

THE REACTIONS OF INDANDIONES WITH ACTIVE METHYLENE COMPOUNDS

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ABSTRACT

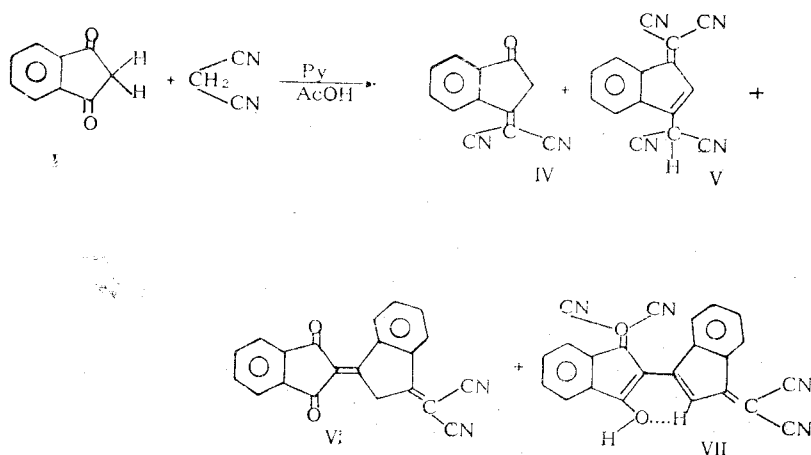
We have studied the reactions of 1,3-indandione (I), 2-methyl-1,3-indandione (II) and 2,2-dimethyl-1,3-indandione (III) with malonitrile and methyl cyanoacetate. Both, I and II, reacted with malonitrile to give several compounds. The reaction of methyl cyanoacetate with I gave a dark, resinous material under similar conditions, while II gave mono imine of the indandione in poor yield. The reaction of III with malonitrile and methyl cyanoacetate did not take place. The structure of the compounds were confirmed on the basis of IR, UV, ¹HNMR and mass spectral studies.

INTRODUCTION

It has been shown that the oximes, dioximes, phenylhydrazones and diphenylhydrazones can be obtained by the condensation of ammonia derivatives with I, II and III (Wislicenus-1889) some reactions where I regarded as active methylene compound have also been reported (Kalnins-1954). On the other hand, there are recent studies on the Japp-Klingemann reaction of II (Hocaoğlu-1987) and the coupling on 2-position of I with aromatic diazonium salts (Hocaoğlu). But we have not seen any information about the Knoevenagel reaction with I, II and III. Accordingly, it will be interesting to investigate, whether or not, the indandiones will be able to react with active methylene compounds such as malonitrile and methyl cyanoacetate. Thus, this paper deals with the carbonyl condensation reactions of indandiones and the structural identification of the product obtained.

RESULTS AND DISCUSSION

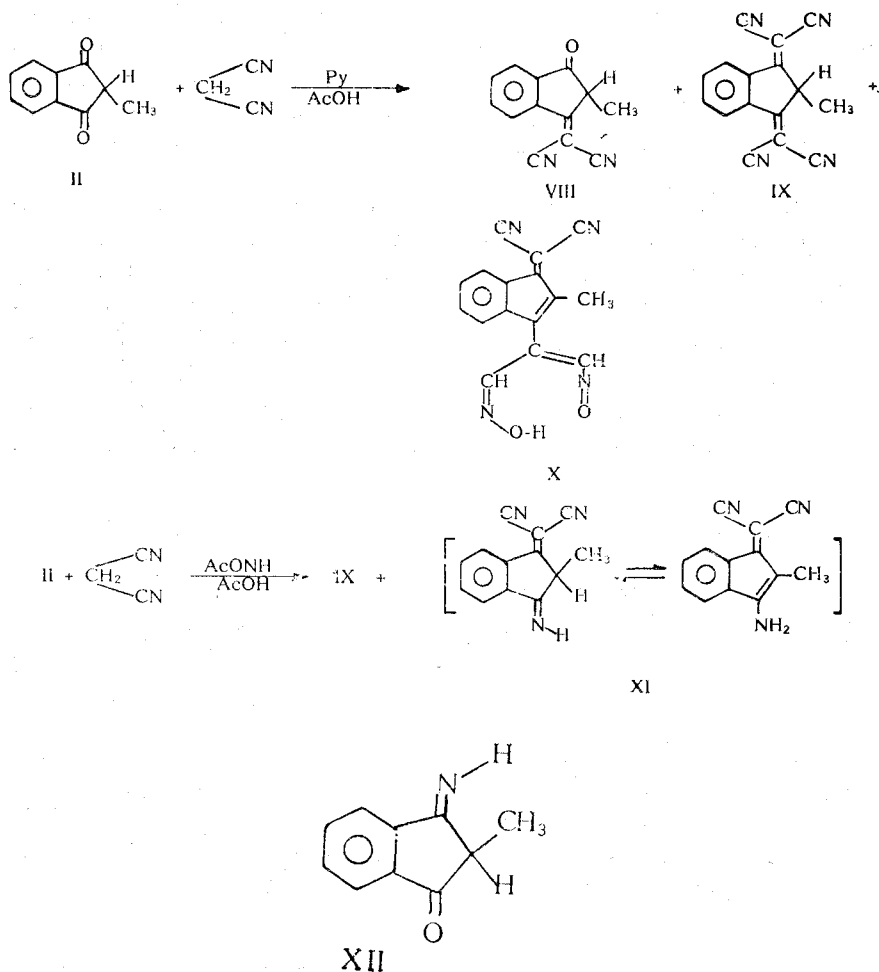
When I was treated with malononitrile in the presence of acetic acid and pyridine, four new compounds IV, V, VI and VII were obtained as products.



We attempted to condense methyl cyanoacetate with the carbonyl groups of I and obtained dark, resinous material under similar conditions. No pure compounds could be separated by TLC or CC.

II was treated with malononitrile in the presence of acetic acid and pyridine and the compounds of VIII, IX and X were obtained. When ammonium acetate was added, into the reaction medium, instead of pyridine, IX yielded in higher percentage, but the other compound (IX) existed in low yield. When the reaction time of the above reaction was extended to four hours the main product was IX with 6% of XI. These results seem to confirm Crowell and Peck's (1953), Robertson's (1960) and Charles (1963) assumptions for the mechanism of Knoevenagel reaction.

When II was treated with methyl cyanoacetate in the presence of acetic acid and ammonium acetate, the imino derivative of the indandione (XII) was obtained in low yield, instead of the condensation products of active methylene compounds. We recovered 74% of II.



The condensation reactions were failed in the presence of pyridine, piperidine or sodium ethoxide, and the recovered II was 96 %, 92 % and 94 %, respectively.

We also attempted to react III with malononitrile or methyl enoacetate under the various conditions, but no product could be obtained. We recovered III, in each case, almost in the initial quantities.

EXPERIMENTAL

The melting points were determined on a Buchi apparatus. The UV spectra were measured on a Coleman Double Beam Spectrophoto-

meter, model Hitachi 124. The IR spectra were recorded in KBr pellets on a Perkin-Elmer 257 Spectrophotometer. ^1H NMR spectra were recorded in the stated solvents on a Varian A60 (60 MHz) instrument with TMS as internal standard. Mass spectra were taken with A.E.I., MS 902 Mass Spectrometer.

The Reaction of I with Malononitrile: To a solution of malononitrile (3,96 g), acetic acid (3,60 g) and pyridine (1 ml) in benzene (40 ml), a solution of I (4,40 g) in benzene (20 ml) was added, drop by drop in thirty minutes with stirring and refluxing. The mixture was refluxed for an additional 2 hours. After cooling the reaction mixture to room temperature and evaporating the solvent at a reduced pressure, the residue was chromatographed on a column of Kieselgur. Elution with petrol-acetone (70:30) yielded IV (9%), V (63%), VI (12%) and VII(17%).

Compound IV: mp 147°C (from chloroform-petrol); IR (KBr) ν_{max} : 2215 ($\text{C}\equiv\text{N}$), 1725 ($\text{C}=\text{O}$) cm^{-1} , UV (MeOH), λ_{max} : 303, 241, 238, 227 nm, ^1H NMR (CD_3Cl) δ : 3,74 (2H,s) ($-\text{CH}_2-$), 7,7-8,10 (3H, m) (3 phenylic hydrogen), 8,80 (1 H, m) (1 phenylic hydrogen); MS m/e: 194 (M^+), 167 ($\text{M}-\text{HCN}$) $^+$, 166 ($\text{MC}-\text{O}$) $^+$, 165 ($\text{M}-\text{CO}-\text{H}$) $^+$, 139 ($\text{M}-\text{NCH}-\text{CO}$) $^+$, 77; Formula: $\text{C}_{12}\text{H}_6\text{N}_2\text{O}$ (by peak matching).

Compound V: mp 198-201°C (decomp.) (from chloroform-petrol); IR (KBr) ν_{max} : 2200 ($-\text{C}\equiv\text{N}$), no $-\text{C}=\text{O}$ band; UV (MeOH) λ_{max} : 729, 715, 680, 644, 365, 246 nm, ^1H NMR ($\text{CD}_3-\text{CO}-\text{CD}_3$) δ : 3,96 (1 H,s), 5,87 (1 H, s), 7,70 (4H, m); MS m/e: 242 (M^+), 216 ($\text{M}-\text{CN}$) $^+$, 215 ($\text{M}-\text{HCN}$) $^+$, 189 ($\text{M}-\text{CN}-\text{HCN}$) $^+$, 188 ($\text{M}-2\text{HCN}$) $^+$; Formula: $\text{C}_{15}\text{H}_6\text{N}_2$ (peak matching).

Compound VI: mp 236-240 (decomp.) (from chloroform-petrol); IR (KBr) ν_{max} : 3610, 3440, 2220 ($-\text{CN}$), 2200 ($-\text{CN}$), 1680 ($-\text{C}=\text{O}$), 1640 ($\text{C}=\text{O}$), 1588 ($\text{C}=\text{C}$); UV (MeOH) λ_{max} : 692, 635, 595, 290, 240 nm; ^1H NMR ($\text{CD}_3-\text{CO}-\text{CD}_3$) δ : 2,84 (2H, s) ($-\text{CH}_2-$), 7,30-7,92 (8H, m) (aromatic); MS m/e: 322 (M^+), 321 ($\text{M}-\text{H}$) $^+$, 296 ($\text{M}-\text{CN}$) $^+$, 295 ($\text{M}-\text{HCN}$) $^+$, 294 ($\text{M}-\text{HCN}-\text{H}$) $^+$ and ($\text{M}-\text{CO}$) $^+$; Formula: $\text{C}_{21}\text{H}_{10}\text{N}_2\text{O}_2$ (by peak matching).

Compound VII: mp 282-290°C (decomp.) (from chloroform-petrol); IR (KBr) ν_{max} : 3435 ($-\text{OH}$), 2215 ($-\text{CN}$), no $\text{C}=\text{O}$ band, 1640 ($\text{C}=\text{C}$), 1500 cm^{-1} , UV (MeOH) λ_{max} : 490, 295, 268 nm; ^1H NMR (DMSO) δ : 5,07 (2H, m), 7,20-8,00 (8H, m); MS m/e: 370 (M^+), 308, 194, 165, 139; Formula: $\text{C}_{24}\text{H}_{10}\text{N}_4\text{O}$ (by peak matching).

The reaction of II with Malononitrile: Malononitrile (3,96), acetic acid (3,60 g) and pyridine (1 ml) were added to a solution of II (4,80 g) in benzene (65 ml). The solution was refluxed for 2 hours. After cooling it to room temperature and evaporating the solvent in reduced pressure, it was first shaken with water (100 ml) and then extracted with ether (50 ml x 3). The ether phase was evaporated and the residue was chromatographed on a column of Kieselgur. Elution with chloroform-acetone (80:20) yielded VIII (8%), IX (57%) and X (32%). VIII and IX were crystallized from the mixture of chloroform-petrol. X was purified on preparative TLC by eluting it with chloroform-acetone (80:20) mixture and crystallized from chloroform-petrol.

Compound VIII: mp 186–187°C; IR (KBr) ν_{\max} : 2240 (—CN), 1730 (C=O), 3440 and 1610 (enol) cm^{-1} ; UV (MeOH) λ_{\max} : 304, 255, 248, 230 nm, $^1\text{HNMR}$ (CDCl_3) δ : 1,62 (3H, d) (— CH_3), 3,60 (1H, q) (C—H), 7,97 (3H, m) and 8,80 (1H, m) (aromatic); MS m/e : 208 (M^+), 207 (M—H^+), 193 (M—CH_3^+), 182 (M—CN^+), 181 (M—HCN^+), 165 ($\text{M—C}_2\text{H}_3\text{O}^+$), 125 ($\text{M—C}_3\text{H}_5\text{O—CN}^+$), 77; Formula: $\text{C}_{13}\text{H}_8\text{N}_2\text{O}$ (by peak matching).

Compound IX: mp 205–207°C (decomp.); IR (KBr) ν_{\max} : 2200 cm^{-1} (—CN), UV (MeOH) λ_{\max} : 660, 615, 575, 248 nm; $^1\text{HNMR}$ (CD_3OD) δ : 2,30 (3H, s) (— CH_3), 7,49 (4H, m) (aromatic); MS m/e : 256 (M^+), 255 (M—H^+), 241 (M—CH_3^+), 230, 215, 204, 203; Formula: $\text{C}_{16}\text{H}_8\text{N}_4$ (by peak matching).

Compound X: mp 218–221°C; IR (KBr) ν_{\max} : 3350, 3280, 3220, 3180, 2250, 2235, 2210 cm^{-1} ; UV (MeOH) λ_{\max} : 315, 250, 235 nm; $^1\text{HNMR}$ (CD_3OD) δ : 1,74 (3H, s), 4,76 (2H, s), 7,50–8,00 (4H, m) (aromatic), 8,17–8,40 (1H, d); MS m/e : 290 (M^+), 273 (M—OH^+), 272 ($\text{M—H}_2\text{O}^+$), 271 ($\text{M—H}_2\text{O—H}^+$), 248 (M—CNO^+), 246 (M—HCN—OH^+), 230 (M—2NO^+), 218 (M—NO—CNO^+), 204 (M—2HCNO^+), 77; Formula: $\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_2$ (by peak matching).

The second reaction of II with ammonium acetate instead of pyridine gave IX (73%) and XI (18%). The extension of the reaction time to 4 hours also gave IX (89,5%) and XI (6%).

Compound XI: mp 201–203 (decomp.); IR (KBr) ν_{\max} : 3260 and 3230 (— NH_2), 2220 (—CN), 1680 cm^{-1} (imine); UV (MeOH) λ_{\max} : 523, 355, 320, 287, 278, 230 nm; $^1\text{HNMR}$ (DMSO) δ : 2,04 (3H, s) (CH_3), 3,38 (1–2H, s) (C=N—H), 7,20–8,00 (3H, m) and 8,65 (1H, m) (aro-

matic); MS m/e : 207 (M^+), 206 ($M-H$)⁺, 181 ($M-CN$)⁺, 180 ($M-HCN$)⁺, 179 ($M-C_2H_4$)⁺, 152 ($M-2CN$)⁺, 151 ($M-CN-HCN$)⁺, 77; Formula: $C_{13}H_9N_3$ (by peak matching).

The reaction of II with methyl cyanoacetate: Methyl cyanoacetate (6,54 g), acetic acid (3,60 g) and ammonium acetate (0,92 g) were added to a solution of II (4,80 g) in benzene (65 ml). The solution was refluxed for 2 hours. After cooling it to room temperature and evaporating the solvent at reduced pressure, the residue was chromatographed on a column of Kieselgur. Elution with chloroform- acetone (80:20) yielded XII (23 %) and II (75 %). No reaction was observed when pyridine, piperidine or sodium ethoxide were used instead of ammonium acetate. We recovered the indandione in the yield more than 90 %.

Various attempts were failed in reacting III with malononitrile or methyl cyanoacetate in the presence of ammonium acetate or pyridine under the similar conditions.

Compound XII: mp 128°C, IR (KBr) ν_{max} : 3350 and 3170 (imine), 1685, 1640, 1615, 1550 cm^{-1} ; UV (MeOH) λ_{max} : 630, 590, 510, 260, 254 nm; 1NMR (TFA) δ : 1,82 (3H, d), 4,14 (1H, q) (C—H); 8,52–8,69 (4H, m); MS m/e : 159 (M^+), 158 ($M-H$)⁺, 131 (M/CO)⁺, 130 ($M-CO-H$)⁺, 105, 104, 103, 77; Formula: $C_{10}H_9NO$ (by peak matching).

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