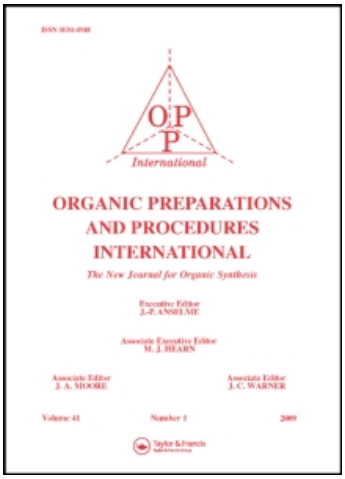

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A FACILE SYNTHESIS OF N-BENZOYLBENZIMIDAZOLES BY PHASE-TRANSFER CATALYSIS

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A FACILE SYNTHESIS OF N-BENZOYLBENZIMIDAZOLES BY PHASE-TRANSFER CATALYSIS

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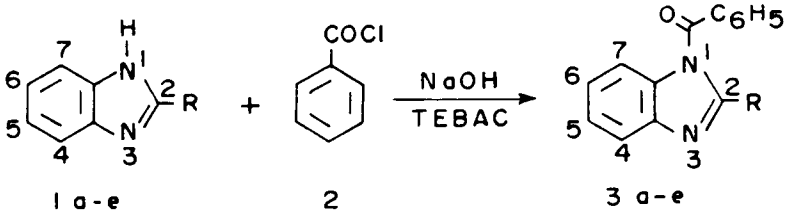
A survey of literature revealed that some reports are on record for the synthesis of N-benzoylbenzimidazoles.[1-6] However, most of them are patents and detailed experimental procedures are not accessible. Benzoylation by the Schotten-Baumann procedure results in the formation of dibenzoyl derivatives of the corresponding o-phenylenediamines, due to the cleavage of the imidazole ring; only small amounts of N-benzoylbenzimidazole derivatives are reported to have formed by this method.[1]

We now report a novel and facile phase-transfer catalytic method for the synthesis of N-benzoylbenzimidazoles in yields of about 50%, using ben-



1 a-e 2 3 a-e

a) R=H; b) R=CH_3; c) R=C_2H_5; d) R=C_6H_5; e) R=C_5H_4N

zyltriethylammonium chloride as catalyst. Thus condensation of

benzimidazoles (1a-e)[7,8] with benzoyl chloride (2) in a mixed organic (benzene) and aqueous phase in the presence of sodium hydroxide (10% w/v) and of a catalytic amount of benzylytriethylammonium chloride yielded N-benzoylbenzimidazoles (3a-e). The yields of 3a-e in the present investigation are substantially higher than the reported methods.[1-3]

The IR spectra of 3 showed the amide carbonyl absorption at ca 1700 cm^{-1}. In the ^1H NMR spectrum of 3b, the C_2 methyl protons were observed as a singlet at δ 2.72 (3H) and all the aromatic protons between δ 7.00-8.00 (9H) as a multiplet; in contrast, in the ^1H NMR spectrum of 1b, the C_2 methyl protons were observed as a singlet at δ 2.40 (3H) while the aromatic C_4, C_7 protons and C_5, C_6 protons appeared as two multiplets between δ 7.30-7.52 (2H) and δ 6.98-7.20 (2H) respectively. The mass spectra of 3b, 3d and 3e indicated the respective molecular ions [$M^{+\cdot}$ = 236, $M^{+\cdot}$ = 298 and $M^{+\cdot}$ = 299 respectively for 3b, 3d and 3e] and the fragmentation patterns are in agreement with the assigned structures. The N-benzoylbenzimidazoles (3a-e) were found to be unstable, slowly hydrolyzing back to the respective benzimidazoles (1a-e), as shown by daily TLC monitoring. The N-benzoylation of 2-methylimidazole by this method led to an intractable mixture.

EXPERIMENTAL SECTION

Melting points were taken in open capillary tubes using a conc. sulfuric acid bath and are uncorrected. IR and NMR spectra were recorded on a Perkin-Elmer-221 spectrophotometer and Varian A60-D instrument respectively. The MS were obtained on a Hitachi RMU 6L mass spectrometer.

2-Methyl-N-benzoylbenzimidazole. Typical Procedure.- To a stirred mixture of 2-methylbenzimidazole (0.66 g, 0.005 mole) in benzene (50 ml), aqueous sodium hydroxide (10% w/v, 50 ml) and a catalytic amount of benzyltriethylammonium chloride (0.02 g) at room temperature, was added dropwise over a period of 30 min. a solution of benzoyl chloride (0.70 g, 0.005 mole) in

benzene (10 ml). Stirring was continued for another 90 min. The benzene

TABLE. N-Benzoylbenzimidazoles (3a-e)

Product	R	mp[a] (°C)	lit.[b] mp (°C)	IR(CO)[c] (cm^{-1})	Yield (%)	Stability[d] (decomposition time in days)
3a[e]	H	92	92	1700	60	18-20
3b	CH_3	85	86	1710	55	13-15
3c	C_2H_5	88	89	1700	35	8-10
3d[f]	C_6H_5	95-6	--	1705	35	8-10
3e[f]	C_5H_4N	124-6	--	1710	35	8-10

a) Crystallization from pet. ether (60-80°). b) Ref. 2. c) IR(KBr) cm^{-1}. d) By TLC study silica gel G: chloroform:acetone (8:2 v/v) and exposed to iodine vapors, complete decomposition time indicated. e) Organic phase used was chloroform since 1a was only sparingly soluble in benzene. f)

Anal. Calcd. for $C_{20}H_{14}N_2O$ (3d): C, 80.53; H, 4.69; N, 9.39
Found: C, 80.44; H, 4.61; N, 9.33

Anal. Calcd. for $C_{19}H_{13}N_3O$ (3e): C, 76.25; H, 4.34; N, 14.05
Found: C, 76.20; H, 4.29; N, 14.01.

layer was separated, washed with water until it was free from alkali and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue crystallized from pet. ether to give 0.71 g (55%) of 2-methyl-N-benzoylbenzimidazole, mp. 85°, lit.[2] mp. 86°. Compounds 3a, 3c, 3d and 3e were similarly prepared from 1a, 1c, 1d and 1e respectively (Table).

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REFERENCES

1. R. C. Elderfield, "Heterocyclic Compounds", Vol. 5, p. 267, John Wiley & Sons, Inc., New York, 1957.

2. L. Wolf, R. Grun and F. Kolasius, Ann., 399, 297; Chem. Abstr., 7, 3742 (1913).

3. A. Dornow and H. Theidel, Chem. Ber., 88, 1267 (1955).

4. M. Haga, R. K. Ness and H. G. Fletcher, J. Org. Chem., 33, 1810 (1968).

5. M. Inoue, T. Saito, K. Arai, S. Kidokoro and H. Okuzawa, Japan. Kokai, 74,76,876 (1974); C. A. 82, 16840c (1975).

6. H. D. Brown and L. H. Sarrett, U. S. Patent 3,055,906 (1962); C. A. 58, 2456c (1963).

7. M. A. Phillips, J. Chem. Soc., 2397 (1928).

8. V. Prabhakar Reddy, P. L. Prasunamba, P. S. N. Reddy and C. V. Ratnam, Indian J. Chem., 22B, 917 (1983).

SYNTHESIS OF 2-NITROCYCLOOCTANONE

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The synthetic utility of cyclic α-nitroketones as well as the preparation of these useful synthetic intermediates has recently been reviewed.[1] α-Nitrocyclooctanone can be prepared by reaction of cyclooctene with dinitrogen tetroxide,[2] but this procedure requires a tedious work-up. On the other hand, two methods are known to prepare the title compound starting from cyclooctanone. Feuer and Pivawer[3] proposed the nitration of cyclooctanone by amyl nitrate at -50° but unfortunately the reaction gave amyl 8-nitrooctanoate as an undesired product while the title compound was obtained in a very low yield. Feuer et al.[4] reported the synthesis of 2-nitrocyclooctanone by nitration of cyclooctanone with potassium amide and amyl nitrate in liquid ammonia at -45° and the title compound was obtained in 60% yield; however, at the same time, amyl 8-nitrooctanoate (21%) was