SYNTHESIS OF α-BENZAMIDO-
β-(2-METHOXYNAPHTHYL)-ACRYLIC ACID

S. P. DHOUBHADHEL, P. P. WAGLEY AND
SABITRI DEVI PRADHAN

Chemistry Instruction Committee
Tribhuban University, Kirtipur
Kathmandu, Nepal

In connection with our studies on α-β-substituted acrylic acid (I), α-benzamido-β-(2-methoxynaphthyl)-acrylic acid (II) was required in quantity. Literature survey indicated that the compound was still unreported. This communication reports the synthesis of the new compound starting with 2-methoxy-1-naphthaldehyde (III) obtained from 2-methoxynaphthalene by for-rylation using phosphorus oxychloride and dimethylformamide according to the procedure of Vincent et al. The aldehyde was converted into 2-phenyl-
4-(2-methoxynaphthaldene)-5-oxazolone (II), which on partial hydrolysis with baryta water afforded the compound (I) the structure of which was confirmed by analytical and spectroscopic methods.

The u.v. spectrum of the compound (I) showed a high intensity band with $\lambda_{max}$ at 225 nm and a broad low intensity band with $\lambda_{max}$ at 342 nm indicating the presence of the chromophore –CH=CH–CO–. The i.r. spectrum showed absorptions in the regions 815–650, 1275–1250, 3550–3250 cm$^{-1}$ and 2950, 1925, 1640, 1601, 1525, 1350 cm$^{-1}$ revealing the presence of =N–H, =CH$_3$, –C=–COH, substituted amide and –C=– structural groupings in conformity with the structure of the compound.

The nmr spectrum displayed a three proton singlet at δ 4.05 (–OCH$_3$) and a broad singlet at δ 4.8 measuring one proton (=N–H). The vinyl proton was seen at δ 8.6 as an ill-defined singlet measuring one proton. The aromatic protons were as a hystack multiplet measuring eleven protons in the range δ 7.2–8.2 ppm. The mass spectrum displayed molecular ion at m/e 347 (1%). The base peak was seen at m/e 105 (C$_9$H$_5$CO$_3^+$). Significant ions occurred at m/e 77 (C$_9$H$_5$CO$_2^+$); at m/e 197 (M–COOH and C$_9$H$_5$CO); at m/e 182 (M–COOH and C$_9$H$_5$CONH) and at m/e 167 (C$_9$H$_7$O$_3^+$). The compound gave positive response to Lassaigne's test for nitroger and formed the azlactone (II) on heating with acetic anhydride.

Experimental

All melting points were uncorrected. UV spectrum was taken on Varian Tectron u.v. vis spectrophotometer model 635; IR spectra were recorded on S.P. 1000 i.r. spectrophotometer. NMR spectra were recorded on Varian-EM-360, 60 MHz nmr spectrometer with TMS as internal reference. Mass spectrum was taken on Hitachi RMU-6E mass spectrometer.

2-Methoxy-1-naphthaldehyde (III) : β-naphthyl methyl ether (5.3 g) was treated with dimethylformamide (3 g) and phosphorus oxychloride (3.4 ml) in ice cold and anhydrous condition. The reaction mixture was then heated over a water bath for 16 hours,
cooled in ice and treated carefully with solid sodium carbonate and water. The solid separated was recrystallised from ethanol to get colourless crystals, m.p. 84-85°C (lit. value 84°C; yield 5%). The analytical values for C and H agreed with the calculated values within the limits of experimental accuracy. i.r. ν max cm⁻¹ 1675 aldehydic C=O; 1600 (ar.m. C=C); 2875-2975 (weak aldehydic C=H), nmr (CDCl₃) δ: 4.05 (3H, s, -OCH₃); 7.1-8.1 (6H, complex m, arom. protons); 9.2 (1H, broad bifurcated singlet, -C=O).

2-phenyl-4-(2-methoxynaphthalene)-5-oxazolone (II): 2-methoxy-1-naphthaldehyde (5 g), hippuric acid (4.8 g), fused sodium acetate (3.2 g) acetic anhydride (75 ml) were heated over water bath for two hours at 60-70°C. The yellow azlactone formed was collected, washed with a little alcohol and recrystallised from alcohol into bright yellow needles m.p. 177°C-178°C; lit. (3) m.p. 178-179°C, yield (50%). The elemental analysis for C, H, and N agreed with the calculated values within the limits of experimental accuracy. u.v. λ max nm (ε) 319 (978), 300 (10,400) nmr (CDCl₃) δ: 4.0 (3H, s, -OCH₃); 7.3-8.1 (11H, complex multiplet in two groups, arom. protons); 8.2 (1H, vinyl proton fused with aromatic proton signals). i.r. ν max cm⁻¹ 1805 (C=O); 1670 (C=N); 1600; 1575; 1525 (arom. C=C).

α-Benzamido-β-(2-methoxynaphthyl)-acrylic acid (I): 2-phenyl-4-(2-methoxynaphthyl)-5-oxazolone (II) (3.0 g), Ba (OH)₂, 2 H₂O (5.7 g), water (103 ml) and alcohol (20 ml) were mixed and the mixture was refluxed for 8 hours. The mixture was filtered hot and the filtrate was acidified with dil. HCl. The solid separated on cooling was washed with water and recrystallised from ethanol to get (I) m.p. 198-200°C, yield 62%. The compound on heating with acetic anhydride gave back (II) as yellow crystalline needles m.p. and the mixed m.p. with authentic sample, 166-167°C. The analytical values for C, H, and N agreed with the calculated values within the limits of experimental accuracy. U.V. λ max nm 255 (E = 74,930); 310 (E = 15,730); 342 (E = 11,100). IR ν max cm⁻¹ 3550-3250 (m, br); 2950 (w); 1725 (s); 1640 (s); 1600 (w); 1525 (s); 1475 (s); 1350 (w); 1275 (s); 1195 (w); 1160 (w); 1125 (w); 1100 (s); 1030 (m); 925 (w); 815 (s); 750 (s). NMR (CDCl₃) δ: 0.05 (6H, complex m, 11H, arom. protons); 8.6 (ill-defined s) (1H, vinyl proton).

Mass spectrum. m/z: 347 (M⁺, 1%); 303 (M⁻CO₂, 4%); 270 (M⁻C₆H₃, 1%); 226 (M⁻H and -C₆H₅CONH, 8%); 211 (M⁻H and -C₆H₅CONH and -CH₂, 8.5%); 197 (M⁻CO₂H and -C₆H₅CO, 12%); 171 (M⁻CO₂H and -C₆H₅CONH, 40%); 167 (M⁻CO₂H and -C₆H₅CONH and -CH₂, 32-5%); 105 (C₆H₅CO²⁺, 100%); 77 (C₆H₅⁺, 54%).

The authors thank Chemistry Chairmen for research facilities. Thanks are also due to Royal Drug Research Laboratory and Centre for Applied Science and Technology, Kirtipur, for the spectra reported. Two of the authors (P. F. W. and S. D. P.) gratefully acknowledge the scholarship from the Institute of Science, TU.

May 14, 1980.


N-ACYLATION AND N-BENZYLLATION OF FUSED BENZOPYRANO-BENZODIAZEPINONES UNDER PHASE TRANSFER CATALYSIS CONDITIONS

G. JAGATH REDDY AND A. V. SUBBA RAO
Department of Chemistry, Osmania University, Hyderabad 500007, A.P., India

Benzodiazepines exhibit varying physiological properties such as psychopharmacological activity, anti-anxiety and sedative. The diazepines when N-acylated or N-alkylated, their physiological activity was enhanced. The present communication deals with the synthesis of a few fused benzopyrano-benzodiazepinones and their N-acyl or N-benzyl products under phase transfer catalysis (PTC) conditions.

Recently Fittón et al. reported the synthesis of 5α, 11-Dihydro[1]benzopyran [2, 3-h][1, 5] benzodiazepine-13(6H)-ones (Iα-b)² by reacting equimolar quantities of chromone-3-carboxaldehydes (Iα-b) and α-phenylendiamine in chloroform and oxidation of Iα-b to 11 benzopyran [2, 3-b] [1, 5] benzodiazepine-13 (6H)-ones (IIα-b) with chloranil. In the present investigation, we report the condensation of chromone-3-carboxaldehydes (Iα-d) with α-phenylendiamine under different conditions. Coloured products were separated as soon as Iα-d were mixed with α-phenylendiamine in acetic acid and characterised as dihydro compounds Iα-d. These dihydro compounds Iα-d were also obtained by condensing Iα-d with α-phenylendiamine in methanol. Keeping the dihydro compounds Iα-d alone in acetic acid or allowing the reaction mixture of Iα-d and α-phenylendiamine in acetic acid