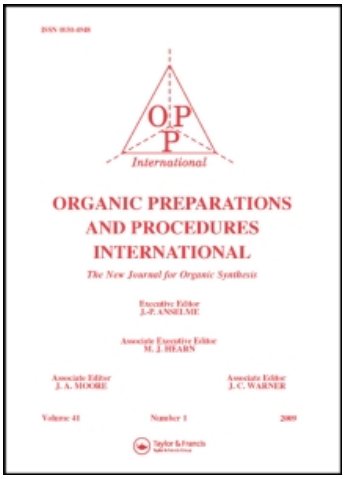

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PYROLYSIS OF 1,1-DIMETHYL-1-PHENYLAMINE-2-BENZOYLIMIDE

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PYROLYSIS OF 1,1-DIMETHYL-1-PHENYLAMINE-2-BENZOYLIMIDE

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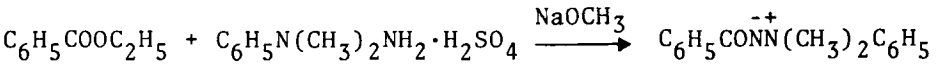

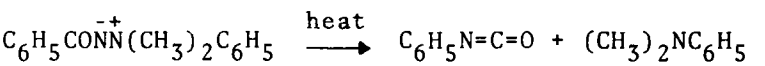

Aroylaminimides substituted with alkyl groups are not suitable as starting materials for the preparation of aryl isocyanates; side reactions occur between the isocyanate and the other products formed in the reaction. For example, pyrolysis of 1,1,1-trimethylamine-2-benzoylimide gave mainly the phenyl isocyanate trimer;[1-3] other products obtained in smaller amounts were benzanilide, 1,3-diphenylurea, carbon dioxide and 2-phenylbenzimidazole.[4] Similarly, 1,1-dihexyl-1-methylamine-2-benzoylimide underwent elimination and rearrangement and gave 1-hexene, dihexylmethylamine, benzanilide, 1,3-diphenylurea, 2-phenylbenzimidazole, carbon dioxide and 1-phenyl-3-methylurazole.[5]

These complications can be avoided by using a 1,1-dimethyl-1-phenylamine-2-aroylimide; the corresponding benzoyl derivative on pyrolysis gives a 94% yield of phenyl isocyanate. This isocyanate is not trimerized by

dimethylaniline and can be separated from the latter by fractional distillation and is isolated in 69% yield.

1,1-Dimethyl-1-phenylamine-2-benzoylimide was prepared by the base catalyzed condensation of ethyl benzoate with 1,1-dimethyl-1-phenylhydrazinium hydrosulfate.

EXPERIMENTAL[6]

1,1-Dimethyl-1-phenylamine-2-benzoylimide. A mixture of 1,1-dimethyl-1-phenylhydrazonium hydrosulfate[7] (97.1g) and sodium methoxide (57.9g) in anhydrous tetrahydrofuran (650 ml) was stirred at -22° for several hours. The resulting suspension was treated at -22° with ethyl benzoate (80.5g) and the mixture was allowed to come to room temperature; stirring was continued for 46 hr. Removal of the tetrahydrofuran gave a residue which was treated with water and extracted with chloroform. The chloroform extract upon removal of the solvent and addition of ether gave a crystalline solid (13.8g, 13.9%) which was recrystallized from a mixture of benzene and hexane; yield, 13.0g; (13.0%); mp 158-9°; ir(nujol) 1560cm^{-1}(CO); nmr($DCCl_3$) δ 7.60 (m, 10, $(C_6H_5)_2$), δ 3.68 (s, 6, $N(CH_3)_2$).

Anal. Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.68; H, 6.56; N, 11.62.

Pyrolysis of 1,1-Dimethyl-1-phenylamine-2-benzoylimide. 1,1-Dimethyl-1-phenylamine-2-benzoylimide (8.83g) was heated at 170° for two hours under anhydrous conditions. The resulting liquid upon distillation gave 7.99g of a mixture,

b.p. 165-195°, of phenyl isocyanate and dimethylaniline. Analysis by gas chromatography using a silicon rubber W98 column at 150° indicated that the ratio of phenyl isocyanate to dimethylaniline was 51.5; 48.5. Fractional distillation at 95 mm using an 8-plate column gave 3.01g (69%) of phenyl isocyanate; b.p. 94-6°.

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