Note

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Reaction of Amide Homologs. XV.[*1] Preparation of N,N′-Alkylidenebisacetamides.

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The well-known condensation between aldehyde and amide is one that takes place to give N,N′-alkylidenebisamide. Generally the reaction is processed on heating the mixture in the presence of acid catalyst such as acetic acid.

$$\mathrm{RCHO} + 2\mathrm{R'CONH_2} \longrightarrow \mathrm{RCH(NHCOR')_2} + \mathrm{H_2O}$$

In views of the previous papers[1,2] and of the repeated experiments in this laboratory, the method appeared to be appropriate chiefly for relatively reactive aldehydes such as formaldehyde and benzaldehyde, and not for higher aldehyde analogs, giving very poorer yield of the bisamide. It was found in this laboratory that perchloric acid was an efficient catalyst for the reaction with acetamide and this employment was convenient for the preparation of rather higher analogs of the bisacetamide. The reaction with a variety of aldehydes proceeded smoothly under milder condition and, as Table I shows, higher yields were obtainable by this method than by the methods using acetic acid catalyst previously reported. It can be said that the present method using perchloric acid catalyst is a convenient and general one.

Experimental

General Procedure——A mixture of 0.36 mole of acetamide, 0.15 mole of aldehyde, and 1.5 ml. of 60% $HClO_4$ was heated on a boiling water bath for 1 hr. On cool, the product, N,N′-alkylidenebisamide, was crystallized in the reaction solution. A slightly excess amount of EtOH required for dissolving crystals of the accompanying acetamide was added. Then, the product was collected by filtration, washed with a small amount of H_2O, and recrystallized from EtOH or acetone to pure crystals which weighed.

Table I. N,N′-Alkylidenebisacetamides

Bisacetamide	Yield[b] (%)	m.p. (°C)	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
Ethylidene-	60 (lit.,[c] 44; lit.,[d] 38)	180～181	$C_6H_{12}O_2N_2$	49.98	8.39	19.43	49.79	8.20	19.60
Propylidene-	61 (lit.,[c] 7.5; lit.,[d] 35)	190～191	$C_7H_{14}O_2N_2$	53.17	8.92	17.71	53.34	9.02	17.53
n-Butylidene-	60 (lit.,[c] 11.5)	188～189	$C_8H_{16}O_2N_2$	55.79	9.36	16.27	55.91	9.27	16.09
n-Heptylidene-	86 (lit.,[c] 6.5)	171～172	$C_{11}H_{22}O_2N_2$	61.65	10.35	13.07	61.82	10.29	12.95
γ-Phenylpropylidene-[a]	82	210～211	$C_{13}H_{18}O_2N_2$	66.64	7.74	11.96	66.80	7.64	11.80

a) A new compound
b) Based on the starting aldehyde
c) Ref. 1); catalyst=AcOH
d) Ref. 2); catalyst=AcOH

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