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THE SYNTHESIS OF ENAMIDES

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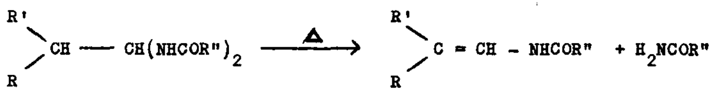
Alkylidenebisamides (I) which are easily prepared from aldeydes and primary amides[1], have been found to undergo thermal decomposition to the corresponding enamides (II) in 40 - 70% yield. The reaction was carried out in a distillation or a sublimation apparatus, at 220-280° (oil bath) under reduced pressure (1-40 mm.).



I

II

a, R=R'=H; R"=C_6H_5.
b, R=R'=H; R"=CH_3.
c, R=CH_3; R'=H; R"=C_6H_5.
d, R=CH_3; R'=H; R"=CH_3.
e, R=C_6H_5; R'=H; R"=C_6H_5.
f, R=R'=CH_3; R"=C_6H_5.
g, R=R'=CH_3; R"=CH_3.

Thus, heating ethylidenebisbenzamide (Ia)[2] to 250° for 35 min., in a sublimation apparatus under reduced pressure (10 mm.), affords a mixture of *N*-vinylbenzamide and benzamide. The mixture was separated by chromatography on silicic acid to give the *N*-vinylbenzamide (IIa; m.p. 102-103°)[3] in 45% yield. Similarly, heating propylidenebisbenzamide (Ic; m.p. 221°) to 240°, in a distillation apparatus under reduced pressure (1 mm.), afforded both *cis*-*N*-(1-propenyl)benzamide (m.p. 77°; 47%) and *trans*-*N*-(1-propenyl) benzamide (m.p. 111°; 23%). Treatment of β-phenylethylidenebisbenzamide (Ie) at 260-270° in a sublimation apparatus as described above, gave *cis*-*N*-β-styrylbenzamide (m.p. 58°; 30%) and *trans*-*N*-β-styrylbenzamide (m.p. 180°[4]; 38%).

Bisacetamides were also found to undergo pyrolysis to the corresponding enamides. *N*-vinylacetamide (IIb; m.p. 53°; 54%) was obtained by heating ethylidenebisacetamide (Ib)[1] to 220° in a distillation apparatus under reduced pressure (40 mm.) and subsequent chromatographing the distillate on basic alumina. Under similar conditions, propylidenebisacetamide (Id) afforded *cis*-*N*-(1-propenyl)acetamide (IId; m.p. 73°; 37%) and *trans*-*N*-(1-propenyl)acetamide (m.p. 72°; 28%).

N-(1-Isobutenyl)benzamide (IIf; m.p. 71°) and *N*-(1-isobutenyl)acetamide (IIg; m.p. 51°) were obtained by the pyrolysis of the corresponding bis-adducts. However, the direct condensation of isobutyraldehyde with benzamide or acetamide in boiling benzene in the presence of a sulfonic acid catalyst[5], afforded a better yield of *N*-(1-isobutenyl) benzamide (62%) and *N*-(1-isobutenyl)acetamide (89%).

The enamides, described above, decolorized bromine solution and were converted, by catalytic hydrogenation, into the corresponding saturated secondary amides. The enamides showed characteristic NH absorptions at 3500 cm^{-1} and 1510 cm^{-1} and CO absorptions at 1660-1680 cm^{-1} in the infrared. In the case of the vinylamides and styrylamides separate C=C absorption bands at 1650 cm^{-1} were also observed. The *trans* enamides showed the characteristic band at 975 cm^{-1} in the infrared. The n.m.r. spectra support the enamide structure. Two different olefinic protons were observed in the spectra, the α protons absorbed at 2.8 - 3.6 τ and the peaks of the β-protons appeared at 4.6 - 5.6 τ. The acidic NH proton appeared as a broad band at 1.3 - 2.1 τ.

N-Vinylbenzamide is very sensitive to acid; it polymerized at room temperature in dry benzene in the presence of sulfonic acid catalyst. Under similar experimental conditions *N*-(1-propenyl)benzamides (*cis* and *trans*) dimerized to 1.3-dibenzamido-2-methyl-1-pentene (m.p. 132°; 50%). The structure of the dimer was established by its oxidation to 3-benzamido-2-pentanone.

In absolute ethanol in the presence of sodium ethoxide, *N*-vinylbenzamide and *N*-(1-propenyl)benzamides were found to add ethanol to the double bond to give *N*-(1-ethoxy)ethylbenzamide (m.p. 61°; 55%) and *N*-(1-ethoxy) propylbenzamide (m.p. 82°; 62%). In boiling dry benzene in the presence of sodium hydride, *N*-(1-propenyl)benzamides and *N*-β-styrylbenzamides underwent *cis* - *trans* isomerization.

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