J. Indian Chem. Soc.,
Vol. 76, March 1999, pp. 140-144

Studies on synthesis of 2-acetylbenzimidazole and related benzimidazole derivatives

K. Ramaiah[a], J. S. Grossert[b], D. L. Hooper[b], P. K. Dubey*[a] and J. Ramanatham[a]

[a]Department of Chemistry, College of Engineering, J. N. T. University, Kukatpally, Hyderabad-500 072, India

[b]Department of Chemistry, Dalhousie University, Halifax, N.S., B3H 4J3, Canada

Manuscript received 10 February 1998, revised 7 August 1998, accepted 18 November 1998

Condensation of *o*-phenylenediamine (1) with propanoic acid under Phillips' conditions gives 2-ethylbenzimidazole (2). Attempts to oxidise 2 to 2-acetylbenzimidazole (3) using H_2O_2, SeO_2, $KMnO_4$/acetone were unsuccessful. Condensation of 2 with benzaldehyde yields 2-(α-methylstyryl)benzimidazole (4) which on oxidation with $KMnO_4$ gives benzimidazole-2-carboxylic acid (5) as the sole product. Reaction of 1 with pyruvic acid results in 3-methylbenzo-1*H*-dihydropyrazine-2-one (7) rather than 3 as the major product. Treatment of 1 with formic acid gives the known compound benzimidazole (9) which with acetic anhydride in the presence of NaOAc does not yield 3. Reaction of 1 with lactic acid under Phillips' conditions gives 2-(α-hydroxyethyl)benzimidazole (10) which on oxidation with acid dichromate, however, yields 3. Studies on syntheses and spectral properties of related benzimidazoles are reported.

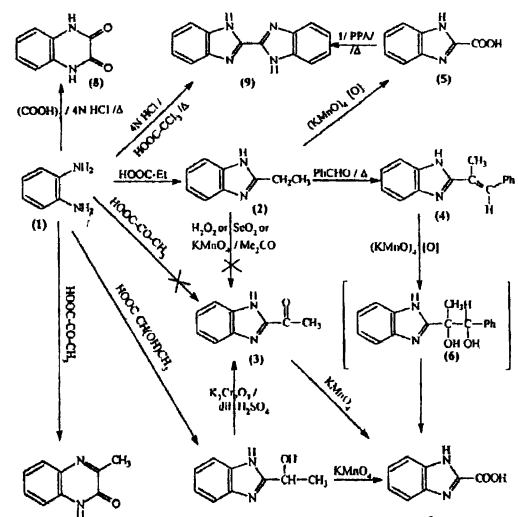
Benzimidazoles are an important group of heterocyclic compounds having a wide spectrum of biological activities[1,2]. Among benzimidazoles, the 2-substituted derivatives have been found to be biologically most potent. In this communication different routes have been explored for the preparation of 2-acetylbenzimidazole which is a crucial intermediate for the preparation of several 2-substituted-benzimidazoles.

Results and Discussion

Condensation of *o*-phenylenediamine (**1**) with propanoic acid under Phillips' conditions[3] gave 2-ethylbenzimidazole (**2**). Attempted oxidation of **2** with H_2O_2/AcOH[4], SeO_2/$PhNO_2$ [5] or $KMnO_4$/acetone[6] with a view to get 2-acetylbenzimidazole[2,7,8] (**3**) led to the recovery of the starting material. In an alternative approach, **2** was condensed with benzaldehyde to obtain 2-(α-methylstyryl)-benzimidazole[9] (**4**). Once again, attempted oxidation of **4** with H_2O_2/AcOH[4] led to the recovery of the starting material. However, oxidation of **4** with aq. $KMnO_4$ under neutral, alkaline or acidic conditions gave benzimidazole-2-carboxylic acid[10] (**5**) as the sole product. Obviously, the latter reactions of **4** proceed through the intermediacy of the vicinal dihydroxy compound **6**.

Treatment of **1** with sodium pyruvate under Phillips' conditions (i.e. in 4 *N* HCl) or of **1** with pyruvic acid in aqueous solution alone yielded, in both cases, the same pyrazine derivative, 3-methylbenzo-1*H*-dihydropyrazine-2-one[11](**7**) rather than **3**. Condensation of **1** with oxalic acid under Phillips' conditions led to the isolation of benzo-1,4(2*H*)-dihydropyrazine-2,3-dione[11](**8**) rather than bisbenzimidazole (**9**). The latter compound was, however, obtained by the known reaction[12] of **1** with trichloroacetic acid. Treatment of **5** with **1** under Phillips' conditions[3] resulted in the failure of the condensation. Instead of the expected **9**, compound **5** was recovered unchanged. Compound **9** was however obtained from **1** and **5** by condensation in polyphosphoric acid[13] at 180–90°.

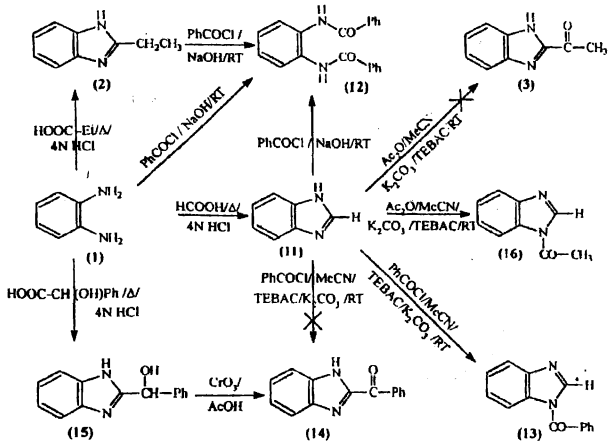
Reaction of **1** with lactic acid under Phillips' conditions[3] gave the known 2-(α-hydroxyethyl)benzimidazole[3,8] (**10**). Oxidation of **10** with aq. $KMnO_4$ independently under neutral, alkaline or acidic conditions gave the same over-oxidised product, i.e. benzimidazole-2-carboxylic acid (**5**). However, oxidation of **10** with $K_2Cr_2O_7$ in dil H_2SO_4 yielded the expected **3**. The reported procedure[7,8] was modified to obtain **3** in higher yields (over 70%) and in purer form (see Experimental).



Scheme 1

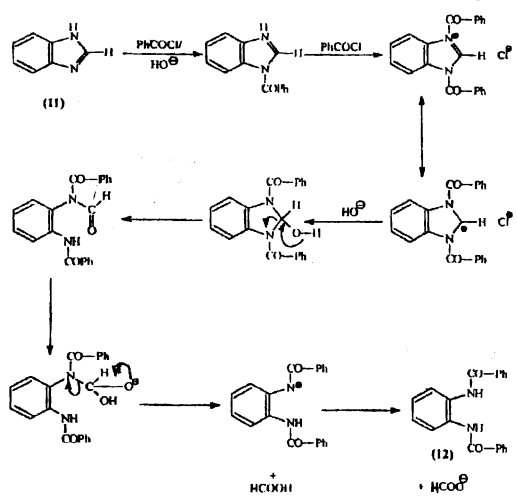
Treatment of **3** with aq. acidic $KMnO_4$ gave **5**, indicating **5** to be the stable end-product of the oxidation of the 2-substituted-benzimidazoles. The above reactions are summarised in Scheme 1.

Condensation of **11**[3,14] with benzoyl chloride in the presence of aq. NaOH gave 1,2-dibenzamidobenzene (**12**)



Scheme 2

(Scheme 2). The formation of **12** in the reaction takes place as shown in Scheme 3. This is further supported by the fact



Scheme 3

that treatment of **2** with benzoyl chloride in aq. NaOH at RT also yielded **12**. An authentic sample of **12** was obtained for comparison purpose by direct reaction of **1** with benzoyl chloride under Schotten-Baumann conditions[15]. Condensation of **11** with benzoyl chloride in CH_3CN in the presence of anhyd. K_2CO_3 as base and triethylbenzylammonium chloride (TEBAC) as phase-transfer catalyst[16] yielded 1-benzoylbenzimidazole (**13**) as the only product and no evidence of 2-benzoylbenzimidazole (**14**) could be found on careful examination by the analyses of the reaction mixture or of crude product. An authentic sample of **14**[5,8] was obtained for comparison purposes by CrO_3 oxidation of the known 2-(α-hydroxybenzyl)benzimidazole (**15**). The latter was prepared[8,11] from **1** by reaction with mandelic acid under Phillips' conditions[3].

Heating **11** with Ac_2O in the presence of anhyd. NaOAc resulted in the recovery of **11** on processing the reaction mixture. Treatment of **11** with Ac_2O in the CH_3CN medium in the presence of anhyd. K_2CO_3 as base and TEBAC as phase-transfer catalyst, however, gave the 1-acetyl derivative, i.e. 1-acetylbenzimidazole (**16**). Once again, no evidence for the presence of the expected compound, i.e. 2-acetylbenzimidazole (**3**), could be found on careful examination by tlc analyses of the reaction mixture or of the crude product. The above reactions are briefly summarised in Scheme 2.

Table 1. Preparation of some substituted benzimidazoles and related compounds

Starting material	Reagent/ condition*	Product (Yield %)	M.p.°C (Lit.)**
1	Propanoic acid[a]	**2**	174–75
		(70)	(177[g], 174.5[h])
10	$K_2Cr_2O_7$[b]	**3**	190–91
		(76)	(188–89[i], 190–91[i], 191–92[j])
10	$KMnO_4$[c]	**5**	168–69
		(68)	(174d[k])
1	Sod. pyruvate[a]	**7**	247–49
		(75)	(244–45[h])
1	Pyruvic acid[d]	**7**	247–49
		(60)	(251–52[j])
1	Oxalic acid dihydrate[a]	**8**	>270
		(73)	(>350[g])
1	Trichloroacetic acid[a]	**9**	>260
		(56)	(>360[m])
1	Lactic acid[a]	**10**	180–81
		(78)	(178–89[g])
1	Formic acid[a]	**11**	171–72
		(72)	(170[g], 172–73[h])
1	Benzoyl chloride[e]	**12**	>270
		(70)	(301[n])
1	Chromium trioxide[f]	**14**	213–15
		(70)	(215–16[j])
1	Mandelic acid[a]	**15**	199–200
		(70)	(202–03[g])

*Condition : [a]Phillips' condition (4 *N* HCl, Δ, 3 h); [b]Dil. H_2SO_4, RT; [c]Aq. Na_2CO_3, Δ, 1–2 h; [d]Water, RT, 15 min; [e]Schotten-Baumann conditions; [f]AcOH, 100°, 0–5 h.

**Lit. m.p.(°C) : [g]Ref. 3; [h]Ref. 18; [i]Ref. 7; [j]Ref. 8; [k]Ref. 10; [l]Ref. 19; [m]Ref. 20; [n]Ref. 21.

Experimental

o-Phenylenediamine and solvents were purified by distillation before use. M.ps. were recorded in open capillary tubes in sulphuric acid bath and are uncorrected. Ir spectra (KBr) were recorded on a Perkin -Elmer 2000 FT-IR or on a Pye-Unicam SP3-200 spectrophotometer, nmr spectra

Table 2. Spectral data of some substituted benzimidazoles and related compounds

Comp. no	ν_{max}	^{1}H nmr δ	^{13}C nmr δ	*m/z* (%I)
2	2885 (broad, vs), 1615, 1584, 1538 etc. (series of sharp signals, medium C=C, C=N etc.)	1.45 (3H, t, CH_3), 2.95 (2H, q, CH_2), 7.2–7.65 (4H, AA′BB′ benzene protons)	12.25 (CH_3), 22.00 (CH_2), 144.36, 121.08 (aryl carbons), 156.18 (imidazole quaternary carbons)	146 (M^+, 70) 145 (100), 131 (25), 118 (9), 104 (4), 92 (7) etc.
3	3305 (sharp, strong, chelated NH), 1669 (sharp, vs, chelated C=O), 1575, 1502, 1414 etc. (series of sharp signals, medium, C=C, C=N etc.)	2.78 (3H, s, CH_3), 7.3–8.1 (4H, complex m, benzene protons), 13.42 (1H, s, NH)	26.07 (CH_3), 112.31, 121.97, 123.93, 126.63, 133.78, 143.46, 147.76 (aryl carbons and imidazole quaternary carbons), 192.25 (C=O)	160 (M^+, 50), 145 (10), 118 (100), 91 (38), 90 (37), 63 (38), 43 (100)
5	3040–2590 (broad, strong, NH), 1651 (vs, sharp C=O), 1512, 1470, 1409, 1386, 1341, 1231 etc.	7.26–9.21 (complex m, ArH)	115.2, 116.08, 122.03, 124.1, 136.6, 137.6 (aryl and quaternary carbons)	162 (M^+, 12) 144 (12), 119 (12), 118(100), 117 (7), 91 (34), 90 (19), 64 (19), 63 (24)
7	3325 (w, sharp, NH), 3175–2790 (broad, strong, bonded NH and C–H stretching), 1660 (vs, sharp, amide C=O), 1599 (vs, sharp), 1577, 1495, 1485, 1425 etc. (series of sharp absorptions)	2.41 (3H, s, CH_3), 7.2–7.9 (4H, complex m, ArH), 12.35 (1H, s, NH)	20.55 (CH_3), 116.22, 122.99, 127.86, 129.26, 131.66, 131 92, (aryl carbons), 154.93 (N=C–CH_3), 159.19 (C=O)	160 (M^+, 80), 133 (13), 132 (99), 131 (100), 130 (3), 105 (16), 104 (9), 91 (8), 90 (29), 78 (10), 77 (9), 76 (15), 65 (8) etc.
8	3050 (w), 2990 (w), 2900 (w), 2800 (vw) (series of sharp absorptions due to CH stretching), 1700 (shoulder), 1690 (vs, C=O), 1600 (m), 1500 (w), 1490 (w), 1410 (w), 1400 (s) etc.	7.0–7.4 (4H, m, ArH), 11.9 (2H, s, 2 × NH)	115.172, 123.03, 125.64 (six aryl carbons), 155.25 (two carbonyl carbons)	162 (M^+, 100), 146 (2), 134 (7), 106 (3)
9	3365 (s, NH), 3190 (s, CH), 1630 (s, C=C and C=N), 1592 (s), 1499 (vs), 1457 (m), 1277 (vs), 1252 (w), 1156 (w) etc.	–	–	234 (M^+, 90), 233 (M-1, 10), 228 (12), 158 (15), 155 (12), 129 (100), 128 (90), 127 (15)
10	2890 (broad, vs, NH and OH), 1614, 1587, 1547 (series of sharp, strong absorptions, C=C C=N etc.)	1.98 (3H, d, *J* 6.43 Hz, CH_3), 5.41 (1H, q, *J* 6.43 Hz, CH), 6.29(1H, s, OH), 7.58–7.93 (4H, AA′BB′, ϕ-H), 12.74 (1H, broad s, NH)	23.03 (CH_3), 63.73 (CH), 111.3, 118.4, 120.9, 121.6, 134 1, 143 0, 158.6 (six aryl carbons, and one imidazole carbon)	162 (M^+, 100), 161 (10), 147 (80), 144 (40), 119 (98), 118 (50), 92 (22), 91 (25), 65 (20), 64 (18) etc.
11	2900 (broad, s, NH), 1600, 1475, 1450 etc. (series of sharp absorptions, medium to strong C=C, C=N etc.)	7.2–7.6 (4H, AA′BB′, ϕ-H) 8.22 (1H, s, CH), 12.45 (1H, broad, s, NH)	123.44, 143.67 (phenyl carbons, imidazole quat. carbon)	118 (M^+, 100)
12	3300 (s, strong, NH), 1701(s, strong, C=O), 1590, 1530, 1485, 1430 etc. (series of sharp, medium to strong absorptions)	–	–	–
14	3300 (s, chelated NH), 1660 (s, chelated C=O)	7.26–8.72 (9H, complex m, phenyl and ϕ-H protons), 10.77 (1H, broad s, NH)	112.01, 122.37, 123.80, 126.50, 128.57, 131.34, 133.20, 133.94, 143.98, 147.76 (aryl carbons and imidazole quat. carbon), 184.12 (C=O)	222 (M^+, 57), 221 (12), 195 (15), 194 (100), 105 (55), 77 (60), 51 (15)
15	2910 (broad, s, imidazole, NH, OH), 1615, 1522, 1486, 1447 etc. (series of sharp absorptions)	6.40 (1H, s, CH), 7.02 (1H, broad, OH), 7.56–7.98 (9H, complex m, ArH)	70.06 (CH), 121.4, 126.4, 127.4, 128.2, 142.5, 157.03 (aryl carbons)	224 (M^+, 100), 223 (25), 207 (20), 206 (70), 205 (24), 195 (12), 194 (14), 147 (20), 119 (35), 118 (28), 105 (12), 103 (10), 91 (12), 71 (20)

($CDCl_3$/DMSO-d_6) on a Varian (Gemini) (100 MHz) or on a Bruker instrument at 250 MHz for proton and at 62.9 MHz for carbon probe, and mass spectra on a SCIEX-API-III instrument (70 eV) under electron-impact conditions.

Most of the compounds obtained are known in literature. Therefore, reported procedures were followed for preparing them with appropriate modifications in reaction conditions and/or in work-up of reaction mixtures. The details of the compounds are shown in Table 1. All the compounds were characterised by spectral methods (Table 2).

Preparation of **4** : An intimate mixture of **2** (1.46 g, 10 mmol) and benzaldehyde (3 ml, 30 mmol) was heated at 180–90° in an oil-bath for 4 h. The reaction mixture was then cooled to RT and triturated with n-hexane (5 × 10 ml). The combined hexane washings was decanted out and the residue dried to obtain crude styrylated product **4** (1.77 g, 76%). It was crystallised twice from hot methanol to obtain a tlc-pure product, m.p. 242–44° (lit.[9] 245°); ν_{max} (KBr) 2890 br. strong (imidazole NH), 1627, 1586, 1515 cm^{-1} (series of sharp bands C=C, C=N etc.); ^1H nmr δ (DMSO-d_6/TMS) 2.4 (3H, s, *J* 0.9 Hz, CH_3), 7.1–7.6 (10H, complex m, five phenyl, one vinylic and four aryl protons of heterocyclic ring), 12.6 (1H, br s, NH); ^{13}C nmr δ (DMSO-d_6/TMS) 15.30 (CH_3), 122.00, 127.51, 127.59, 128.55, 129.32, 139.26, 136.52, 154.00 (benzene ring carbons, imidazole quaternary carbon and two vinyl carbons); *m/z* (%I) 234 (M^+, 57, $C_{16}H_{14}N_2^+$), 233 (M-1, 100), 232 (10), 158 (4), 157 (44), 155 (8), 142 (5), 141 (5), 129 (13), 128 (6.5), 127 (16). HRMS for M-1 = $C_{16}H_{13}N_2^+$, found : 233.1079 amu, calcd. : 233.1079 amu.

Oxidation of **3** *and* **4**. *General procedure* : *(a) With alkaline $KMnO_4$* : To a hot solution of $KMnO_4$ (4.8 g, 30 mmol) in water (50 ml) was added a suspension of **3** or **4** (10 mmol) in aq. Na_2CO_3 (2.12 g in 10 ml water). The mixture was heated on a steam-bath (100°) for 1 h. Ethanol (5 ml) was then added to the hot mixture and reaction mass filtered. The clean, hot, basic filtrate was neutralised with gl. AcOH to a pH of 5.5–6.0 and refrigerated for 12 h. The separated precipitate of **5** was filtered, washed with ice-cold water (2 × 5 ml) and dried (1.2 g, 74% from **3** and 0.8 g, 49% from **4**), m.p. 167–69° d. The m.p., m.m.p. and tlc of this product were found to be identical with those of an authentic sample[10].

(b) With acidic $KMnO_4$: To a solution of **3** or **4** (10 mmol) in gl. AcOH (20 ml) was added slowly with stirring at RT a solution of $KMnO_4$ (4.8 g, 30 mmol) in aq. AcOH (1 : 1, v/v; 20 ml) over a period of 0.5 h. Then stirring was continued at RT for a further 2 h, and the unreacted/excess $KMnO_4$ was reduced with $NaHSO_3$ and the mixture filtered. The filtrate was treated with aq. Na_2CO_3 (10%; 5 ml) when the sodium salt of **5** separated out. The latter was filtered, washed with water (2 × 5 ml), resuspended in water and treated with gl. AcOH to a pH of 5.5–6.0. The separated solid (**5**) was washed with ice-cold water (2 × 5 ml) and dried (1.2 g, 74% from **3** and 0.6 g, 37% from **4**), m.p. 167–69° d. The m.p., m.m.p. and tlc of this product were found to be identical with those of an authentic sample[10].

(c) With neutral $KMnO_4$: To a suspension of **4** (2.34 g, 10 mmol) in water (25 ml) was added at RT solid $KMnO_4$ (4.8 g, 30 mmol) over a period of 0.5 h with stirring. The mixture was then stirred at RT for 3 h. Then the unreacted/excess of $KMnO_4$ was reduced with $NaHSO_3$ and the colourless solution filtered. The filtrate was treated with aq. Na_2CO_3 (10%; 5 ml) when the sodium salt of **5** separated out, which was washed with water (2 × 5 ml), resuspended in water and treated with gl. AcOH to a pH of 5.5–6.0. The separated solid (**5**) was washed with ice-cold water (2 × 5 ml) and dried (0.6 g, 37%), m.p. 167–69° d. The m.p., m.m.p. and tlc of this product were found to be identical with those of an authentic sample[10].

Preparation of **9** *from* **1** *and* **5** *by condensation in PPA* : To a freshly prepared, hot, syrupy solution of polyphosphoric acid (30 ml) at 100°, was added an intimate mixture of **1** (2.7 g, 25 mmol) and **5** (4.05 g, 25 mmol). The dark coloured mixture was then heated at 180–90° in an oil-bath for 3 h. Then the reaction mixture was cooled to RT, diluted with water (100 ml) and the acidic solution neutralised with aq. NaOH (40%) to a pH >8.0. The separated solid was washed with water (free of alkali) and dried (2.34 g, 40% based on **5**), m.p. >260°. The tlc and ir of this compound were found to be identical with those of **9** obtained using a reported procedure.

Oxidation of **10** *with acidic $K_2Cr_2O_7$* : To a solution of **10** (8.1 g, 50 mmol) in dil. H_2SO_4 (5%; 40 ml) was added dropwise with stirring a solution of $K_2Cr_2O_7$ (19.8 g, 150 mmol) in aq. H_2SO_4 (25%, v/v; 80 ml) at RT over a period of 20 min. The mixture was then stirred further at RT for 2 h. The separated orange solid (which is the chromium complex of **3**) was washed with water (3 × 10 ml), then suspended in water (50 ml) and treated with aq. NH_3 (1.1) to a pH of 6.0–6.5. The separated solid was washed with water (3 × 10 ml), dried (5.76 g, 72%) and crystallised from boiling ethyl acetate to give a tlc pure product, m.p. 190° (lit.[7,8] 191–93°). Spectral data are presented in Table 2.

Condensation with benzoyl chloride : (a) Of **2** *or* **11** *under Schotten-Baumann conditions. General procedure* : A mixture of **2** or **11** (10 mmol), aq. NaOH (10%; 25 ml) and benzoyl chloride (3.0 ml, 21 mmol) was stirred at RT for 3 h. The separated solid was then washed with water (3 × 20 ml) free of alkali and dried to obtain **12** (2.0 g, 63% from **2** or from **11**), m.p. of both >260°. Tlc and ir (KBr) of this product were found to be identical with those of an authentic sample.

(b) Of **11**, *under phase-transfer catalytic conditions* : To a suspension of anhyd. K_2CO_3 (2.8 g, 20 mmol) in MeCN (25 ml) was added triethylbenzylammonium chloride TEBAC (2.28 g, 10 mmol) and the mixture stirred at RT for 10 min. To it was added **11** (1.18 g, 10 mmol) and stirring continued further for 10 min, followed by the addition of a solution of benzoyl chloride or acetic anhydride (12 mmol) in MeCN (5 ml). The progress of the reaction was monitored by tlc for the disappearance of **11**. On completion of reaction (within 15 min), the mixture was filtered (to remove inorganic salts). The insoluble material was washed with MeCN (2 × 5 ml) and the combined filtrate evaporated to dryness yielding a residue.

In case of benzoyl chloride the residue was taken up in $CHCl_3$ (50 ml) and washed with water (2 × 10 ml). The $CHCl_3$ layer was separated, dried over anhyd. $MgSO_4$ and evaporated to obtain a residue. Trituration of residue with hexane at RT gave a free-flowing solid (**13**; 1.3 g, 59%), m.p. 115–17° (lit.[22] 118°); ν_{max} (KBr) 1680, 1600, 1595, 1520, 1500, 1470, 1450, 1320, 1300.

In case of acetic anhydride, the residue was extracted and crystallised out with hot hexane giving **16** (1.0 g, 63%), m.p. 110–11° (lit.[23] 113–14°); ν_{max} (KBr) 3058, 2925, 2848, 1731 (C=O), 1606, 1507, 1457, 1386, 1288 cm^{-1}.

Acknowledgement

The authors are grateful to U.G.C., New Delhi, and NSERC, Ottawa, Canada, for extending financial support. They are also thankful to Dr. K. Syam Sunder, Professor and Head, Chemistry Department, J. N. T. University, Hyderabad, for facilities and constant encouragement.

References

1. "Benzimidazoles and Congeneric Tricyclic Compounds", ed. P. N. Preston, Interscience-Wiley, New York, 1980, Part 2, Chap.10, p. 531; M. R Grimmet in "Comprehensive Heterocyclic Chemistry", ed. K. T. Potts, Pergamon, Oxford, 1984, Vol. 5, Chap. 4.08, p. 457; K. Hoffmann, 'Imidazole and its Derivatives' in "The Chemistry of Heterocyclic Compounds", ed. A. Weissberger, Wiley-Interscience, New York, 1953, Part I, p. 247, B. V. Kumar and V. M. Reddy, *Indian J. Chem. Sect. B*, 1985, **24**, 928.
2. P. N. Preston, *Chem. Rev.*, 1974, **74**, 279.
3. M. A. Phillips, *J. Chem. Soc.*, 1928, 2393
4. "Oxidation – Techniques and Applications – in Organic Syntheses", ed R. L. Augustine, Marcel Dekker, New York, 1969, Vol. I, Chap V, p. 215; "Synthetic Reagents", ed J. S Pizey, Ellis Harwood, Chichester, 1985, Vol. 6, Chap. 2, p. 62
5. Donau-Pharmazie G.m.b.h., *Chem. Abstr* , 1965, **59**, 6415.
6. L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Interscience-Wiley, New York, 1967, Vol. I, p. 942.
7. H. Matrick, Ph.D. Thesis, University of Pennsylvania, 1960; Ref. 2, p. 93; Merck & Co., Neth. Pat. 6413815/1965 (*Chem. Abstr* , 1965, **63**, 16357); G. W. H. Cheeseman, *J. Chem. Soc.*, 1964, 4645.
8. H Zellner, G. Zellner, F. Kopple and J Dirnberger, *Monatsh. Chem.*, 1967, **98**, 643.
9. Fr. Pat. 818/1937 (*Chem. Abstr.*, 1938, **32**, 2251).
10. V. B. Brasynas, *Chem Abstr* , 1961, **55**, 22293; S. Rosemann, *J. Am. Chem. Soc.*, 1953, **75**, 3854.
11. M. A. Phillips, *J. Chem. Soc.*, 1928, 2393.
12. K. H. Buechel, *Z. Naturforsch. Teil B*, 1970, **25**, 945 (*Chem Abstr.*, 1971, **74**, 22759)
13. D. W. Hein, R. J. Alheim and J. J. Leavitt, *J. Am. Chem. Soc.*, 1957, **79**, 427.
14. E. C. Wagner and W. H. Millet, *Org. Synth.*, 1943, **2**, 65.
15. "Vogel's Textbook of Practical Organic Chemistry Including Qualitative Organic Analysis", ed. B. S. Furniss, ELBS, London, 1978.
16 E. V. Dehmlow and S. S. Dehmlow, "Phase-Transfer Catalysis", Verlag-Chemie, Stuttgart, 1980, Chap 1; W. P. Weber and G. W Gokel, "Phase-Transfer Catalysis in Organic Syntheses", Springer-Verlag, Stuttgart, 1977.
17. W. O. Pool, H. J. Harwood and A. W. Ralston, *J. Am. Chem Soc.*, 1937, **59**, 178.
18. O. Hinsberg, *Annalen*, 1896, **292**, 245
19 H. Suschitzky, B. J. Wakefield and R A. Whittaker, *J. Chem. Soc., Perkin Trans 1*, 1975, 401.
20. G. Holan, E. L. Samuel, B. C. Ennis and R. W. Hinde, *J. Chem. Soc. (C)*, 1967, 20.
21. "Heilbron's Dictionary of Organic Compounds", Eyre and Spottiswoode, London, 1965, Vol. 4, p. 2685.
22. P. Rajakumar, *Indian J. Chem., Sect. B*, 1986, **25**, 1273
23. B. Oddo and F. Ingraffia, *Gazz Chim. Ital.*, 1932, **62**, 1092 (*Chem. Abstr.*, 1933, **27**, 2686).