pillets; 1, 5, 12, 17 on Perkin-Elmer 137 B infracord and other compounds were recorded on Backmann IR-4 spectrophotometer as mulls in Nujol, equipped with a rock salt prism as the monochromator and calibrated by standard methods. The ultraviolet spectra were recorded on a Hilger and Watts Ultrascan spectrophotometer using 10-mm matched quartz cells.

ACKNOWLEDGMENT

The authors are grateful to Jagdish Shankar, B.A.R.C., Bombay, for permitting one of them (D.R.A.) to work as a guest worker. They are obliged to T. R. Govindachari, CIBA laboratory, for the microanalysis of the compounds. Thanks are due to the Principal, Government College of Science, Raipur, for facilities.

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RECEIVED for review June 16, 1971. Accepted October 23, 1971. Work partially supported by Ravishankar University.

Reactions of Primary Amines with 2-Acyl-1,3-indandiones

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Ethyl- and isopropylamine react with various 2-acyl-1,3-indandiones to form the corresponding 2[1-(alkylimino)alkyl]-1,3-indandiones or 3-alkylimino-2-acyl-1-indanones. Tertiary butylamine forms the tertiary butyl ammonium salts of 2-acyl-3-hydroxyindones. Spectral data (infrared, ultraviolet, nuclear magnetic resonance) are given for the compounds.

As a continuation of our work on the condensation of amines with 2-diphenylacetyl-1,3-indandione (*1*, *5*), we investigated the reactions of primary amines with 2-acyl-1,3-indandiones having straight and branched-chain acyl groups.

Ethyl- and isopropylamine react with 2-acyl-1,3-indandiones to give the imines **1** when 2-propionyl-1,3-indandione is used and imines **2** when 2-isobutyryl- and 2-pyvalyl-1,3-indandione are used (Figure 1). The structures of these compounds are based on elemental analyses and spectral data. The uv absorption peaks of imines **1** are slightly shifted bathochromically in comparison with those of imines **2**, and the extinction coefficients at each peak are similar, with the exception of the extinction coefficients at 325–30 mμ, which increase from 5000 for compounds **2** to 31,000 for compounds **1**.

The similarities of the uv spectra of imines **2** with that of 2-(diphenylacetyl)-3-isopropylamino-1-indanone, prepared by Bechara (*1*) from 2-(diphenylacetyl)-1,3-indandione, 1-hydrazone, and excess isopropylamine, support the assigned position of the imino group in compounds **2**. This structure proof of imines **2** is obviously an indirect proof for the structure of imines **1**, since the latter can have only the alternative structure.

The positions of the imino groups in these compounds are further substantiated by the fact that four equivalent aromatic protons at δ7.7 ppm are present in the nmr spectra of imines **1**, and three equivalent aromatic protons at 7.6, along with one nonequivalent or deshielded proton at 7.8, are present in imines **2** (*4*).

Tertiary butylamine reacts with 2-propionyl-, 2-isobutyryl-, and 2-pyvalyl-1,3-indandione to give the tertiary butyl ammonium salts of the corresponding 2-acyl-3-hydroxyindones (**3a–c**) (Figure 1). The structures of these compounds are based on elemental analyses and are consistent with the ir and nmr spectra.

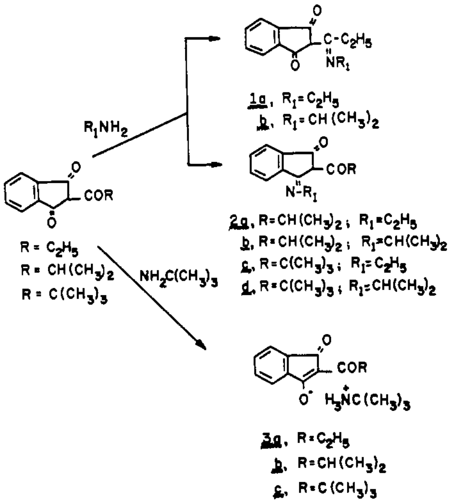

Figure 1. Reactions of primary amines with 2-acyl-1,3-indandiones

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Table I. Indandiones (1a, b) and Indanones (2a-d)[a]

Compound	%	Mp, °C
1a	45	105-6
b	38	65.5-67
2a	38	107-8
b	40	134-5
c	30	155-6
d	30	147-8

[a] Elemental analyses (C, H, and N) of the compounds listed have been submitted for review and are in agreement with the theoretical values.

Table II. Tertiary Butyl Ammonium Salts of 2-Acyl-3-hydroxyindones (3a, b, c)[a]

Compound	Refluxing time, hr	Yield, %	Mp, °C
3a	14	35.0	196-8[b]
b	20	35.0	224-5[c]
c	24	37.5	202-3[d]

[a] Elemental analyses (C, H, and N) of the compounds listed have been submitted for review and are in agreement with the theoretical values. [b] Recrystallized 3 times from methylcyclohexane methanol (90:10). [c] Recrystallized first from methylcyclohexane methanol (90:10) then from a minimum amount of methanol. [d] Recrystallized twice from a minimum amount of ethanol.

EXPERIMENTAL

Melting points were determined on a modified Fisher melting point apparatus. The uv spectra were obtained in ethanol using a Cary spectrophotometer, Model 13. The ir spectra were measured on a Perkin-Elmer Model 257 spectrophotometer as Nujol mulls between sodium chloride plates. The nmr spectra were obtained on a Varian Associates Spectrometer Model A 60, with TMS as internal standard and dimethylsulfoxide as solvent. Elemental analyses were performed by Wyeth Laboratory, Radnor, Pa.

2-[1-(Ethylimino)propyl]-1,3-indandione (1a), 3-Ethylimino-2-isobutyryl- and 3-Ethylimino-2-pyvalyl-1-indanones (2a and 2c). The general procedure used was as follows. A 250-ml pressure bottle was charged with the appropriate 2-acyl-1,3-indandione (*2*) (0.05 mol), methanol (75 ml), type 4A Molecular Sieve (20 grams) and ethylamine (0.5 mol), quickly sealed, cooled by means of an ice bath until the charge remained at room temperature without any further cooling. After 24 hr (48 hr for compounds **2a** and **2c**), the reaction mass was filtered and the filtrate concentrated to about 25 ml and cooled in an ice bath. The crystals were collected by filtration and dried at 30° overnight to give yellow needles. An analytical sample was prepared by "dry column" chromatography (*3*), followed by recrystallization from methylcyclohexane. The yields and mp of compounds **1a, 2a,** and **2c** are listed in Table I. Compound **1a**: uv λ_{max} mμ ($\epsilon \times 10^{-3}$) 226 (20.0), 282 (13.1), 293 (29.5), 319 (22.1), and 332 (32.4); ir 1680 (C=N), 1635 (C=O in conjugation with C=C), 1580, (C=O, C=N, caused by intramolecular bonding), 1600 and 1470 cm^{-1} (C=C for aromatic hydrocarbons); nmr δ1.1, 1.25, 1.35 (t, 3H); 1.2, 1.3, 1.45 (t, 3H); 2.9, 3.0, 3.15, 3.25 (q, 2H); 3.4, 3.5, 3.65, 3.75 (q, 2H); 7.7 (s, 4H arom); 11.9 ppm (1H enolic, D_2O exchanged). Compound **2a**: uv λ_{max} mμ ($\epsilon \times 10^{-3}$) 230 (24.3), 265 (22.6), 278 (25.1), 288 (30.9), and 325 (5.8); ir 1670 (C=N), 1615 (C=O in conjugation with C=C), 1570 (C=O, C=N, caused by intramolecular bonding), 1595 and 1480 cm^{-1} (C=C for aromatic hydrocarbons); nmr δ1.05, 1.15 (d, 6H); 1.3, 1.45, 1.65 (t, 3H); 3.7 to 4.3 (sym. heptet, 1H); 2.5-2.7 (q, 2H); 7.6 (s, 3H arom.); 7.8 (s, 1H arom); 11.9 ppm (1H enolic, D_2O exchanged). Compound **2c** shows uv and ir spectra similar to those of compound **2a**.

2-[1-(Isopropylimino)propyl]-1,3-indandione (1b), 3-Isopropylimino-2-isobutyryl-, and 3-Isopropylimino-2-pyvalyl-1-indanones (2b and 2d). The general procedure was as follows. A mixture of the appropriate 2-acyl-1,3-indandione (*2*) (0.05 mol), methanol [75 ml (for compound **2d**: 100 ml)], type 4A Molecular Sieve (20 grams) and isopropylamine (0.5 mol) was refluxed for 12 hr. The reaction mixture was then worked up as described in the above method to give yellow needles. The yields and mp of these compounds are listed in Table I. Compound **1b**, uv λ_{max} mμ ($\epsilon \times 10^{-3}$) 226 (20.2), 282 (12.6), 293 (29.2), 319 (21.0), and 332 (31.4); ir similar to that of compound **1a**; nmr δ1.1, 1.25 (masked) (t, 3H); 1.3, 1.4 (d, 6H); 2.9, 3.0, 3.15, and 3.25 (q, 2H); 3.8-4.3 (sym. heptet, 1H); 7.7 (s, 4H arom); 11.9 ppm (1H enolic, D_2O exchanged).

Compound **2b**: uv λ_{max} mμ ($\epsilon \times 10^{-3}$) 230 (23.2), 265 (22.6), 278 (24.7), 288 (30.1), and 325 (5.9). [2-Diphenylacetyl-3-isopropylimino-1-indanone (**1**) 228 (28.7) 265 (19.8), 278 (22.8), 288 (33.6), and 325 (11.9).] Ir similar to that of compound **2a**; nmr δ1.0, 1.15 (d, 6H); 1.4, 1.55 (d, 6H); 3.5 to 4.0 (sym. heptet, 1H); 4.3-4.8 (sym. heptet, 1H); 7.6 (s, 3H arom); 7.8 (s, 1H arom) and 11.9 ppm (1H enolic, D_2O exchanged). Compound **2d** shows uv and ir spectra similar to those of compound **2b**.

Tertiary Butylammonium Salts 3a, 3b, 3c. A mixture of the appropriate 2-acyl-1,3-indandione (*2*) (0.05 mol), methanol (75 ml), type 4A Molecular Sieve (20 grams) and tertiary butylamine (0.5 mol) was reacted and worked up as described above for compound **2b** to give yellow crystals. The yields and mp are listed in Table II. Compound **3a**; uv λ_{max} mμ ($\epsilon \times 10^{-3}$) 220 (22.0), 245 (10.7), 281 (29.7), 310 (11.4), 322 (12.0); ir 2700, 2620, and 2520 (NH stretching of tertiary amine salts); 1689 (C=O), 1625 (C=O in conjugation with C=C); 1585 cm^{-1} (C=O caused by intramolecular bonding); nmr δ0.9, 1.0, 1.15 (t, 3H), 1.35 (s, 9H), 2.7, 2.8, 2.95, 3.05 (q, 2H), 7.45 (s, 4H arom), 7.8 to 8.3 ppm (br 3H, D_2O exchanged, assigned to $\overset{+}{N}H_3$). The enolic proton at 11.9 ppm present in the spectra of compounds **1** and **2** was not observed. Compounds **3b** and **3c** show uv and ir spectra similar to those of compound **3a**.

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RECEIVED for review June 21, 1971. Accepted December 9, 1971.