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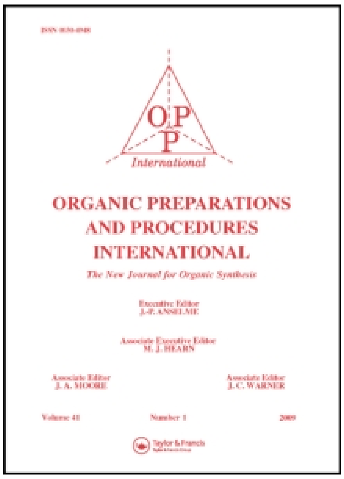

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SYNTHESIS OF AROYL CHLORIDES FROM SUBSTITUTED BENZOTRICHLORIDES

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SYNTHESIS OF AROYL CHLORIDES FROM SUBSTITUTED BENZOTRICHLORIDES

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(4/21/78)

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Detailed procedures for the synthesis of aroyl chlorides by the reaction of benzotrichlorides with hexamethyldisiloxane catalyzed by ferric chloride[1] are given.

$$XYC_6H_3CCl_3 + (Me_3Si)_2O \xrightarrow{FeCl_3} XYC_6H_3COCl + 2\ Me_3SiCl$$

a) X = Y = H b) X = H, Y = o-Cl c) X = H, Y = p-Cl

d) X = o-Cl, Y = p-Cl e) X = H, Y = m-CCl_3 f) X = H, Y = p-CCl_3

EXPERIMENTAL

Melting points and boiling points were uncorrected. IR spectra were recorded on a Hitachi Model EPI-G3 spectrophotometer. GC analyses were performed with an Ohkura Model 802 gas chromatograph. All starting halides were purchased commercially. Hexamethyldisiloxane was supplied by Toshiba Silicone Company. Each reaction was conveniently followed by GC. All acid chlorides synthesized were identified by comparison of their IR spectra with those previously reported.[2]

Benzoyl chloride.- To a mixture of 26.4 g (135 mmoles) of benzotrichloride and 22.7 g (139 mmoles) of hexamethyldisiloxane was added 1.0 g (6 mmoles) of ferric chloride. The mixture was then stirred at room temperature. After 7 min., an exothermic reaction occurred and the temperature rose to 65°. Stirring was continued for 10 min. After removal of trimethylchlorosilane from the resulting mixture by flush distillation, vacuum distillation gave 14. 6 g (77%) of benzoyl chloride as a colorless liquid, bp. 71-72°/18 mm, lit.[3] bp. 93°/20 mm.

o-Chlorobenzoyl chloride.- Ferric chloride (0.9 g, 6 mmoles) was added to a mixture of o-chlorobenzotrichloride (23.0 g, 100 mmoles) and hexamethyl-

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disiloxane (16.2 g, 99 mmoles). The mixture was stirred for 25 min. at room temperature and then for 35 min. at 90°. Essentially the same work-up as above gave 13.8 g (79%) of o-chlorobenzoyl chloride, bp. 71-72°/2.5 mm, lit.[4] bp. 94°/10 mm.

p-Chlorobenzoyl chloride.- A mixture of p-chlorobenzotrichloride (23.0 g, 100 mmoles), hexamethyldisiloxane (16.2 g, 99.7 mmoles) and ferric chloride (0.9 g, 6 mmoles) was stirred for 50 min. at 90°. Work-up gave 14.7 g (84%) of p-chlorobenzoyl chloride as a colorless liquid, bp. 99°/5 mm, lit.[5] 107°/10 mm.

2,4-Dichlorobenzoyl chloride.- A mixture of 2,4-dichlorobenzotrichloride (19.4 g, 73.4 mmoles), hexamethyldisiloxane (11.9 g, 73.3 mmoles) and ferric chloride (0.6, 3.7 mmoles) was stirred for 1 hr at 90°. After removal of trimethylchlorosilane, vacuum distillation of the mixture gave 12.9 g (84%) of 2,4-dichlorobenzoyl chloride as a colorless liquid, bp. 88°/2 mm, lit.[6] bp. 150/34 mm.

Terephthaloyl chloride.- α,α,α,α',α',α'-Hexachloro-p-xylene (23.0 g, 73.5 mmoles), hexamethyldisiloxane (23.8 g, 147 mmoles) and ferric chloride (0.6 g, 3.7 mmoles) were mixed and stirred for 70 min. at 90°. After removal of trimethylchlorosilane from the resulting mixture, vacuum distillation gave 11.2 g (76%) of terephthaloyl chloride as a white solid, bp. 87-88°/2 mm, mp. 78.5-79°, lit.[7] bp. 157-160°/25 mm, mp. 78-80°.

Isophthaloyl chloride.- α,α,α,α',α',α'-Hexachloro-m-xylene (23.0 g, 73.5 mmoles), hexamethyldisiloxane (23.8 g, 147 mmoles) and ferric chloride (0.6 g, 3.7 mmoles) were mixed and then stirred for 2 hr at 80°. Similar treatment as mentioned above gave 11.0 g (74%) of isophthaloyl chloride as a white solid, bp. 103-104°/2 mm, lit.[8] bp. 136°/11 mm.

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AN IMPROVED SYNTHESIS OF s-TRIAZOLO[1,5-x]AZINES

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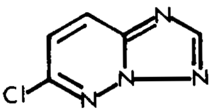
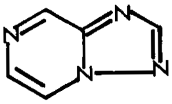
The synthesis of V by an improved method (also suitable for the preparation of III and IV) *via* previously unknown II is described.

$$\underset{\text{I}}{\text{ArNHCH=NOH}} \longrightarrow \underset{\text{II}}{\text{ArNHCH=N-OAc}} \longrightarrow \text{III or IV or V}$$

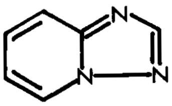
a) Ar = 3-(6-Chloropyrimidyl) b) Ar = 2-Pyrazinyl c) Ar = 2-Pyridyl



III



IV



V

EXPERIMENTAL

Melting points were determined on a Kofler hot stage and mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6L instrument.