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Note

Reactions of cyclic anhydrides with aromatic primary amines: Part 3†—Synthesis of novel 3-(*N*-arylcarbamoyl)- and 3-(*N*-naphthylcarbamoyl)carboxylic acids

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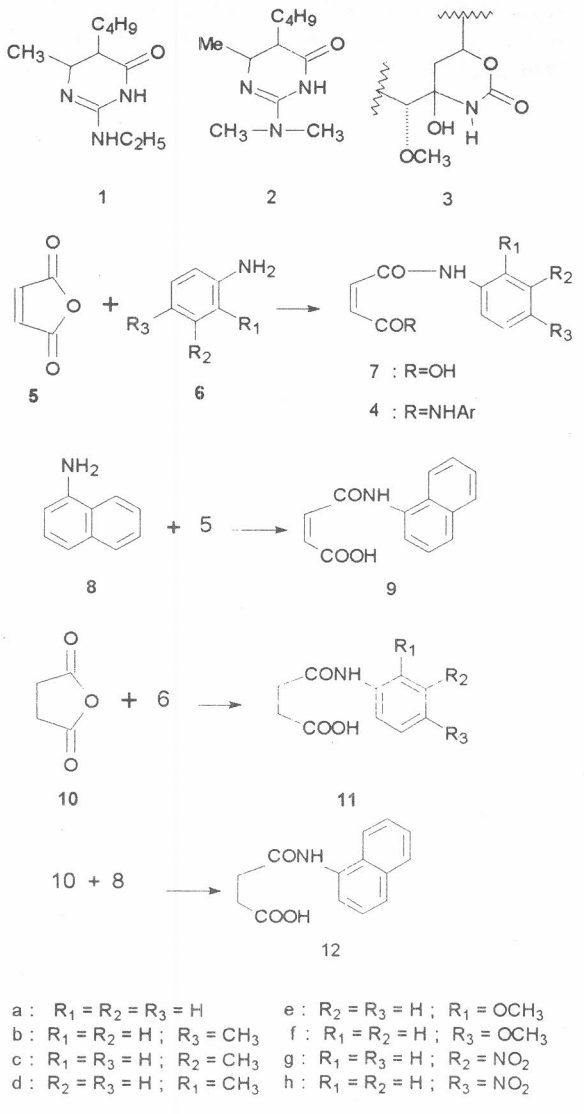
Some hitherto unreported 3-(*N*-arylcarbamoyl)propenoic acids **7a-h** and 3-(*N*-naphthylcarbamoyl)propenoic acid **9** have been synthesized in excellent yields, together with some propanoic acid analogues **11a-h** and **12** as potential pesticides. Structural assignments of the products are based on elemental analyses and spectral (IR, ^{1}H NMR, mass) data.

It has been recognised that the $NSCCl_3$ group is responsible for the fungicidal activity of Captan and other related compounds. Systemic fungicides such as Ethirimol **1** and Dimethirimol **2** are potent also because of the carbamoyl moiety[1]. The insecticidal carbamates and pyrimidine analogues also have this toxophore. The cyclic carbinolamide moiety **3** has also been proposed as a reactive site responsible for the cytotoxic, antimitotic and antileukemic properties of the maytansinoids[2]. Several amides are known to elicit various biological activities[3-7]. Motivated by the results of the insecticidal activity of structurally similar anilinic acids[8], the author describes herein the synthesis of acrylic acid derivatives, **7a-h, 11a-h, 9** and **12** (Scheme I) and their spectral data. These target molecules are structurally attractive as insecticides[9,10], herbicides[11] and surface fungicides[12] and may readily be converted into other anilides **4** thus introducing dual toxophores within the same molecule.

The target amides were prepared by the reaction of appropriate cyclic anhydrides with aromatic amines using the methods reported in literature[13,14].



Scheme I

Preliminary studies on these compounds as insecticides are encouraging and details will be communicated in subsequent reports.

Experimental Section

General. Melting point are uncorrected. IR spectra were recorded in KBr on a Perkin-Elmer 157G spectrophotometer (ν_{max} in cm^{-1}), ^{1}H NMR spectra in $CDCl_3$ on a Varian Associates A60 using TMS as internal standard (chemical shifts in δ, ppm), and mass spectra on an AE1 MS 902 instrument.

†For Part 2, see *Indian J Chem*, SCCB 4761/94

Synthesis of propenoic acids 7a-h, 9 and propanoic acids 11a-h and 12: General procedure. A mixture of the appropriate anhydride **5** or **10** (0.05 mole) and amine **6a-h** or **8** (0.05 mole) in benzene[14] (100 mL) was refluxed for 2 hr. The mixture was allowed to cool and the precipitate filtered, dried under suction and crystallised from ethanol to give the corresponding propanoic or propenoic acid. The characterization data of the compounds are given below:

Compound 7a: mp 207-08°C, yield 6.80 g (71%). Anal. Calcd for $C_{10}H_9NO_3$: C, 62.8; H, 4.7; N, 7.3. Found: C, 62.7; H, 4.7, N, 7.2%; IR (KBr): 3250, 2995, 1705, 1675, 1640; ^{1}H NMR ($CDCl_3$): 11.96 (1H, s, COOH), 9.36 (1H, brs, CONH), 7.35 (1H, d, vinyl-H, *J*=9 Hz), 7.20 (5H, m, Ar-H); 6.38 (1H, d, *J*=9 Hz); MS: m/z 191 (M^+), 174, 146, 120.

Compound 7b: mp 188-90°C, yield 7.51 g (73%). Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.4; H, 5.4; N, 6.8. Found: C, 64.3, H, 5.4; N, 6.8%; IR (KBr): 3220, 2995, 1705, 1670, 1640; ^{1}H NMR ($CDCl_3$): 11.97 (1H, s, COOH), 9.35 (1H, brs, CONH), 7.34 (1H, d, vinyl-H, *J*=9 Hz), 7.18 (2H, d, ArH, *J*=8.5 Hz), 7.05 (2H, d, ArH, *J*=8.5 Hz), 6.35 (1H, d, vinyl-H, *J*=9 Hz), 2.37 (3H, s, $ArCH_3$); MS: m/z 205 (M^+), 188, 160, 134, 133.

Compound 7c: mp 170-72°C, yield 7.50 g (73%). Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.4; H, 5.4; N, 6.8. Found: C, 64.4; H, 5.4; N, 6.7%; IR (KBr): 3225, 2995, 1710, 1675, 1645; ^{1}H NMR ($CDCl_3$): 11.98 (1H, s, COOH), 9.33 (1H, brs, CONH), 7.34 (1H, d, olefinic, *J*=9 Hz), 6.96 (4H, m, ArH), 6.36 (1H, d, olefinic, *J*=9 Hz), 2.38 (3H, s, $ArCH_3$); MS: m/z 205 (M^+), 188, 187, 160, 134, 133.

Compound 7d: mp 104-05°C, yield 8.25 g (81%). Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.4; H, 5.4; N, 6.8. Found: C, 64.4; H, 5.3; N, 6.7%; IR (KBr): 3220, 2990, 1705, 1670, 1640; ^{1}H NMR ($CDCl_3$): 11.97 (1H, s, COOH), 9.30 (1H, brs, CONH), 7.35 (1H, d, vinyl-H, *J*=9 Hz), 7.02 (4H, m, ArH), 6.38 (1H, d, vinyl-H, *J*=9 Hz), 2.36 (3H, s, $ArCH_3$); MS: m/z 205 (M^+), 188, 187, 160, 134, 133.

Compound 7e: mp 139-40°C, yield 9.28 g (84%). Anal. Calcd for $C_{11}H_{11}NO_4$: C, 59.7, H, 5.0; N, 6.3. Found: C, 59.7; H, 4.9; N, 6.2%; IR (KBr): 3215, 2990, 1700, 1670, 1645; ^{1}H NMR ($CDCl_3$): 11.97, 1H, s, COOH), 9.20 (1H, brs, CONH), 7.34 (1H, d, vinyl-H, *J*=9 Hz), 6.90 (4H, m, ArH), 6.6 (1H, d, vinyl-H, *J*=9 Hz), 3.82 (3H, s, $ArOCH_3$); MS: m/z 221 (M^+), 206, 204, 189.

Compound 7f: mp 184-85°C yield 9.56 g (87%). Anal. Calcd for $C_{11}H_{11}NO_4$: C, 59.7; H, 5.0; N, 6.3. Found: C, 59.7; H, 5.0; N, 6.2%; IR (KBr): 3210, 2990, 1700, 1670, 1645; ^{1}H NMR ($CDCl_3$): 11.98 (1H, s, COOH), 9.21 (1H, brs, $CONH_2$), 7.35 (1H, d, vinyl-H, *J*=9.5 Hz), 6.90 (2H, d, *J*=8.5 Hz, ArH), 7.22 (2H, d, *J*=8.5 Hz, ArH), 6.36 (1H, d, vinyl-H, *J*=9.5 Hz), 3.80 (3H, s, $ArOCH_3$); MS: m/z 221 (M+), 206, 204, 189.

Compound 7g: mp 185-86°C, yield 9.60 g (81%). Anal. Calcd for $C_{10}H_8N_2O_5$: C, 50.9; H, 3.4; N, 11.9. Found: C, 50.8; H, 3.3; N, 11.8%; IR (KBr): 3380, 2995, 1715, 1670, 1625, 1520, 1340; ^{1}H NMR ($CDCl_3$): 12.00 (1H, s, COOH), 9.42 (1H, brs, CONH), 8.28 (4H, m, ArH), 7.42 (1H, d, *J*=9.0 Hz, vinyl-H), 6.40 (1H, d, vinyl-H, *J*=9.0 Hz); MS: m/z 236 (M^+), 219, 191.

Compound 7h: mp 187-88°C, yield 9.42 g (80%). Anal. Calcd for $C_{10}H_8N_2O_5$: C, 50.9; H, 3.4; N, 11.9. Found: C, 50.9; H, 3.4; N, 11.8%; IR (KBr): 3360, 3000, 1710, 1670, 1630, 1530 and 1350 (N=O); ^{1}H NMR ($CDCl_3$): 12.02 (1H, s, COOH), 9.46 (1H, brs, CONH), 8.25 (2H, d, *J*=8.5 Hz, ArH), 8.62 (2H, d, *J*=8.5 Hz, ArH), 7.40 (1H, d, vinyl-H, *J*=9 Hz), 6.41 (1H, d, *J*=9 Hz, vinyl-H); MS: m/z 236 (M^+), 219, 191.

Compound 9: mp 132°C, yield 10.10 g (85%). Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.7; H, 4.6; N, 5.8. Found: C, 69.6; H, 4.5; N, 5.7%; IR (KBr): 3240, 2995, 1710, 1685, 1640; ^{1}H NMR ($CDCl_3$): 11.98 (1H, s, COOH), 9.28 (1H, brs, CONH), 7.70 (7H, m, ArH), 7.38 (1H, d, *J*=9 Hz, vinyl-H), 6.45 (1H, d, *J*=9 Hz, vinyl-H); MS: m/z 241 (M^+), 224, 196.

Compound 11a: mp 149.5°C, yield 6.95 g (72%). Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.2; H, 5.7; N, 7.3. Found: C, 62.1; H, 5.7; N, 7.4%; IR (KBr): 3240, 3000, 1710, 1675, 1630; ^{1}H NMR ($CDCl_3$): 10.68 (1H, s, COOH), 9.34 (1H, brs, CONH), 7.25 (5H, m, ArH), 2.62 (4H, m, H-2 and H-3 protons); MS: m/z 193 (M^+), 176, 148.

Compound 11b: mp 148-49°C, yield 8.10 g (78%). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.8; H, 6.3; N, 6.8. Found: C, 63.8; H, 6.3; N, 6.9%; IR (KBr): 3220, 2990, 1710, 1670, 1640; ^{1}H NMR ($CDCl_3$): 10.66 (1H, s, COOH), 9.32 (1H, brs, CONH), 7.22 (2H, d, *J*=8.5 Hz, ArH), 7.10 (2H, d, *J*=8.5 Hz, ArH), 2.61 (4H, m, H-2 and H-3 protons), 2.36 (3H, s, $ArCH_3$); MS: m/z 207 (M^+), 206, 190, 189, 162, 161.

Compound 11c: mp 101-02°C, yield 7.91 g (76%). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.8; H, 6.3; N, 6.8. Found: C, 63.7; H, 6.3; N, 6.9%; IR (KBr): 3225, 2995, 1710, 1675, 1640; ^{1}H NMR ($CDCl_3$): 10.67 (1H, s, COOH), 9.33 (1H, brs, CONH), 7.01 (4H, m, ArH), 2.58-2.64 (4H, m, H-2 and H-3 protons), 2.38 (1H, s, $ArCH_3$); MS: m/z 207 (M^+), 206, 190, 189, 162, 161.

Compound 11d: mp 155-56°C, yield 8.30 g (80%). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.8; H, 6.3; N, 6.8. Found: C, 63.8; H, 6.3; N, 6.7%; (IR (KBr): 3220, 2990, 1705, 1660, 1635; ^{1}H NMR ($CDCl_3$): 10.68 (1H, s, COOH), 9.32 (1H, brs, CONH), 7.02 (4H, m, ArH), 2.61 (4H, m, H-2 and H-3 protons), 2.37 (1H, s, $ArCH_3$); MS: m/z 207 (M^+), 206, 190, 189.

Compound 11e: mp 138°C, yield 9.37 g (84%). Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.2; H, 5.8; N, 6.3. Found: C, 59.1; H, 5.7; N, 6.1%; IR (KBr): 3215, 2990, 1700, 1660, 1640; ^{1}H NMR ($CDCl_3$): 10.68 (1H, s, COOH), 9.30 (1H, s, CONH), 6.98 (4H, m, ArH), 2.62 (4H, m, H-2 and H-3 protons), 3.80 (1H, s, $ArOCH_3$); MS: m/z 223, 208, 206, 191.

Compound 11f: mp 110-11°C, yield 9.37 g (84%). Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.2; H, 5.8; N, 6.3. Found: C, 59.2; H, 5.8; N, 6.2%; IR (KBr): 3210, 2990, 1700, 1670, 1630; ^{1}H NMR ($CDCl_3$): 10.69 (1H, s, COOH), 9.31 (1H, s, CONH), 7.04 (2H, d, J=8.5 Hz, ArH), 7.23 (2H, d, J=8.5 Hz, ArH), 2.63 (4H, m, H-2 and H-3), 3.81 (3H, s, $ArOCH_3$); MS: m/z 223 (M^+), 208, 206, 191.

Compound 11g: mp 124-25°C, yield 9.62 g (81%). Anal. Calcd for $C_{10}H_{10}N_2O_5$: C, 50.4; H, 4.2; N, 11.8. Found: C, 50.4; H, 4.1; N, 11.7%; IR (KBr): 3340, 3000, 1710, 1680, 1630, 1520, 1320; ^{1}H NMR ($CDCl_3$): 11.24 (1H, s, COOH), 9.44 (1H, brs, CONH), 8.30 (4H, m, ArH), 2.62 (4H, m, H-2 and H-3); MS: 238 (M^+), 221, 193.

Compound 11h: mp 130-31°C, yield 9.51 g (80%). Anal. Calcd for $C_{10}H_{10}N_2O_5$: C, 50.4; H, 4.2; N, 11.8. Found: C, 50.3; H, 4.2; N, 11.7%; IR (KBr): 3340, 3000, 1710, 1680, 1640, 1520, 1310; ^{1}H NMR ($CDCl_3$): 11.30 (1H, s, COOH), 9.42 (1H, brs, CONH), 8.24 (2H, d, J=8.5 Hz, ArH), 8.60 (2H, d, J=8.5 Hz, ArH), 2.61 (4H, m, H-2 and H-3); MS: m/z 238 (M^+), 221.193.

Compound 12: mp 150-51°C, yield 10.35 g (85%). Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.1; H, 5.4; N, 5.8. Found: C, 69.2; H, 5.3; N, 5.7%; IR (KBr): 3250, 2995, 1710, 1675, 1640; ^{1}H NMR ($CDCl_3$): 11.12 (1H, s, COOH), 9.24 (1H, brs, CONH), 7.68 (7H, m, ArH), 2.62 (4H, m, H-2 and H-3); MS: m/z 243 (M^+), 226, 198.

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