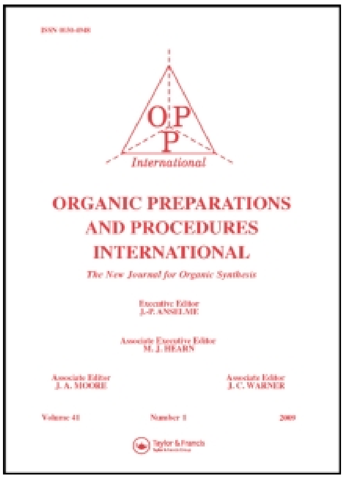

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1,1-DIARYLHYDRAZINES

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1,1-DIARYLHYDRAZINES

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The preparation of 1,1-diphenylhydrazine(IIIa) and N-aminocarbazole(IIIb) by the sequence carbamyl azide to carbazate to hydrazine has been recently reported.[1] The present procedures incorporate several improvements over the previous method. The reaction time has been shortened from *5-10 days* to *15-20 hrs*. The number of manipulations has been reduced from two to one, i.e., the hydrazine can be produced from the azide in a "one pot" operation. Furthermore, the overall yield has been improved by 7-9%. The key factors in these improvements are the utilization of the *t*-amyl group instead of the *t*-butyl group and the hydrolysis of the carbazate without isolation.

In separate experiments, the *t*-amyl carbazates were isolated and characterized. The *t*-amyl is as easily cleaved as the *t*-butyl group by hydrochloric acid[1] as shown by the formation of 1,1-diphenylhydrazine hydrochloride in a practically quantitative yield.

$$Ar_2NCON_3 \xrightarrow{t\text{-AmylOH}} Ar_2NNHCO_2t\text{-Amyl} \xrightarrow[2.\ OH^-]{1.TosOH} Ar_2NNH_2$$

EXPERIMENTAL

1,1-Diphenylhydrazine

A solution of 23.0 g. (0.1 mole) of diphenylcarbamyl azide[1] in 150 ml. of *t*-amyl alcohol was heated under reflux overnight.[2] The small amount of tetraphenylcarbohydrazide (1 g.) was removed by filtration. To the filtrate was added 5 g. of *p*-toluenesulfonic acid and 20 ml. of water and the mixture heated under reflux for 5 hrs. The reaction mixture was cooled to room temperature, 50 ml. of ether added,[3] and washed with 100 ml. of 10% aqueous sodium hydroxide. The organic layer was dried and evaporated *in vacuo*. Distillation gave 13.1 g. (72.4%) of *pure*, *colorless* 1,1-diphenylhydrazine, bp. 130-134°/1.1 mm. Its infrared spectrum was identical to that of an authentic sample.[1]

N-Aminocarbazole

A solution of 1 g. (4.3 mmoles) of biphenylylcarbamyl azide[1] in 10 ml. of *t*-amyl alcohol was heated under reflux overnight. Upon cooling, less than 0.1 g. of *bis*-(biphenylyl) carbohydrazide precipitated and it was removed by filtration. To the filtrate was added 0.2 g. of *p*-toluenesulfonic acid and 5 ml. of water and the mixture heated under reflux for 1 hr. The reaction mixture was cooled, 30 ml. of ether was added,[3] and washed with 5 ml. of 10% aqueous sodium hydroxide. Removal of the solvent gave 0.55 g., 82.2% (after recrystallization from ethanol) of N-aminocarbazole as pale yellow needles, mp. 148-149°, mixtured mp. with an authentic sample[1] undepressed.

t-Amyl 3,3-diphenylcarbazate

A solution of 11.5 g. (0.05 mole) of diphenylcarbamyl azide in 100 ml. of t-amyl alcohol was heated under reflux for 15 hrs. Removal of the solvent left 15 g. of white solid. The solid was dissolved in 100 ml. of ether and the insoluble tetraphenylcarbohydrazide (1.1 g.) was removed by filtration. Evaporation of the filtrate gave 13.5 g. of t-amyl 3,3-diphenylcarbazate. Recrystallization from n-hexane-benzene gave 13 g. (87%) of pure product, mp. 99-100°. The product can be distilled without decomposition, bp. 170°/1 mm.

Anal. Calc'd for C, 72.45; H, 7.43; N, 9.39
Found: C, 72.16; H, 7.45; N, 9.55

t-Amyl 3,3-biphenylylcarbazate

A solution of 1 g. (4.3 mmoles) of biphenylylcarbamyl azide in 10 ml. of t-amyl alcohol was heated under reflux overnight. The small amount of the carbohydrazide was removed by filtration and the filtrate evaporated to give 1.05 g., 84% (after recrystallization from n-hexane-benzene) of t-amyl 3,3-biphenylylcarbazate, mp. 119-120°.

Anal. Calc'd for C, 72.94; H, 6.81; N, 9.44
Found: C, 72.92; H, 6.90; N, 9.52

1,1-Diphenylhydrazine Hydrochloride

A solution of 15 g. (0.05 mole) of t-amyl 3,3-diphenylcarbazate in 100 ml. of methanol containing 5 ml. of conc. hydrochloric acid was heated under reflux for 2 hrs. Removal of the solvent gave a white solid which was washed with 50 ml. of ether; 10.8 g. (97%) of 1,1-diphenylhydrazine hydrochloride was obtained as silky white needles, mp. 160-165°.

REFERENCES

[*] Fellow of the Alfred P. Sloan Foundation

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2. On that scale, the decomposition of the azide is complete after 15 hrs. but not after 8 hrs. (monitoring by IR).

3. Ether is added to prevent the formation of emulsions.

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