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

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In connection with our studies on α - β -substituted acrylic acid (I), α -benzamido- β -(2-methoxynaphthyl)-acrylic acid (I) 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 formylation using phosphorus oxychloride and dimethylformamide according to the procedure of Vincent *et al.*². The aldehyde was converted into 2-phenyl-4-(2-methoxynaphthalidene)-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 λ_{\max} at 225 nm and a broad low intensity band with λ_{\max} at 342 nm indicating the presence of the chromophore $-\text{CH}=\text{CH}-\text{CO}-$. The i.r. spectrum showed absorptions in the regions 815-650, 1275-1250, 3550-3250 cm^{-1} and at 2950, 1925, 1640, 1600, 1525, 1350 cm^{-1} revealing the presence of $=\text{N}-\text{H}$, $-\text{CH}_3$, $-\text{C}=\text{C}-\text{COCH}$, substituted amide and $-\text{C}=\text{C}-$ structural groupings in conformity with the structure of the compound.

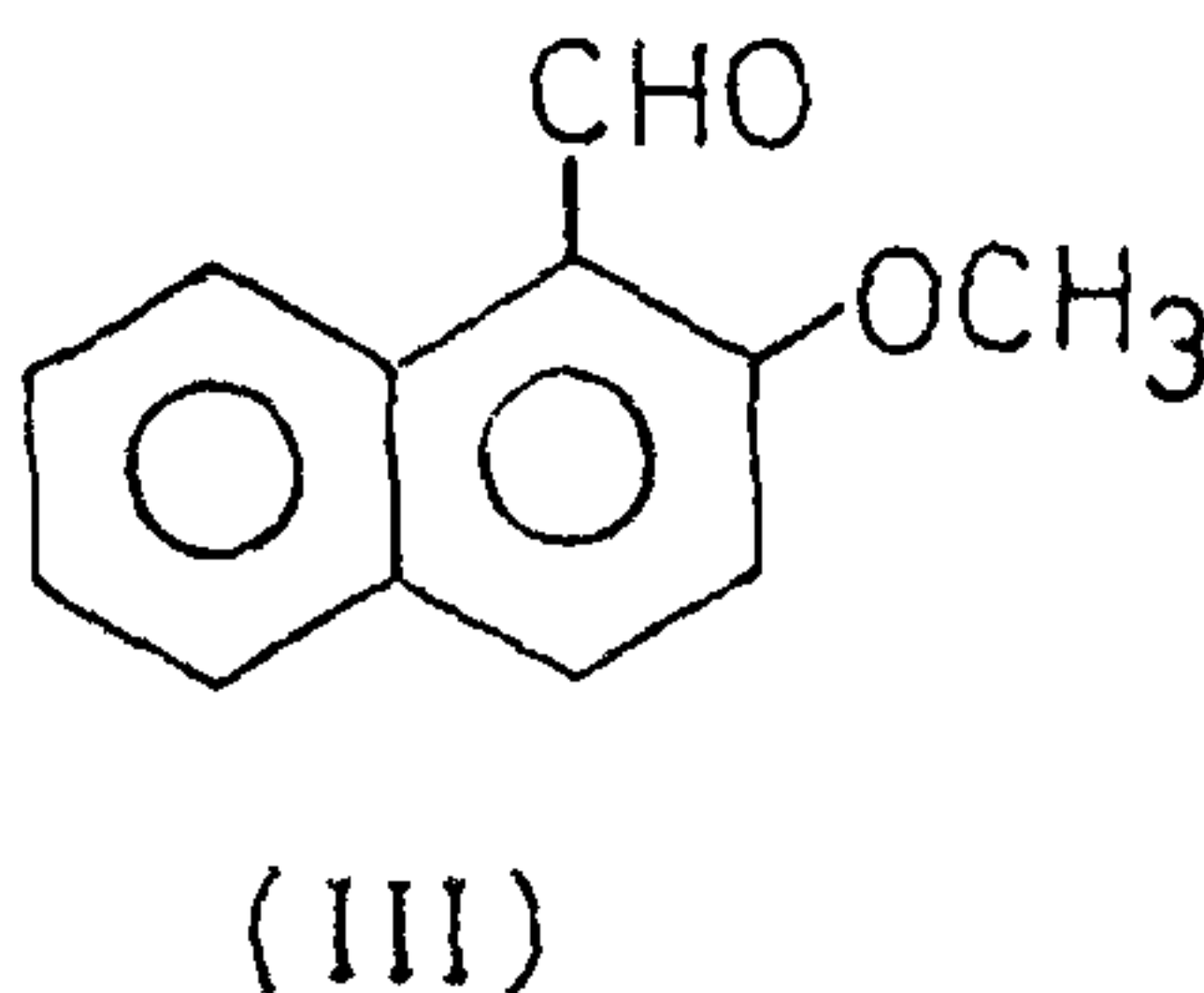
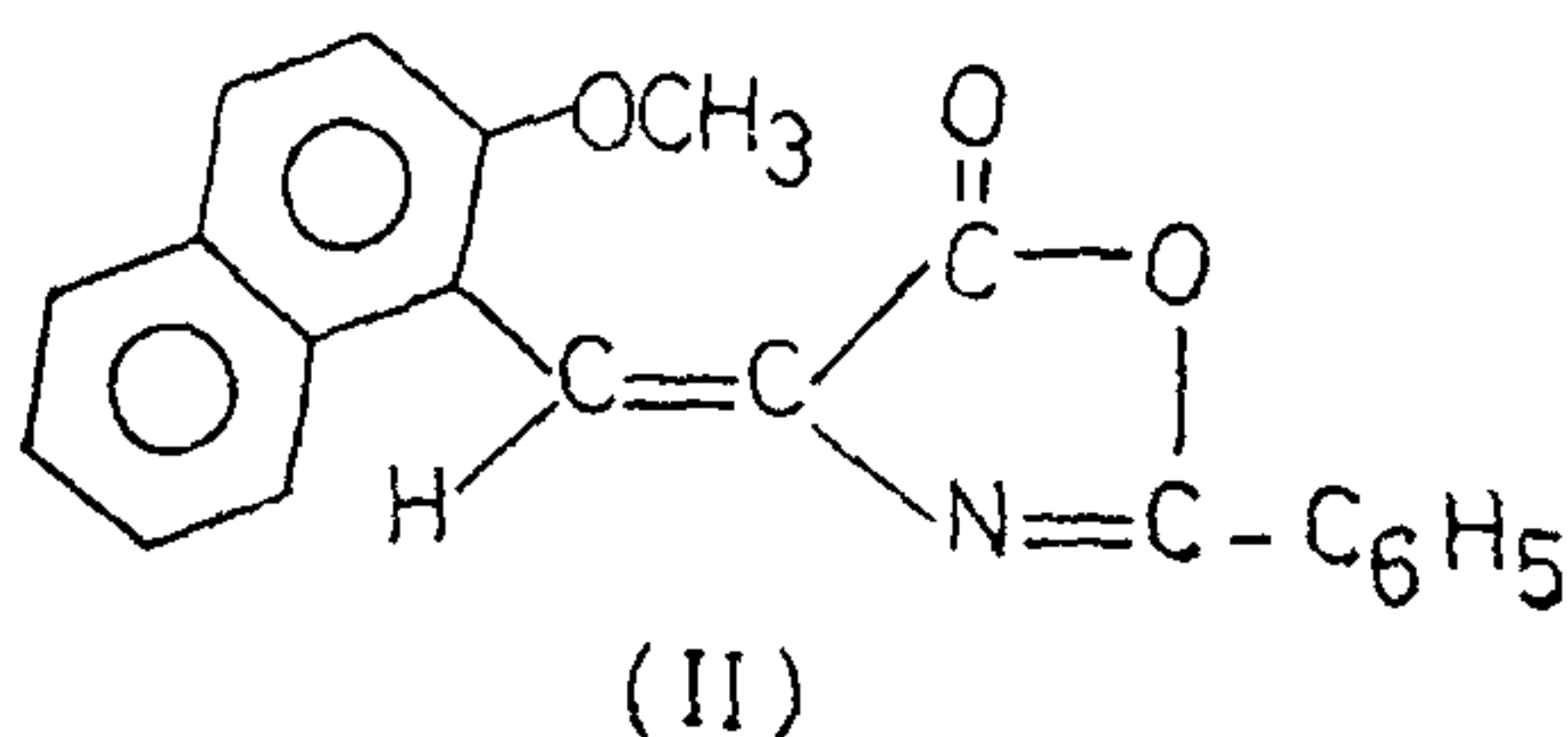
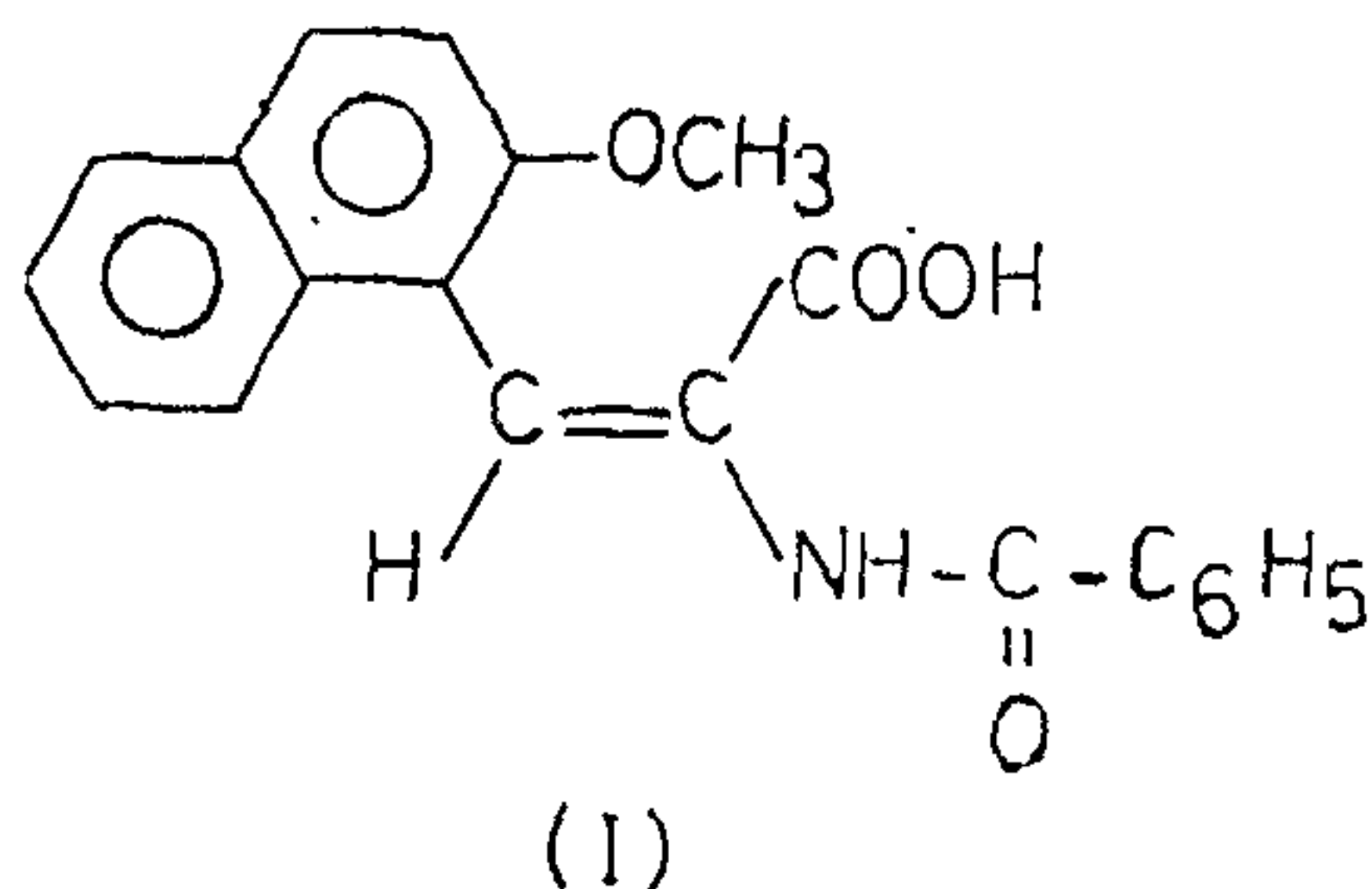
The nmr spectrum displayed a three proton singlet at δ 4.05 ($-\text{OCH}_3$) and a broad singlet at δ 4.8 measuring one proton ($=\text{N}-\text{H}$). The vinylic proton was seen at δ 8.6 as an ill-defined singlet measuring one proton. The aromatic protons were as a haystack multiplet measuring eleven 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 ($\text{C}_6\text{H}_5\text{CO}^{2+}$). Significant ions occurred

at m/e 77 ($\text{C}_6\text{H}_5^{7+}$); at m/e 197 ($\text{M}-\text{COOH}$ and $-\text{C}_6\text{H}_5\text{CO}$); at m/e 182 ($\text{M}-\text{COOH}$ and $-\text{C}_6\text{H}_5\text{CONH}$) and at m/e 167 ($\text{C}_{12}\text{H}_7\text{O}^{7+}$). The compound gave positive response to Lassaigne's test for nitrogen and reformed the azlactone(II) on heating with acetic anhydride.

Experimentals

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 53%). The analytical values for C and H agreed with the calculated value within the limits of experimental accuracy. i.r. ν_{\max}^{KBr} cm^{-1} 1675 (aldehydic C=O); 1600 (arom. C=C); 2875–2975 (weak aldehydic C–H). nmr (CDCl_3) δ : 4.05 (3H, s, $-\text{OCH}_3$); 7.1–8.1 (6H, complex m, arom. protons); 9.2 (1H, broad bifurcated

H
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singlet, $-\text{C}=\text{O}$).

2-phenyl-4-(2-methoxynaphthalidene)-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. $\lambda_{\max}^{\text{CHCl}_3}$ nm (ϵ) 419 (9976), 300 (10,400) nmr (CDCl_3) δ : 4.0 (3H, s, $-\text{OCH}_3$); 7.3–8.1 (11H, complex multiplet in two groups, arom. protons); 8.2 (1H, vinylic proton fused with aromatic proton signals). i.r. ν_{\max}^{KBr} cm^{-1} 1805 (C=O); 1670 (C=N); 1600; 1575; 1525 (arom. C=C).

***o*-Benzamido- β -(2-methoxynaphthyl)-acrylic acid (I):** 2-phenyl-4-(2-methoxynaphthalidene)-5-oxazolone (II) (3.0 g), Ba(OH) $_2$ · 2 H $_2$ O (5.7 g), water (100 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. UV $\lambda_{\max}^{\text{EtOH}}$ nm 255 ($E = 74,030$); 310 ($E = 15,730$); 342 ($E = 11,160$). IR ν_{\max}^{KBr} cm^{-1} 3550–3250 (m, br); 2950 (w); 1725 (s); 1640 (s); 1600 (w); 1525 (s); 1475 (s); 1400 (w); 1350 (w); 1275 (s); 1195 (w); 1160 (w); 1125 (w); 1100 (m); 1030 (m); 925 (w); 815 (s); 750 (s). NMR (CDCl_3) δ : 4.05 (s) (3H, $-\text{OCH}_3$); 4.8 (br. s.) (1H, N=H); 7.2–8.2 (complicated m) (11H, arom. protons); 8.6 (ill-defined s) (1H, vinylic proton).

Mass spectrum. : m/e 347 (M^+ , 1%); 303 ($\text{M}-\text{CO}_2$, 4%); 270 ($\text{M}-\text{C}_6\text{H}_5$, 1%); 226 ($\text{M}-\text{H}$ and $-\text{C}_6\text{H}_5\text{CONH}$, 8%); 211 ($\text{M}-\text{H}$, $-\text{C}_6\text{H}_5\text{CONH}$ and $-\text{CH}_3$, 8.5%); 197 ($\text{M}-\text{COOH}$ and $-\text{C}_6\text{H}_5\text{CO}$, 12%); 182 ($\text{M}-\text{COOH}$

and $\text{C}_6\text{H}_5\text{CONH}$, 40%); 167 ($\text{M}-\text{COOH}$, $-\text{C}_6\text{H}_5\text{CONH}$ and CH_3 , 32.5%); 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100%); 77 (C_6H_5^+ , 54%).

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

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BENZODIAZEPINES exhibit varying physiological properties such as psychopharmacological activity, anti-anxiety and sedative^{1,2}. The diazepines when N-acylated or N-alkylated, their physiological activity was enhanced^{3,4}. 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 Fitton *et al.* reported the synthesis of 5a, 11-Dihydro[1]benzopyrano [2, 3-b][1, 5] benzodiazepin-13(6H)-ones (IIa-b)⁵ by reacting equimolar quantities of chromone-3-carboxaldehydes (Ia-b)⁶ and *o*-phenylenediamine in chloroform and oxidation of IIa-b to [1] benzopyrano [2, 3 b] [1, 5] benzodiazepin-13 (6H)-ones (IIIa-b) with chloranil. In the present investigation, we report the condensation of chromone-3-carboxaldehydes (Ia-d) with *o*-phenylenediamine under different conditions. Coloured products were separated as soon as Ia-d were mixed with *o*-phenylenediamine in acetic acid and characterised as dihydro compounds IIa-d. These dihydro compounds IIa-d were also obtained by condensing Ia-d with *o*-phenylenediamine in methanol. Keeping the dihydro compounds IIa-d alone in acetic acid or allowing the reaction mixture of Ia-d and *o*-phenylenediamine in acetic acid