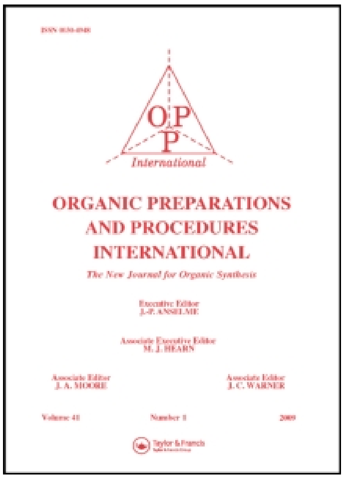

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1-ACYL- AND 1,1-DIACYL-2,2-DIMETHYLHYDRAZINES

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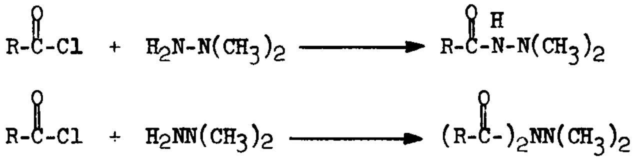

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + H_2N\text{-}N(CH_3)_2 \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{N}\text{-}N(CH_3)_2$$

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + H_2NN(CH_3)_2 \longrightarrow (R\text{-}\overset{O}{\overset{\|}{C}}\text{-})_2NN(CH_3)_2$$

1-Acyl-and 1,1-diacyl-2,2-dialkylhydrazines have been used as intermediates in the preparation of aminimides[2] and polysubstituted hydrazines.[3] The published synthesis used the Schotten-Baumann method which, however, gave low yields. Furthermore, the purification of the monoacylhydrazines was very difficult owing to traces of the diacyl compound. The diacylhydrazine was formed if the monoacyl compound remained in solution and was thus susceptible to further acylation. The monoacylhydrazines were the sole product if a solvent was chosen so that the monoacyl derivatives precipitated as soon as they are formed; hexane, pentane and ethyl ether were suitable for this purpose.

If the diacylhydrazine was desired, a solvent in which the monoacylhydrazine was readily soluble was used; benzene was one of the best solvents for the preparation of the diacyl derivatives which we studied. Hinman always found diacylhydrazines as minor products in the preparation of the monoacyl derivatives.[3] We believe that our results provide an explanation for his findings.

EXPERIMENTAL

1-Benzoyl-2,2-dimethylhydrazine. - To a well stirred solution of 120 g (2 moles) of 1,1-dimethylhydrazine[4,5] in 1000 ml hexane was added dropwise a solution of 140.5 g (1 mole) of benzoyl chloride in 500 ml hexane. The reaction mixture was maintained at 0° throughout the addition. After the addition, the mixture was allowed to warm to 25°, and 100 ml of water was added. The mixture of hydrazide, dimethylhydrazine hydrochloride, water and hexane was neutralized with 0.5N KOH and filtered. The crude hydrazide was air dried (185 g) and recrystallized from carbon tetrachloride, yielding 131 g, (80%), mp 106-7°, lit.[3] yield 24%, mp 106-107°.

1,1-Dibenzoyl-2,2-dimethylhydrazine. - To a stirred solution of 140.5 g (1 mole) benzoyl chloride in 600 ml benzene was added dropwise a solution of 30 g (0.5 mole) 1,1-dimethylhydrazine and 104 g (1 mole) triethylamine in 200 ml benzene. A precipitate was formed immediately. The reaction mixture was maintained at 15-20°. After completion of the addition, the mixture was allowed to warm to 25°. The solid (triethylamine hydrochloride) was filtered and the filtrate evaporated *in vacuo*. The resulting yellow solid was dissolved in refluxing 95% ethanol, brought to the cloud point with water and allowed to cool, yielding in two crops 106 g (80%) 1,1-dibenzoyl-2,2-dimethylhydrazine, mp 152-153°, lit.[3] yield 57%, mp 152-153°.

Anal. Calcd for $C_{16}H_{16}N_2O_2$; C, 71.63; H, 6.01; N, 10.45. Found C, 71.34; H, 6.05; N, 10.50.

1-(4-Vinylbenzoyl)-2,2-dimethylhydrazine[2(f)]. - A solution of 132 g (0.8 mole) of 4-vinylbenzoyl chloride[6] in 250 ml hexane was added dropwise to a solution of 96 g (1.6 moles) of 1,1-dimethylhydrazine in

600 ml of hexane. A precipitate was formed immediately, and the reaction mixture was maintained at 15-20°.

After completion of the addition, 100 ml of water was added, 0.5N KOH added until neutral and the solid collected by filtration. After air drying, the solid (105-140 g)[7] was recrystallized from benzene, yielding 98.7-124.7 g (77-97%)[7] of the hydrazide, mp 125-126°.[2(f)]

Anal. Calcd for $C_{11}H_{14}N_2O$; C, 69.45; H, 7.42; N, 14.72. Found: C, 69.40; H, 7.39; N, 14.62.

1,1-(4-Vinylbenzoyl)-2,2-dimethylhydrazine. - To a solution of 5.4 g (0.033 mole) of 4-vinylbenzoyl chloride in 75 ml of benzene was added dropwise 3.0 g (0.05 mole) of 1,1-dimethylhydrazine in 10 ml benzene. The mixture was stirred at room temperature for 10 hours. The mixture was filtered and the filtrate was washed with water. After the solution was dried over sodium sulfate, the solvent was removed in vacuo. The residue, a yellow solid, 3.5 g, was recrystallized from 80% ethanol, yielding 2.8 g (42%), mp 117-119°.

The infrared spectrum (halocarbon mull) showed absorptions at 3050, 2890, 1775, 1625, 1601 and 1555 cm^{-1}. The nmr spectrum (τ, $CDCl_3$) showed a singlet at 7.10 ($-CH_3$), a quartet centered at 2.50 (AB aromatic) and vinyl multiplet between 4.75 and 3.0 in the expected ratio of 3:4:3.

Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74. Found: C, 74.94; H, 6.35; N, 8.70.

1-Cinnamoyl-2,2-dimethylhydrazine. - To a stirred solution of 52 g (0.86 mole) of 1,1-dimethylhydrazine in 200 ml hexane and 200 ml ether was added a solution of 43 g (0.27 mole) of cinnamoyl chloride[8] in 75 ml ether. The reaction mixture was maintained at 10° throughout the addition, then was allowed to warm to room temperature. After neutralization with 0.5N KOH, the reaction mixture was filtered, washed with water and then air dried, yielding 44.3 g of a white solid, mp 93-99°. Recrystallization from benzene gave 37 g (73%), mp 110-111.5°.

The infrared spectrum (halocarbon mull) showed major absorptions at 3180, 3045, 2950, 1655, 1610 and 1555 cm^{-1}. The nmr spectrum (τ, $CDCl_3$) showed a singlet 7.15 ($-CH_3$), multiplets centered at 3.15 and 1.95 (trans H), aromatic complex centered at 2.30 and N-H singlet at 2.67 in the expected area ratio of 6:2:5:1.

Anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.72. Found: C, 69.50; H, 7.43; N, 14.71.

Ethyl 2,2-dimethylcarbazate. - To a stirred solution of 21.7 g (0.2 mole) of ethyl chloroformate in 50 ml hexane was added dropwise a solution of 24 g (0.4 mole) of 1,1-dimethylhydrazine in 25 ml hexane. The rate of addition was controlled to maintain the reaction temperature below 40°.

The solid (dimethylhydrazine hydrochloride) was filtered and the solvent removed from the filtrate in vacuo. The oil, 26 g, was distilled, bp 90-92° (8 mm), yielding 23.4 g (90%) of an oil which crystallized upon standing, mp 25-28° (hygroscopic); lit.[3,9] yield 30% (bp 83-84°/14 mm) and 44% (bp 45-9°/0.2 mm).

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4. Purchased from FMC Corp. as "Dimazine"$_{TM}$ and redistilled, bp 62-64°

5. An equivalent of dimethylhydrazine is used as an acid acceptor, although other bases e.g., triethylamine, have been utilized.

6. The acid chloride was prepared from thionyl chloride and 4-vinylbenzoic acid. The acid was prepared by the method of E. Oswawa, Makromol. Chem., 83, 100 (1965).

7. Range of ten preparations.

8. Technical grade cinnamoyl chloride was used as received from Eastman Kodak Co.

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