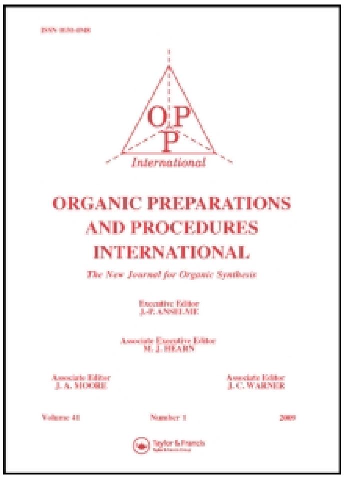

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E AND *Z*-CYANOACRYLAMIDES FROM DIAMINOMALEONITRILE

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E AND Z-CYANOACRYLAMIDES FROM DIAMINOMALEONITRILE

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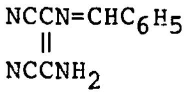
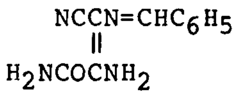
A recent report described a reaction of the monobenzylidene derivative 1 of diaminomaleonitrile and hydrogen peroxide (30%) in ethanol at room temperature for 18 hours which gave Z-α-amino-β-cyano-β-benzylidenaminoacrylamide 2 (37%; 81% in the presence of sodium molybdate), without a trace of either the E-isomer 3 or the position isomer 4.[1,2]



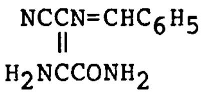
$\begin{array}{l} NCCN{=}CHC_6H_5 \\ \quad \| \\ NCCNH_2 \end{array}$

1



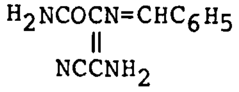
$\begin{array}{l} \quad NCCN{=}CHC_6H_5 \\ \qquad \| \\ H_2NCOCNH_2 \end{array}$

2



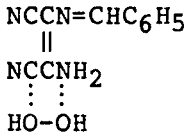
$\begin{array}{l} \quad NCCN{=}CHC_6H_5 \\ \qquad \| \\ H_2NCCONH_2 \end{array}$

3



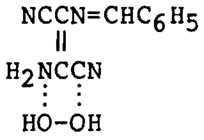
$\begin{array}{l} H_2NCOCN{=}CHC_6H_5 \\ \qquad \| \\ \quad NCCNH_2 \end{array}$

4



$\begin{array}{l} NCCN{=}CHC_6H_5 \\ \quad \| \\ NCCNH_2 \\ \ \vdots \ \vdots \\ HO{-}OH \end{array}$

5



$\begin{array}{l} \quad NCCN{=}CHC_6H_5 \\ \qquad \| \\ H_2NCCN \\ \quad \vdots \ \vdots \\ \quad HO{-}OH \end{array}$

6

We have obtained predominantly the E-amide 3 with trace amount of the Z-isomer 2 by treatment of the Schiff base 1 with a complex prepared from hydrogen peroxide and 1,4-diazabicyclooctane (DABCO·$2H_2O_2$) in tetrahydrofuran (THF) at room temperature for 30 days. Amides 2 and 3 were not present in the residue after solvent removal but were formed on the addition of water. Amide 4, the position isomer, was not detected, thereby confirming the necessity for a regiospecificity in the reaction. Such control was previously attributed to the proposed intermediate 5[1] and can be extended to its readily available tautomer 6, a possible precursor for amide 3; however, the absence of products with N-O bonding tended to discredit intermediates 5 and 6. In dimethyl sulfoxide at room temperature for five weeks the amide 3 slowly isomerized to its isomer 2 whereas in *o*-dichlorobenzene at 180° the reverse isomerization 2 ⟶ 3 occurred.

EXPERIMENTAL

Instruments included Perkin Elmer 237B and 521 grating ir, Varian A-60 and T-60 and Bruker WP-80 and A.E.I. MS30 double-beam mass spectrometers. Yields were based on starting materials consumed. Elemental analyses were provided by Micro-Tech Laboratories, Skokie, Illinois. DAMN was commercially available.

Benzylidenediaminomaleonitrile and DABCO·H_2O_2. - A solution of benzylidenediaminomaleonitrile[1] (1.0 g, 5 mmol) in THF (50 ml) was treated with DABCO·$2H_2O_2$[4] (2.0 g, 11.1 mmol) and stirred at room temperature for 30 days. Removal of the solvent followed by treatment of the residue with water and filtration gave 0.7 g (65%) of a solid, (two spots tlc) of the *E*-monoamide 3 of benzylidenediaminomaleonitrile with a trace of the *Z*-isomer 2. The amide 3, mp. 225-227° (dec.), separated from solution in dimethylformamide and tetrahydrofuran.

IR (KBr): 3420, 3200-3300, 2185, 1695, 1610, 1560, 1420 cm^{-1}; m/e(70 ev): 214 M^+.

Anal. Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 26.15
Found: C, 61.31; H, 4.79; N, 25.90

The structural assignment for amide 3 was supported by ^{13}C-nmr chemical shifts (ppm) at 151.25 (C-2) and at 94.58 (C-3), their close association with 152.11 (C-2) and 92.70 (C-3) reported for the amide 2, and the chemical shift differences in C-2 and C-3: 56.67 for amide 3 and 59.41 for amide 2 which agree with the calculated difference of 60.1 and do not support an alternative assignment as amide 4 for which a chemical shift difference in C-2 and C-3 of 11.7 was calculated.[1] The Z-monamide 2 of benzylidenediaminomaleonitrile was detected by tlc comparison with an authentic sample; mp 211-212° (dec.);[1] m/e(70 ev): 214 M^+.

Both tlc and ^{13}C-nmr revealed an isomerization of the amide 3 into amide 2 in dimethyl sulfoxide-d_6 (solvent used for nmr) in about 30 hours to an extent of 30%. After 5 weeks the isomerization reached 50%. Both isomers 2 and 3 were detected by ^{13}C-nmr: δ 92.58(2), 94.58(3), 114.14(3), 115.29 (2), 127.44(3), 128.17(2) 128.65(2), 128.90(3), 130.17 (2, 3), 136.19(3), 136.49(2), 148.39(3), 150.03(2), 151.25(3), 152.52 (2), 163.09(3), 164.61(2). The assignments for compounds 3 and 2 were determined from two spectra from the same solution, one taken when the solution was freshly prepared and one after an interval of 5 weeks and from spectra of the pure compounds. When the reaction was carried out in aqueous ethanol (90%) benzylidenediaminomaleonitrile and DABCO·$2H_2O_2$ at room temperature for 14 days furnished the amide 2 in 65% yield.

After treatment of the amide 2 (200 mg) with DABCO·$2H_2O_2$ (500 mg) in tetrahydrofuran at room temperature for 40 hrs the presence of the amide 3 was detected (tlc). Heating a sample of amide 2 (200 mg) at 180°C in o-dichlorobenzene (10 ml) for 2 hours afforded the amide 3 in 75% yield, identified by tlc, mp and mixture mp. The amide 3 (10 mg) remained unreactive to ammonium hydroxide (28%, 3 ml) after 3 hrs at 25° and was quantitatively recovered. Under similar conditions the amide 2 cyclized into a pyrrolone.[1]

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2. Amides 2 and 4 were expected Radziszewski reaction[3] products.
3. K. Wiberg, J. Am. Chem. Soc., 77, 2519 (1955).
4. A. A. Oswald and D. L. Guertin, J. Org. Chem., 28, 651 (1963); Y. L. Fan and R. G. Shaw, ibid, 38, 2410 (1973).
5. A referee requested information on the isomerization of compounds 1 and 2 by DABCO. At room temperature DABCO did not bring about an isomerization of either compound; the possibility of such reactions with DABCO at higher temperatures was not investigated.