BENZIMIDAZOLE DERIVATIVES.

XXVI.* WITTIG REACTION IN THE BENZIMIDAZOLONE SERIES

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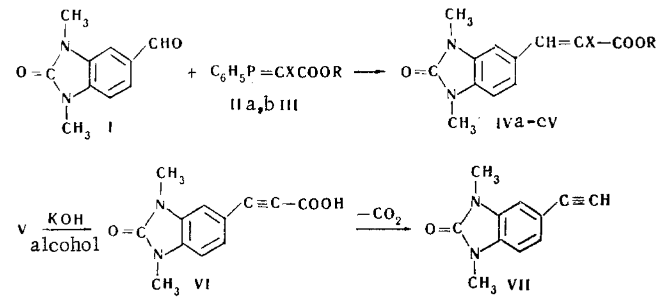
β-(1,3-Dimethyl-5-benzimidazolonyl)acrylic acid, β-(1,3-dimethyl-5-benzimidazolonyl)propiolic acid, and 5-ethynyl-1,3-dimethylbenzimidazolone were synthesized via the Wittig reaction from 5-formyl-1,3-dimethylbenzimidazolone. The UV and IR spectra are presented.

Up to now, the Wittig reaction has found only limited application in the benzimidazole series [1]. Meanwhile, as we have shown, it is a convenient method for obtaining unsaturated acids of this series, particularly the ethynyl derivatives.



II a X = H, R = CH_3; b X = H, R = C_2H_5; III X = Br, R = CH_3; IV a X = H, R = CH_3; b X = H, R = C_2H_5; c X = R = H; V X = Br, R = CH_3

We have synthesized esters of β-(1,3-dimethyl-5-benzimidazolonyl)acrylic acid (IVa,b), the alkaline saponification of which leads to the free acid (IVc), by the reaction of 5-formyl-1,3,-dimethylbenzimidazolone (I) [2] with carbomethoxy- (IIa), and carbethoxymethylenetriphenylphosphoranes (IIb) [3]. IVc is also formed by the condensation of I with malonic acid. Methyl β-(1,3-dimethyl-5-benzimidazolonyl)-α-bromoacrylate, which is converted to β-(1,3-dimethyl-5-benzimidazolonyl)propiolic acid (VI) by treatment with alcoholic alkali, was obtained from bromocarbomethoxymethylenetriphenylphosphorane (III) [4] and I. Carbon dioxide is split out from VI when it is vacuum-sublimed, and it is converted to 5-ethynyl-1,3-dimethylbenzimidazolone (VII). The presence of an acetylenic bond in VII was proved by the formation of copper (yellow color) and silver acetylides. The structures of VI and VII were confirmed by the IR spectra.

EXPERIMENTAL

Methyl β-(1,3-Dimethyl-5-benzimidazolonyl)acrylate (IVa). A solution of 1.9 g (0.01 mole) of I and 3.34 g (0.01 mole) of IIa in 20 ml of chloroform was refluxed for 6-8 h. The solvent was removed by distillation, and the residue was crystallized from ethyl acetate to give 1.74 g (70%) of colorless needles with mp 175° which were readily soluble in alcohol and benzene and insoluble in water. Found %: C 63.5; H 6.0; N 11.2. $C_{13}H_{14}N_2O_3$. Calc. %: C 63.4; H 5.7; N 11.4.

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*See [1] for communication XXV.

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Ethyl β-(1,3-Dimethyl-5-benzimidazolonyl)acrylate (IVb). This was similarly obtained in 81% yield from IIb in the form of colorless prisms with mp 152° (from alcohol) which were soluble in chloroform, benzene, and dioxane. Found %: C 64.4; H 6.5; N 11.0. $C_{14}H_{16}N_2O_3$. Calc. %: C 64.6; H 6.2; N 10.8.

β-(1,3-Dimethyl-5-benzimidazolonyl)acrylic Acid (IVc). A) IVa or IVb was refluxed in 15% alcoholic potassium hydroxide for 4 h to give 95% of colorless plates from dioxane with mp 270° (dec.). Found %: C 62.0; H 5.2; N 12.3. $C_{12}H_{12}N_2O_3$. Calc. %: C 62.0; H 5.2; N 12.1.

B) One drop of piperidine was added to a solution of 0.19 g (1 mmole) of I and 0.11 g (1 mmole) of malonic acid in 1 ml of pyridine, and the mixture was heated at 100° for 1.5 h. The mixture was cooled, and 0.2 g (86%) of a product with mp 270° (from dioxane) was isolated by the addition of 5 ml of 5% hydrochloric acid. The IR and UV spectra* indicated the identity of the compounds obtained. UV spectrum: λ_{max}, nm (log ε): 268 (3.76), 570 (4.27). IR spectrum: ν_{CO} 1700 cm^{-1}.

Methyl α-Bromo-β-(1,3-dimethyl-5-benzimidazolonyl)acrylate (V). A solution of 0.95 g (5 mmole) of I and 2.08 g (5 mmole) of III in 15 ml of benzene was refluxed for 8 h, cooled, and the resulting precipitate was filtered to give 0.86 g (53%) of colorless prisms with mp 182° (dec.) which were readily soluble in chloroform and insoluble in water. Found %: Br 24.9; N 8.9; C 48.2; H 4.2. $C_{13}H_{13}BrN_2O_3$. Calc. %: Br 24.6; N 8.6; C 48.0; H 4.0.

β-(1,3-Dimethyl-5-benzimidazolonyl)propiolic Acid (VI). V [1.63 g (5 mmole)] was refluxed for 4 h in a solution of 2 g of potassium hydroxide in 15 ml of alcohol. The alcohol was removed by vacuum distillation, the residue was dissolved in 25 ml of water, and 1.05 g (91.5%) of colorless plates of VI with mp 183° (from aqueous dioxane) were isolated by the action of 10% hydrochloric acid; the product was slightly soluble in water and dimethylformamide and insoluble in benzene. Found %: C 62.8; H 4.3; N 12.1. $C_{12}H_{10}N_2O_3$. Calc. %: C 62.6; H 4.4; N 12.2. UV spectrum; λ_{max}, nm (log ε): 251 (3.82), 281 (4.18), 293 (4.10), 293 (4.10), and 309 (4.24). The IR spectrum had bands at 1715 cm^{-1} (ν_{CO}) and 2220 cm^{-1} ($\nu_{C\equiv C}$) [5].

5-Ethynyl-1,3-dimethyl-2-benzimidazolone (VII). VI [0.46 g (2 mmole)] was heated at 180-200° and a residual pressure of 8 mm in a vacuum-sublimation apparatus. VI was decarboxylated, and 0.3 g (81%) of colorless prisms of VII with mp 145° (from alcohol) sublimed; the product was readily soluble in chloroform. Found %: C 70.6; H 5.3; N 14.8. $C_{11}H_{10}N_2O$. Calc. %: C 70.94; H 5.4; N 15.0. The IR spectrum of VII contained bands which could be assigned to the valence vibrations $C\equiv C$ (2115 cm^{-1}), $\equiv CH$ (3205 cm^{-1}) [5], and CO (1715 cm^{-1}).† UV spectrum: λ_{max}, nm (log ε): 242 (3.74), 265 (4.2), 279 (3.68), and 298 (4.01).

Silver Acetylide of 5-Ethynyl-1,3-dimethylbenzimidazolone (VIII). This was obtained by the addition of an ammoniacal solution of silver hydroxide to an alcohol solution of VII. Found %: C 44.5; H 3.4; Ag 36.5. $C_{11}H_9AgN_2O$. Calc. %: C 45.0; H 3.1; Ag 36.8.

LITERATURE CITED

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*The IR spectra in mineral oil were obtained with a UR-20 spectrometer, while the UV spectra in methanol were obtained with an SF-4 spectrometer.

†In chloroform.