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SPECTROSCOPIC PROPERTIES AND GAS CHROMATOGRAPHIC BEHAVIOUR OF ARYL β-DIKETONES AND SELECTED CHELATES

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SUMMARY

IR and nuclear magnetic resonance spectra and gas chromatographic data are reported for a series of 33 aryl β-diketones. Elution of the intact ligands is confirmed and predictable from thermoanalytical data. Chromatographic behaviour of chelates derived from these ligands shows several adverse phenomena.

INTRODUCTION

In the analytical applications of gas chromatography to trace metal analyses, β-diketones and β-keto enamines have been the principal ligands employed. Typical procedures involve reaction of excess ligand with the sample which has probably undergone some pretreatment, then injection of the resulting chelate solution into the chromatograph. Since retention time and peak symmetry of the excess ligand can ultimately determine the success or failure of the analysis a knowledge of the chromatographic behaviour of the ligands becomes essential. Even when complete removal of excess ligands is unavoidable, as with a fluorinated β-diketone and electron-capture detection, it is still necessary to consider the chromatographic behaviour of the free ligand because one of the decomposition products of metal chelates may be the parent ligand[1]. This means that the thermal stability and volatility of the ligands, as well as those of the chelates, becomes an important consideration.

Although considerable data on the thermal properties of metal chelates have amassed, it is somewhat surprising that thermoanalytical studies of the parent ligands have been limited to an investigation[2] of the relationship between boiling point and enthalpy of vapourisation of a series of β-diketones. This situation exists despite the simplification afforded by the absence of a central metal ion in ligands (and, consequently, where the extent of hydration and polymerisation, size and orbital structure of the central metal ion can be completely ignored) to highlight the intrinsic volatility

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or stability characteristic of the ligand grouping. Of more importance here is decomposition of the chelate and any relationship to structural weakness in the parent β-diketone.

This paper describes the spectroscopic, chromatographic and thermoanalytical properties of a series of 33 aryl β-diketones considered as potential reagents for analytical application. The β-diketones can be considered as derivatives of 1-phenylbutane-1,3-dione, 4,4,4-trifluoro-1-phenylbutane-1,3-dione, 1-phenyl-4,4-dimethylpentane-1,3-dione and 1,3-diphenylpropane-1,3-dione, with substituents in the aromatic ring including alkyl, fluoroalkyl and halide groups. For purposes of comparison, several β-keto enamines containing an aromatic substituent are also examined.

EXPERIMENTAL

IR spectra

IR spectra* were obtained on a Hitachi EP I IR spectrophotometer in the range 4000–400 cm^{-1}. Halocarbon mulls (4000–1600 cm^{-1}) and potassium bromide discs (4000–400 cm^{-1}) were used jointly.

Nuclear magnetic resonance (NMR) spectra

Proton spectra were obtained on a JEOL-JNM-4H-100 instrument in carbon tetrachloride using a probe temperature of 38°C and a concentration of 0.15 mol fraction of the solute. The proton resonances, given for each β-diketone are quoted in ppm (δ scale) relative to tetramethylsilane as internal standard. Individual resonances of interest are: enolic proton resonance (δ_{OH}), methine proton resonance (δ_{CH}), and aromatic proton resonances (δ_{Ar}).

Thermal analyses

Thermal data were collected, as previously described[3], on an instrument (Rigaku, Thermoflex M8076) combining both thermogravimetry, (TG) and differential thermal analysis (DTA). The DTA data are presented as the temperatures corresponding to peak maxima and to the range of the various energy transitions. For the β-diketones the DTA consisted of a broad ramping endotherm followed by rapid return to the baseline, characteristic of volatilisation (V) processes, and preceded by a sharp fusion endotherm (F) in the case of solid β-diketones. By contrast, the DTA for the β-keto enamines exhibited a fusion endotherm followed by peaks attributable to decomposition (D) and, in some cases, simultaneous volatilisation.

Gas chromatography

An instrument equipped with flame ionization detectors was used for the collection of retention data, t'_R, which are expressed relative to compound 5 (t'_R = 1.00, retention time, = 4.0 min) and were collected as follows. The β-diketone (1 μl; 10 mg/ml in methanol) was injected directly onto a glass column (1.5 m × 4 mm I.D.) packed with SE-30 (10% w/w on Chromosorb W; AW-DMCS; 80–100 mesh). Pure nitrogen, as carrier gas, was maintained at 60 ml/min and the oven temperature was maintained at 115°C.

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* Spectra have been lodged with the Editor in microfiche form.

Synthesis of ligands

β-Diketones* were prepared by Claisen condensation of the appropriate ethyl ester and ketone with sodium hydride as condensing agent or, for compounds 1–4, 6, 8, 9, 14 and 15, using sodium *tert.*-butoxide[4]. Liquid compounds were purified by fractional vacuum distillation and solids by recrystallization from aqueous ethanol to yield white solids, except for compound 32 which was a yellow solid.

(1) 1-Pentafluorophenyl-4,4,4-trifluorobutane-1,3-dione (HF_5bta). Yield 82%. b.p. 71–72°C (1.4 mmHg). t'_R = 0.48. DTA: V, 140°C (63–152). δ_{CH}, 6.25; δ_{OH}, 13.67. (Found: C, 39.1; H, 0.7. Calculated for $C_{10}H_2F_8O_2$: C, 39.2; H, 0.7%).

(2) 1-Pentafluorophenyl-4,4,5,5,5-pentafluoropentane-1,3-dione (HF_5bpb). Yield 79%. b.p. 84–85°C (6.8 mmHg). t'_R = 0.55. DTA: V, 142°C (61–155). δ_{CH}, 6.37; δ_{OH}, 14.08. (Found: C, 37.4; H, 0.5. Calculated for $C_{11}H_2F_{10}O_2$: C, 37.1; H, 0.6%).

(3) 1-(2′,4′-Difluorophenyl)-4,4,4-trifluorobutane-1,3-dione (H2,4F_2bta). Yield 84%. m.p. 29°C. t'_R = 0.70. DTA: F, 29°C (21–40), V 153°C (74–161). δ_{CH}, 6.58; δ_{OH}, 14.15; δ_{Ar}, 6.91, 7.02, 7.12, 7.93, 8.02, 8.10, 8.19. (Found: C, 47.4; H, 1.9. $C_{10}H_5F_5O_2$ requires C, 47.6; H, 2.0%).

(4) 1-(2′-Trifluoromethylphenyl)-4,4,4-trifluorobutane-1,3-dione (HoCF_3bta). Yield 84%. b.p. 85°C (2.2 mmHg). t'_R = 0.74. DTA: V, 155°C (74–162). δ_{CH}, 6.29; δ_{OH}, 14.07; δ_{Ar}, 7.63 (sharp singlet). (Found: C, 46.8; H, 2.0. $C_{11}H_6F_6O_2$ requires C, 46.5; H, 2.1%).

(5) 1-Phenyl-4,4,4-trifluorobutane-1,3-dione (Hbta). Yield 68%. m.p. 39°C (lit.[5] 40°C). t'_R = 1.00. DTA: F, 38°C (29–44) V, 153°C (81–172). δ_{CH}, 6.48; δ_{OH}, 15.00; δ_{Ar}, 7.51, 7.82. (Found: C, 55.9; H, 3.2. Calculated for $C_{10}H_7F_3O_2$: C, 55.6; H, 3.2%).

(6) 1-(3′-Trifluoromethylphenyl)-4,4,4-trifluorobutane-1,3-dione (HmCF_3bta). Yield 79%. b.p. 80–81°C (0.8 mmHg). m.p. 38°C. t'_R = 1.00. DTA: F, 38°C (31–49). V, 160°C (83–172). δ_{CH}, 6.54; δ_{OH}, 14.75; δ_{Ar}, 6.60, 6.72, 6.78, 8.03, 8.15. (Found: C, 46.3; H, 1.9. $C_{11}H_6F_6O_2$ requires C, 46.5; H, 2.1%).

(7) 1-(4′-Fluorophenyl)-4,4,4-trifluorobutane-1,3-dione (HpFbta). Yield 68%. m.p. 39°C (lit.[6] 40–42°C). t'_R = 1.01. DTA: F, 38°C (29–46). V, 157°C (88–170). δ_{CH}, 6.56; δ_{OH}, 14.94; δ_{Ar}, 7.10, 7.25, 7.40, 8.50, 8.60, 8.69. (Found: C, 51.1; H, 2.4. Calculated for $C_{10}H_6F_4O_2$: C, 51.2; H, 2.6%).

(8) 1-(4′-Fluorophenyl)-4,4,5,5,5-pentafluoropentane-1,3-dione (HpFbpb). Yield 78%. m.p. 51°C. t'_R = 1.11. DTA: F, 51°C (48–59). V, 157°C (90–169). δ_{CH}, 6.55; δ_{OH}, 15.10; δ_{Ar}, 7.02, 7.17, 7.31, 7.85, 7.94, 8.01, 8.10. (Found: C, 46.3; H, 2.0. $C_{11}H_6F_6O_2$ requires C, 46.5; H, 2.1%).

(9) 1-(4′-Fluorophenyl)-4,4,5,5,6,6,6-heptafluorohexane-1,3-dione (HpFbhp). Yield 85%. m.p. 41°C. t'_R = 1.27. DTA: F, 41°C (28–46). V, 157°C (95–169). δ_{CH}, 6.52; δ_{OH}, 14.80; δ_{Ar}, 7.02, 7.17, 7.31, 7.83, 7.95, 8.05, 8.15. (Found: C, 43.0; H, 1.8. $C_{12}H_6F_8O_2$ requires C, 43.1; H, 1.8%).

(10) 1-(2′,5′-Dimethylphenyl)-4,4,4-trifluorobutane-1,3-dione (H2,5Me_2bta).

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* Ligands are identified by abbreviations derived from trivial names. Thus, while Hba refers to benzoylacetone, Hbta to benzoyltrifluoroacetone, Hbpb to benzoylpentafluorobutanone, Hbhp to benzoylheptafluoropentanone, Hdbm to dibenzoylmethane and Hbpm to benzoylpivaloylmethane, all other abbreviations refer to ring-substituted derivatives of one of these compounds. For example, HpClba refers to *p*-chlorobenzoylacetone, HmCF_3bta to *m*-trifluoromethylbenzoyltrifluoroacetone and Hp^{t}Bubta to *p*-*tert.*-butylbenzoyltrifluoroacetone.

Yield 59%. b.p. 91–92°C (12 mmHg). t'_R = 2.25. DTA: V, 171°C (89–186). δ_{CH}, 6.29; δ_{OH}, 14.58; δ_{Ar}, 7.05, 7.14, 7.35. (Found: C, 59.4; H, 4.5. $C_{12}H_{11}F_3O_2$ requires C, 59.0; H, 4.5%).

(11) 1-(2′-Chlorophenyl)-4,4,4-trifluorobutane-1,3-dione (HoClbta). Yield 67%. b.p. 102–104°C (3.2 mmHg). t'_R = 2.26. DTA: V, 172°C (92–183). δ_{CH}, 6.55; δ_{OH}, 14.35; δ_{Ar}, 7.32, 7.42, 7.59, 7.65, 7.73. (Found: C, 48.0; H, 2.2; $C_{10}H_6ClF_3O_2$ requires C, 47.9; H, 2.4%).

(12) 1-Pentafluorophenylbutane-1,3-dione (HF_5ba). Yield 39%. b.p. 171–173°C (52 mmHg). t'_R = 0.86. DTA: V, 167°C (88–208). δ_{CH}, 6.08; δ_{OH}, 14.19. (Found: C, 47.8; H, 2.2. $C_{10}H_5F_5O_2$ requires C, 47.6; H, 2.0%).

(13) 1-(4′-Methylphenyl)-4,4,4-trifluorobutane-1,3-dione (HpMebta). Yield 64%. m.p. 42°C (lit.[5] 42°C). t'_R = 2.00. DTA: F, 43°C (38–51). V, 175°C (103–186). δ_{CH}, 6.48; δ_{OH}, 15.07, δ_{Ar}, 7.17, 7.32, 7.73, 7.88. (Found: C, 57.0; H, 3.9. Calculated for $C_{11}H_9F_3O_2$: C, 57.4; H, 3.9%).

(14) 1-(2′,4′-Dimethylphenyl)-4,4,4-trifluorobutane-1,3-dione (H2,4Me_2bta). Yield 78%. b.p. 89–91°C (0.5 mmHg). t'_R = 2.52. DTA: V, 177°C (86–191). δ_{CH}, 6.30; δ_{OH}, 14.67; δ_{Ar}, 6.98, 7.10, 7.42, 7.56. (Found: C, 59.1; H, 4.6. $C_{12}H_{11}F_3O_2$ requires C, 59.0; H, 4.5%).

(15) 1-(3′-Chlorophenyl)-4,4,4-trifluorobutane-1,3-dione (HmClbta). Yield 82%. m.p. 38°C (lit.[5] 39°C). t'_R = 2.19. DTA: F, 38°C (30–45). V, 177°C (93–196). δ_{CH}, 6.50; δ_{OH}, 14.83; δ_{Ar}, 7.40, 7.52, 7.60, 7.75, 7.85. (Found: C, 47.8; H, 2.3. Calculated for $C_{10}H_6ClF_3O_2$; C, 47.9; H, 2.4%).

(16) 1-(4′-Chlorophenyl)-4,4,4-trifluorobutane-1,3-dione (HpClbta). Yield 69%. m.p. 52°C (lit.[5] 61°C). t'_R = 2.00. DTA: F, 53°C (46–65). V, 180°C (93–190). δ_{CH}, 6.50; δ_{OH}, 14.88; δ_{Ar}, 7.30, 7.46, 7.72, 7.97. (Found: C, 47.8; H, 2.4. Calculated for $C_{10}H_6ClF_3O_2$: C, 47.9; H, 2.4%).

(17) 1-(4′-Chlorophenyl)-4,4,5,5,5-pentafluoropentane-1,3-dione (HpClbpb). Yield 70%. m.p. 69°C. t'_R = 2.82. DTA: F, 69°C (60–77). V, 176°C (105–181). δ_{CH}, 6.56; δ_{OH}, 15.00; δ_{Ar}, 7.39, 7.52, 7.81, 7.96. (Found: C, 43.7; H, 1.8. $C_{11}H_6ClF_5O_2$ requires C, 43.9; H, 2.0%).

(18) 1-(2′,4′-Dichlorophenyl)-4,4,4-trifluorobutane-1,3-dione (H2,4Cl_2bta). Yield 59%. b.p. 185°C (59 mmHg). t'_R = 3.85. DTA: V, 182°C (104–194). δ_{CH}, 6.56; δ_{OH}, 14.37; δ_{Ar}, 7.25, 7.28, 7.36, 7.42, 7.48, 7.60, 7.75. (Found: C, 42.0; H, 1.8. $C_{10}H_5Cl_2F_3O_2$ requires C, 42.1; H, 1.8%).

(19) 1-(4′-Bromophenyl)-4,4,4-trifluorobutane-1,3-dione (HpBrbta). Yield 59%. m.p. 56°C (lit.[5] 56°C). t'_R = 3.99. DTA: F, 54°C (47–62). V, 182°C (101–192). δ_{CH}, 6.51; δ_{OH}, 14.84; δ_{Ar}, 7.55, 7.66, 7.77, 7.89. (Found: C, 40.7; H, 2.0. Calculated for $C_{10}H_6BrF_3O_2$: C, 40.7; H, 2.0%).

(20) 1-(2′,5′-Dichlorophenyl)-4,4,4-trifluorobutane-1,3-dione (H2,5Cl_2bta). Yield 65%. b.p. 101–102°C (2.0 mmHg). m.p. 54°C. t'_R = 4.00. DTA: F, 55°C (49–61). V, 189°C (88–203). δ_{CH}, 6.58; δ_{OH}, 14.22; δ_{Ar}, 7.40, 7.66, 7.69, 7.72. (Found: C, 42.1; H, 1.6. $C_{10}H_5Cl_2F_3O_2$ requires C, 42.1; H, 1.8%).

(21) 1-(3′-Bromophenyl)-4,4,4-trifluorobutane-1,3-dione (HmBrbta). Yield 68%. m.p. 41°C (lit.[5] 39°C). t'_R = 3.76. DTA: F, 42°C (35–49). V, 189°C (106–209). δ_{CH}, 6.47; δ_{OH}, 14.78; δ_{Ar}, 7.18, 7.32, 7.45, 7.63, 7.75, 7.80, 7.88, 7.97. (Found: C, 40.3; H, 1.9. Calculated for $C_{10}H_6BrF_3O_2$: C, 40.7; H, 2.0%).

(22) 1-Phenylbutane-1,3-dione (Hba). Yield 54%. m.p. 59°C (lit.[7] 60°C). t'_R

= 2.33. DTA: F, 58°C (50–64). V, 193°C (90–222). δ_{CH}, 6.04; δ_{OH}, 16.29; δ_{Ar}, 7.37, 7.75. (Found: C, 73.8; H, 6.4. Calculated for $C_{10}H_{10}O_2$; C, 74.1; H, 6.2%).

(23) 1-(4′-Fluorophenyl)butane-1,3-dione (HpFba). Yield 57%. m.p. 47°C (lit.[7] 48–49°C). t'_R = 2.20. DTA: F, 47°C (41–58). V, 188°C (103–209). δ_{CH}, 6.16; δ_{OH}, 16.20; δ_{Ar}, 7.01, 7.14, 7.27, 8.30, 8.41, 8.52. (Found: C, 66.5; H, 5.4. Calculated for $C_{10}H_9FO_2$: C, 66.7, H, 5.0%).

(24) 1-(3′-4′-Dimethylphenyl)-4,4,4-trifluorobutane-1,3-dione (H3,4Me$_2$bta). Yield 61%. b.p. 105–107°C (0.7 mmHg). t'_R = 1.50. DTA: V, 187°C (86–213). δ_{CH}, 6.48; δ_{OH}, 14.50; δ_{Ar}, 7.12, 7.26, 7.60, 7.65, 7.69. (Found: C, 58.9; H, 4.6. $C_{12}H_{11}F_3O_2$ requires C, 59.0; H, 4.5%).

(25) 1-Phenyl-4,4-dimethylpentane-1,3-dione (Hbpm). [Sodium methoxide was used as condensing agent for this preparation. Benzoic acid was obtained (46% yield) as an unavoidable by-product.] Yield 21%. b.p. 114°C (7 mmHg) [lit.[8] 151–152°C (13 mmHg)]. t'_R = 6.50. DTA: V, 197°C (97–220). δ_{CH}, 6.20; δ_{OH}, 16.43; δ_{Ar}, 7.41, 7.85. (Found: C, 76.8; H, 8.0. Calculated for $C_{13}H_{16}O_2$: C, 76.5; H, 7.8%).

(26) 1-(3′,4′-Dichlorophenyl)-4,4,4-trifluorobutane-1,3-dione (H3,4Cl$_2$bta). Yield 61%. b.p. 117.5–118°C (0.8 mmHg). m.p. 34°C (lit.[9] 38°C). t'_R = 4.25. DTA: F, 37°C (31–46). V, 201°C (106–218). δ_{CH}, 6.47; δ_{OH}, 14.12; δ_{Ar}, 7.43, 7.58, 7.64, 7.68, 7.81, 7.97. (Found: C, 42.3; H, 1.7. Calculated for $C_{10}H_5Cl_2F_3O_2$: C, 42.1; H, 1.8%).

(27) 1-(4′-*tert.*-Butylphenyl)-4,4,4-trifluorobutane-1,3-dione (Hp^{t}Bubta). (4′-*tert.*-Butylacetophenone was prepared as described by Butler *et al.*[10]). Yield 61%. m.p. 62°C. t'_R = 6.88. DTA: F, 62°C (58–69). V, 203°C (113–216). δ_{CH}, 6.48; δ_{OH}, 14.72; δ_{Ar}, 7.37, 7.52, 7.77, 7.91. (Found: C, 61.6; H, 5.6. $C_{14}H_{15}F_3O_2$ requires C, 61.8; H, 5.5%).

(28) 1-(4′-Chlorophenyl)butane-1,3-dione (HpClba). Yield 46%. m.p. 69°C (lit.[7] 72°C). t'_R = 6.05. DTA: F, 70°C (61–78). V, 208°C (103–229). δ_{CH}, 6.09; δ_{OH}, 16.08; δ_{Ar}, 7.22, 7.37, 7.65, 7.83. (Found: C, 61.3; H, 4.6. Calculated for $C_{10}H_9ClO_2$: C, 61.1; H, 4.6%).

(29) 1-(4′-*tert.*-Butylphenyl)butane-1,3-dione (Hp^{t}Buba). Yield 46%. b.p. 175°C (6 mmHg). [lit.[7] 121°C (1 mmHg)]. t'_R = 18.25. DTA: V, 229°C (131–246). δ_{CH}, 6.08; δ_{OH}, 16.34; δ_{Ar}, 7.32, 7.47, 7.73, 7.83. (Found: C, 77.00; H, 7.7. Calculated for $C_{14}H_{18}O_2$: C, 77.1; H, 8.3%).

(30) 1-(4′-*tert.*-Butylphenyl)-4,4-dimethylpentane-1,3-dione (Hp^{t}Bubpm). Yield 36%. t'_R > 25. DTA: V, 225°C (143–250). δ_{CH}, 6.20; δ_{OH}, 16.58; δ_{Ar}, 7.28, 7.45, 7.75, 7.86. (Found: C, 78.4; H, 9.2. $C_{17}H_{24}O_2$ requires C, 78.5; H, 9.2%).

(31) 1-(4′-Bromophenyl)butane-1,3-dione (HpBrba). Yield 48%. m.p. 96°C (lit.[7] 96.5°C). t'_R = 3.60. DTA: F, 95°C (87–99). V, 221°C (154–248). δ_{CH}, 6.09; δ_{OH}, 15.95; δ_{Ar}, 7.50, 7.59, 7.70, 7.82.(Found: C, 49.7; H, 3.9. Calculated for $C_{10}H_9BrO_2$: C, 49.8; H, 3.7%).

(32) 1-(4′-Nitrophenyl)-4,4,4-trifluorobutane-1,3-dione (HpNO$_2$bta). Yield 31%. m.p. 96–97°C (lit.[11] 97–98°C). t'_R = 6.60. DTA: F, 98°C (94–106). V, 229°C (147–240). δ_{CH}, 6.68; δ_{OH}, 14.37; δ_{Ar}, 8.03, 8.20, 8.28, 8.44. (Found: C, 46.3; H, 2.0. Calculated for $C_{10}H_6F_3NO_4$: C, 46.0; H, 2.3%).

(33) 1,3-Diphenylpropane-1,3-dione (Hdbm). Aldrich Chemicals. m.p. 77°C (lit.[12] 77–78°C). t'_R > 30. DTA: F, 77°C (69–84). V, 275°C (143–285). δ_{CH}, 6.69; δ_{OH}, 16.80; δ_{Ar}, 7.28, 7.35, 7.38, 7.80, 7.88, 7.92, 7.95.

The β-keto enamines were prepared by condensation of the appropriate β-diketone and 1,2-diaminoethane as follows.

The diamine (0.05 mol) was added to an ethanolic solution of the required β-diketone (0.10 mol in 60 ml ethanol) and the mixture heated on the steam bath for 60 min. On cooling, any solid that formed was collected by filtration, washed with alcohol, then ether, and purified by recrystallisation. In the case of compounds 38 and 39, both of which failed to precipitate, the solvent was removed by evaporation and the recovered solid washed with boiling ether, before recrystallising from aqueous ethanol as before.

(34) 1,1′-Diphenyl-3,3′-(ethane-1,2-diyldiimino)bis(but-2-en-1-one). Yield 54%. m.p. 179–180°C (lit.[13] 180.5°C). DTA: F, 181°C (176–184). D, 316°C. (Found: C, 75.6; H, 6.8; N, 7.7. Calculated for $C_{22}H_{24}N_2O_2$: C, 75.9; H, 6.9; N, 8.0%).

(35) 1,1′-Bis(4′-fluorophenyl)-3,3′-(ethane-1,2-diyldiimino)bis(but-2-en-1-one). Yield 48%. m.p. 175–176°C. DTA: F, 178°C (173–182). D, 292°C. D, 326°C. (Found: C, 68.9; H, 5.6; N, 7.2. $C_{22}H_{22}F_2N_2O_2$ requires C, 68.8; H, 5.7; N, 7.3%).

(36) 1,1′-Bis(4′-methylphenyl)-3,3′-(ethane-1,2-diyldiimino)bis(but-2-en-1-one). Yield 59%. m.p. 178–179°C. DTA: F, 183°C (177–188). D, 338°C. (Found: C, 77.0; H, 7.5; N, 7.3. $C_{24}H_{28}N_2O_2$ requires C, 76.6; H, 7.4; N, 7.4%).

(37) 1,1′-Bis(4′-*tert.*-butylphenyl)-3,3′-(ethane-1,2-diyldiimino)bis(but-2-en-1-one). Yield 58%. m.p. 225–227°C. DTA: F, 227°C (221–231). D, 299°C. (Found: C, 77.8; H, 8.8; N, 6.0. $C_{28}H_{40}N_2O_2$ requires C, 78.3; H, 8.7; N, 6.1%).

(38) 1,1′-Bis(2′,5′-dimethylphenyl)-3,3′-(ethane-1,2-diyldiimino)bis(but-2-en-1-one). Yield 47%. m.p. 119°C. DTA: F, 119°C (113–125). D, V 352°C. (Found: C, 77.3; H, 7.6; N, 6.7. $C_{26}H_{32}N_2O_2$ requires C, 77.2; H, 7.9; N, 6.9%).

(39) 1,1′-Bis(3′-trifluoromethylphenyl)-3,3′-(ethane-1,2-diyldiimino)bis(but-2-en-1-one). Yield 61%. m.p. 153°C. DTA: F, 153°C (149–158). V, D 334°C. (Found: C, 59.7; H, 4.3; N, 5.8. $C_{24}H_{22}F_6N_2O_2$ requires C, 59.5; H, 4.5; N, 5.8%).

RESULTS AND DISCUSSION

Spectroscopic properties

Because of the novelty of many of the β-diketones, some comments are presented regarding features of their spectroscopic properties, useful also in establishing the integrity of the ligands recovered from thermal analyses.

IR spectra

It is convenient to divide the spectra into three regions of interest. In the first, the region 4000–1640 cm^{-1}, the most significant absorption is observed as weak bands near 3100 cm^{-1} due to the aromatic C–H stretching modes. In contrast, the region from 1500–400 cm^{-1} is characterised by numerous intense and usually sharp bands, mainly associated with the terminal substituents. However, most characteristic of the spectra is the broad intense band in the region 1620–1595 cm^{-1}, assigned to a vibration involving the enolic ring as a whole. Indeed, repeated dilution of Hba in carbon tetrachloride failed to resolve this band so that the extent of intermolecular interaction appears to be insignificant. Consistent with previous observations[14,15] the frequency of this band does not vary systematically with either the strength of the

intramolecular hydrogen bond, or the steric or electronic demands of the terminal groups of the β-diketone. Thus, the most important contribution of the vibrational spectrum remains the evidence provided for an intramolecularly hydrogen bonded structure.

NMR spectra

The NMR data included in the Experimental Section are readily interpreted unambigously. Excluded from these data, is evidence to show the presence with non-polar solvents of the diketo tautomer (8%) in Hba and its ring-substituted analogues.

Substituent effects on the methine proton resonance

The chemical shift of the methine proton (δ_{CH}) does not vary markedly and exhibits the following trend: Hdbm = $HpNO_2$bta (δ_{CH} = 6.69) > other derivatives of Hbta, Hbpb and Hbhp (δ_{CH} range: 6.58–6.29) > HF_5bta (6.25) > Hbpm = Hp^{t}Bubpm (6.20) > ring-substituted derivatives of Hba (δ_{CH} range: 6.16–6.08) > Hba (6.04). The effect involved in determining this trend in the case of Hbta and its analogues seems to be predominantly that of deshielding, due to inductive electron-withdrawal by the fluoroalkyl group, in agreement with the electron density calculations of Gordon and Koob[16]. Other effects are operative, however, as seen by comparing the relative positions of the ring-substituted derivatives of Hbta [*e.g.* $\delta_{CH}(HF_5bta) < \delta_{CH}(Hp^tBubta)$].

Substituent effects on the enolic proton resonance

In contrast to δ_{CH}, the chemical shift of the enolic proton (δ_{OH}) varies considerably (range: 16.80–13.67) and, where pK_a data are available, a linear correlation exists between δ_{OH} and pK_a. However, the two compounds capable of enhanced resonance contributions (Hdbm and $HpNO_2$bta) do not fit the same linear correlation.

The large variation in δ_{OH} values indicates that the terminal substituents exert a considerable influence on the enolic ring, implying extensive interaction between the two ring systems. Due to the deshielding effects of a stronger inductive withdrawal of charge, a more electronegative group is expected to produce a downfield shift in δ_{OH}. Hence, the predicted trend in δ_{OH} would be Hbta > Hba > Hbpm > Hdbm whereas the reverse is observed and can be summarised as: Hdbm (δ_{OH} = 16.80) > Hp^{t}Bubpm (16.58) > Hbpm (16.43) > Hp^{t}Buba (16.34) > Hba (16.29) > ring-substituted derivatives of Hba (range: 16.20–15.95) > analogues Hbta (range: 15.10–14.08) > $HoCF_3$bta (14.07) > HF_5bta (13.67). This situation is not unique since a parallel situation has been observed[17] with the α-protons of the isopropyl halides which become more shielded as the electronegativity of the halide increases.

Although no single factor accounts for the direction of change in δ_{OH} the most important influence is the strength of intramolecular hydrogen bonding with a stronger bond producing a greater downfield shift[18,19], as predicted by theoretical calculations[20]. This lowfield shift can be ascribed to quenching of the intramolecular paramagnetic effect[21] as a result of the loss of axial symmetry.

Aromatic proton resonances

Two distinct environments are generally observed for the aromatic protons, although spin–spin coupling complicates the spectra. The most significant resonances

are reported in the Experimental Section with the downfield signals being assigned to the protons *ortho-* to the enolic ring. This is consistent with the electron-withdrawing capacity of the enolic ring being greatest at this position, and also with the diamagnetic anisotropic effect of the enolic ring. However, this interpretation is complicated by the presence of other substituents on the aromatic ring.

Thermal analysis

When examined by TG a common feature of the 33 β-diketones examined was complete volatilisation with no accompanying decomposition. Moreover, the numerical listing of compounds 1–33 in the Experimental Section is the order of decreasing volatility. In the case of the β-diketones the temperature corresponding to complete volatilisation ranged from 95°C for compounds 1 and 2 to 260°C for compound 33. This trend in volatility can be rationalised mainly in terms of substituent-group effects on the polarity of the ligands. Thus, the substitution of fluorine into the β-diketones enhances volatility, as expected of a group capable of inductively

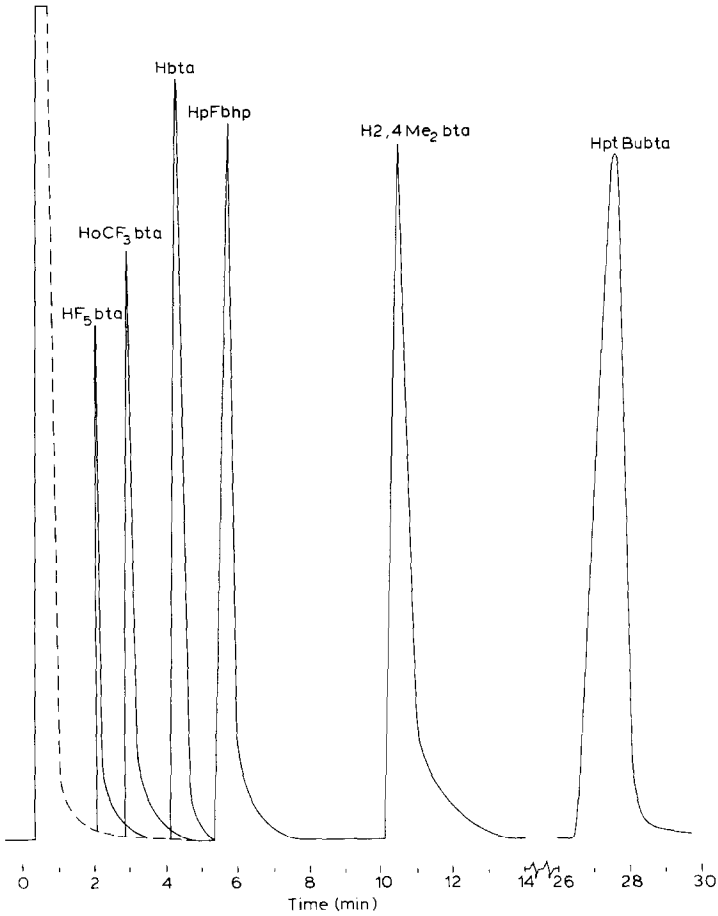

Fig. 1. Chromatograms of β-diketones (10 μg) on SE-30. Column temperature, 115°C (injector/detector, 140°C). Solvent (methanol) is shown as a broken line.

withdrawing charge from the hydrogen bonded enolic ring and, in turn, creating a reduced intermolecular interaction. In marked contrast, the introduction of other halide (chloro or bromo) or pseudo-halide (nitro) groups into the molecule reduces the volatility of the β-diketones relative to the unsubstituted compound. Here, the halogen substituents may function mesomerically to increase electron density in the π system of the aromatic ring and, to a lesser extent, in the enolic ring. This interpretation is supported by NMR data[22,23] and has been used to explain trends in dipole moments[5,24]. The most convincing argument for this type of interaction is the correlation[7,25] between ligand pK_a values and the Hammett's constants.

In contrast to the thermal behaviour of the β-diketones some decomposition was common to all of the β-keto enamines, the extent varying considerably with the aromatic ring substituent. Thus, extensive decomposition was observed for compounds 34–37 and, although copious quantities of a condensate were collected for compound 38, mass spectral examination, in particular, of the condensate demon-

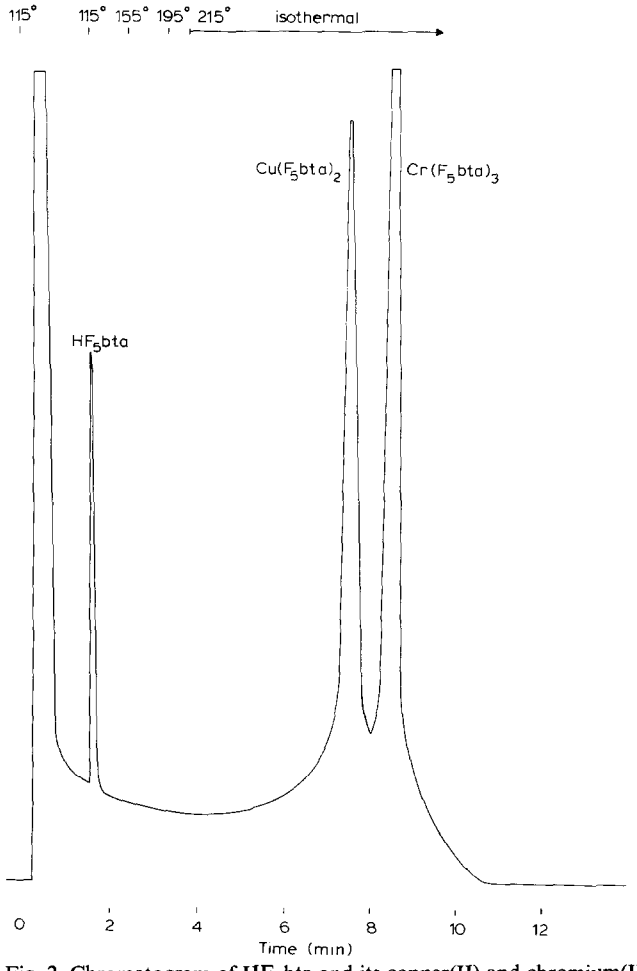

Fig. 2. Chromatogram of HF_5bta and its copper(II) and chromium(III) chelates on SE-30. Column temperature programmed as indicated (injector/detector 220°C).

strated that pyrolytic decomposition had occurred. In contrast, the condensate from compound 39 consisted mainly of unaltered ligand but, here again, thermal decomposition products were detected in the condensate by mass spectrometry. Temperatures of initial mass loss ranged from 260°C for compound 34 to 280°C for compound 39.

Gas chromatography

In the case of compounds 1–11, the order of elution (see Experimental Section) on a SE-30 column is predictable from the volatility sequence obtained using TG. On the other hand, when the less volatile β-diketones (compounds 12–33) are considered several discrepancies are observed between the relative retention time on SE-30 and the volatility as predicted by TG. Most notable are the β-diketones containing either a terminal alkyl group or an alkyl substituent in the aromatic ring. These variations from the predicted retention behaviour can be attributed to the heterogeneous forces prevailing in the chromatography column as compared to the essentially homogeneous forces involved in TG.

Chromatograms are given in Fig. 1 for several of the ligands. Minor tailing

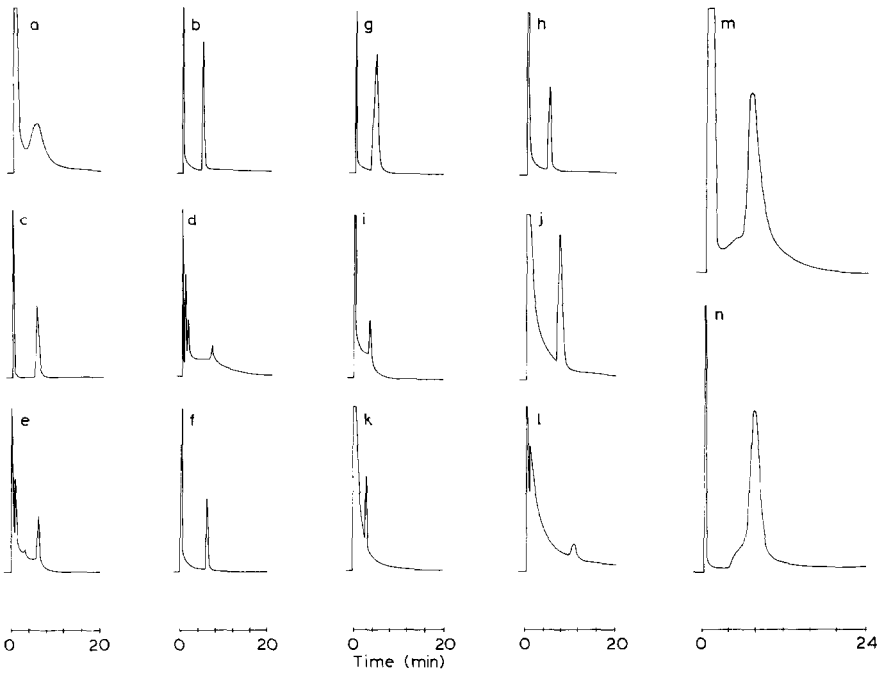

Fig. 3. Chromatograms showing the elution of $Cr(F_5bta)_3$ at, or near, the minimum usable concentration. Column (3% stationary phase), column temperature and quantity of chelate injected are as specified. On-column silanization was used. (a) Uncoated Chromosorb 750, 30 μg, 185°C; (b) OV-17 on Chromosorb W AW, 1 μg, 190°C; (c) OV-17 on Chromosorb 750, 0.6 μg, 200°C; (d) QF-1 on Chromosorb W HP, 1 μg, 190°C; (e) QF-1 on Chromosorb 750, 1 μg, 180°C; (f) OV-3 on Chromosorb 750, 1 μg, 195°C; (g) Kel F Wax on Chromosorb 750, 0.8 μg, 155°C; (h) SE-30 on Chromosorb 750, 0.5 μg, 180°C; (i) Apiezon L on Chromosorb 750, 1.5 μg, 190°C; (j) OV-17 on Porasil F, 1 μg, 195°C; (k) OV-17 on Porasil E, 10 μg, 215°C; (l) OV-17 on Porasil C, 18 μg, 195°C; (m) OV-17 on Ultrabond, 150 μg, 215°C; (n) OV-210 on Chromosorb 750, 10 μg, 180°C; Attenuation is constant for the series.

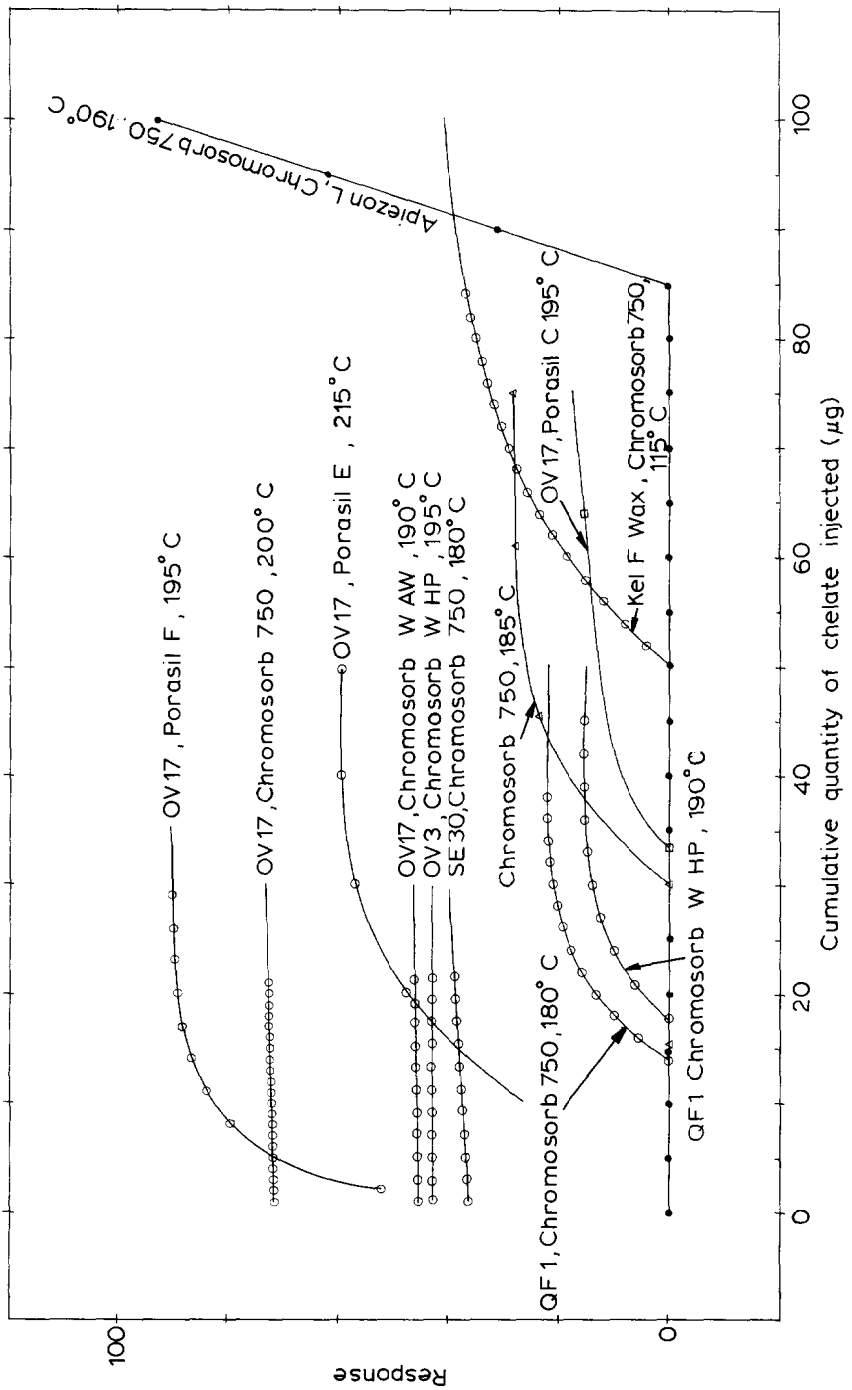

Fig. 4. Retention of $Cr(F_3bta)_3$ on various stationary phases and supports. The curves are identified by the column packing followed by the column temperature. Stationary phase loading is constant at 3%.

was a common feature for all fluorinated ligands, increasing with the fluorine content of the compound. Resolution of free ligand and corresponding metal chelates presents no difficulty as shown in Fig. 2 for HF_5bta. Although chromatographic data for the chelates will be presented in a later communication, the behaviour on different stationary phases and supports is shown in Fig. 3 for the chromium(III) chelate of HF_5bta. The importance of a correct choice of the chromatographic system is evident. Moreover, the adverse behaviour of chelates containing aryl-substituted β-diketones is demonstrated by the elevated baselines observed for $Cr(F_5bta)_3$ on some of the phases and supports. Furthermore, free ligand was detected in the eluent giving rise to the elevated baselines. Loading curves[26] of response against the total amount of chelate injected onto the column are also presented (Fig. 4) for $Cr(F_5bta)_3$ as a further instance of the poorer chromatographic behaviour of the chelates containing aryl substituents. The occurrence of such loading curves, which can be taken as evidence of the unfavourable retention of the chelate by the chromatographic system, will be discussed in a later communication when the corresponding data for several metal ion-ligand systems have been presented. As anticipated from their thermal behaviour, the intact β-keto enamines did not elute from an SE-30 column.

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