4 (1 H, m, CH), 3.95 (3 H, s, OCH_3), and 6.85 (1 H, s, ArH) (Found: C, 76.5; H, 8.0. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.8%); 2,4-*dinitrophenylhydrazone*, m.p. 262—264° (Found: N, 14.9. $C_{19}H_{20}N_4O_5$ requires N, 14.6%).

5-*Methoxy*-3,3,4,7-*tetramethylindan*-1-*one* (12), eluted with light petroleum (b.p. 40—60 °C), gave a yellow oil, b.p 175—178° at 2—2.5 mmHg, $\nu_{max.}$ (CH_2Cl_2) 1 720 cm^{-1} (cyclopentenone), δ ($CDCl_3$) 1.4 (6 H, s, *gem*-Me_2), 2.2 (3 H, s, CH_3), 2.4 (2 H, s, CH_2), 2.65 (3 H, s, CH_3), 3.95 (3 H, s, OCH_3), and 6.7 (1 H, s, ArH) (Found: C, 77.1; H, 8.1. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.2%); 2,4-*dinitrophenylhydrazone*, m.p. 261—263° (Found: N, 13.8. $C_{20}H_{22}N_4O_5$ requires N, 14.1%).

5-*Methoxy*-4,7-*dimethyl*-3-*phenylindan*-1-*one* (13), eluted with light petroleum (b.p. 40—60 °C)–benzene (1 : 9), gave needles, m.p. 152—154° [from light petroleum (b.p. 40—60 °C)], $\nu_{max.}$ (Nujol) 1 720 cm^{-1} (cyclopentenone), δ ($CDCl_3$) 1.85 (3 H, s, CH_3), 2.75 (3 H, s, CH_3), 3.1 (2 H, d, CH_2), 3.85 (3 H, s, OCH_3), 4.5 (1 H, m, CH), 6.75 (1 H, s, ArH), and 7.25 (5 H, m, Ph) (Found: C, 80.8; H, 7.1. $C_{18}H_{18}O_2$ requires C, 81.2; H, 6.8%); 2,4-*dinitrophenylhydrazone*, m.p. 273—275° (Found: N, 12.6. $C_{24}H_{22}N_4O_5$ requires N, 12.6%).

4-*Methoxy*-6,7-*dimethylindan*-1-*one* (14), eluted with benzene, gave yellow needles, m.p. 123—125° [from light petroleum (b.p. 40—60 °C)], $\nu_{max.}$ (Nujol) 1 692 cm^{-1} (cyclopentenone), δ ($CDCl_3$) 2.3 (3 H, s, CH_3), 2.5 (3 H, s, CH_3), 2.7 (2 H, t, CH_2), 2.8 (2 H, t, CH_2), 3.85 (3 H, s, OCH_3), and 6.8 (1 H, s, ArH) (Found: C, 75.4; H, 7.6. $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.6%), 2,4-*dinitrophenylhydrazone*, m.p. >310° (Found: N, 14.9. $C_{18}H_{18}N_4O_5$ requires N, 15.0%).

4-*Methoxy*-2,6,7-*trimethylindan*-1-*one* (15) had m.p. 80—81° [from light petroleum (b.p. 40—60 °C)] (yellow needles), $\nu_{max.}$ (CH_2Cl_2) 1 710 cm^{-1} (cyclopentenone), δ ($CDCl_3$) 1.3 (3 H, d, 2-CH_3), 2.25 (6 H, s, 6- and 7-CH_3), 2.7 (2 H, d, CH_2), 3.2—3.4 (1 H, m, CH), 3.9 (3 H, s, OCH_3), and 6.8 (1 H, s, ArH) (Found: C, 76.5; H, 7.8. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.8%); 2,4-*dinitrophenylhydrazone*, m.p. 238—240° (Found: N, 14.9. $C_{19}H_{20}N_4O_5$ requires N, 14.6%).

7-*Methoxy*-2,4,5-*trimethylindan*-1-*one* (16), eluted with light petroleum (b.p. 40—60 °C), gave yellow needles, m.p. 84—86° [from light petroleum (b.p. 40—60°)], $\nu_{max.}$ (CH_2Cl_2) 1 700 cm^{-1} (cyclopentenone), δ ($CDCl_3$) 1.3 (3 H, d, 2-CH_3), 2.3 (3 H, s, CH_3), 2.6 (3 H, s, CH_3), 3.1 (2 H, d, CH_2), 3.3—3.4 (1 H, m, CH), 3.95 (3 H, s, OCH_3), and 6.9 (1 H, s, ArH) (Found: C, 76.3; H, 7.9. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.8%); 2,4-*dinitrophenylhydrazone*, m.p. 218—220° (Found: N, 14.2. $C_{19}H_{20}N_4O_5$ requires N, 14.6%).

7-*Methoxy*-3,4,5-*trimethylindan*-1-*one* (17), eluted with ethyl acetate, was a yellow oil, b.p. 80—82° at 2—2.5 mmHg (Found: C, 76.3; H, 7.9; $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.8%); 2,4-*dinitrophenylhydrazone*, m.p. 211—213° (Found: N, 14.2. $C_{19}H_{20}N_4O_5$ requires N, 14.6%).

7-*Methoxy*-3,3,4,5-*tetramethylindan*-1-*one* (18), eluted with ethyl acetate, was a yellow oil, b.p. 84—86° at 3—3.5 mmHg (Found: C, 77.3; H, 8.5. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.2%); 2,4-*dinitrophenylhydrazone*, m.p. 247—250° (Found: N, 13.8. $C_{20}H_{22}N_4O_5$ requires N, 14.1%).

7-*Methoxy*-4,5-*dimethyl*-3-*phenylindan*-1-*one* (19), eluted with light petroleum (b.p. 40—60 °C)–benzene (1 : 2), was a yellow oil, b.p. 220—225° at 3—3.5 mmHg (Found: C, 81.6; H, 6.5. $C_{18}H_{18}O_2$ requires C, 81.2; H, 6.8%); 2,4-*dinitrophenylhydrazine*, m.p. 263—265° (Found: N, 12.6. $C_{24}H_{22}N_4O_3$ requires N, 12.6%).

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