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o-Acetylbenzophenone produced yellow 1,2-diaryl-3-(aryliminomethyl)isoindole by the reaction with aromatic amines in the absence of acid. On the reaction of *o*-diacetylbenzene under the similar condition, three types of yellow products were obtained. The structures of these isoindole derivatives were determined and their formation mechanism was proposed.

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o-Acetylbenzophenone (**1**) and *o*-diacetylbenzene (**2**) produce violet reaction mixtures by the reaction with various primary amines in the presence of acetic acid and/or hydrochloric acid. From the reaction mixtures of **1**, one type of red and three types of deep blue pigments had been isolated and their structures were determined by one of the authors previously [1-3]. Because of the active two methyl groups of **2**, the structures of the products with **2** were very complicated and not yet determined.

This paper describes the structures of the yellow products formed by the reactions of **1** and **2** with aniline and *p*-anisidine in the absence of acid, and their formation mechanism was proposed. The reaction of **1** with aniline or *p*-anisidine in benzene or ether afford a yellowish brown mixture. From the mixture of yellow crystals, 1,2-diphenyl-3-(phenyliminomethyl)isoindole (**3a**) or its *p*-methoxyphenyl derivative **3b** were isolated in moderate yields respectively.

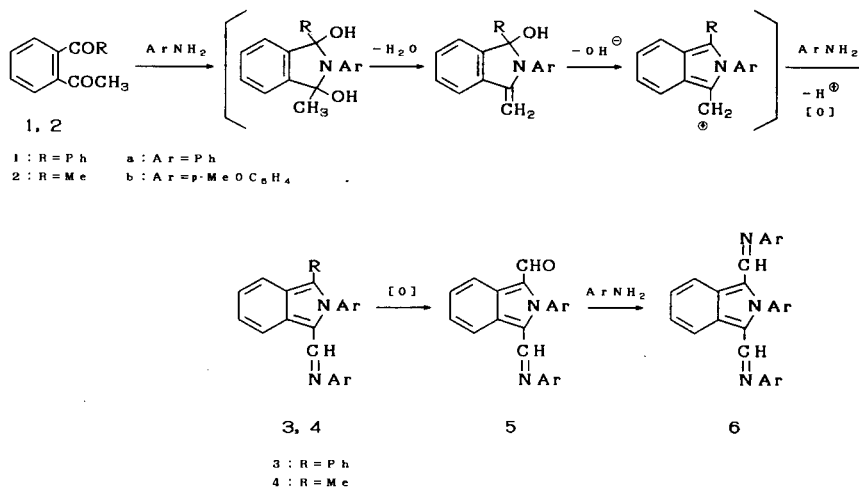
The reaction of **2** under similar conditions, yellow and dark-colored products were obtained. The major part of the yellow products was determined to be 1-methyl-2-phenyl-3-(phenyliminomethyl)isoindole (**4a**) or its *p*-methoxyphenyl derivative **4b** by ms, nmr and ir spectra in compar-

ison with the formation of **3**. By repeated column chromatography for further purification, **4** was changed into 1-formyl-2-phenyl-3-(phenyliminomethyl)isoindole (**5**) and 1,3-bis(phenyliminomethyl)-2-phenylisoindole (**6**) and the other decomposition products owing to oxidation and other reactions with unreacted amine or intermediates. The elute containing **4** was oxidized by cerium(IV) ammonium nitrate to **5** and the structure of **5** was determined on the basis of the ms, nmr and ir spectra. Compound **5** also decomposed slowly on column or preparative layer chromatography as well as on recrystallization. Orange crystals of **6** are stable and constitute the major part of the yellow products when the reaction was performed in the presence of excess aromatic amine. Although the reaction of **5** and aniline or *p*-anisidine gave a certain amount of **6**, it is not clear that the formation of **6** proceeded exclusively *via* compound **5** or from the other intermediate products. The dark-colored products in the reaction of **2** and aromatic amines are to be subject to the further investigation.

EXPERIMENTAL

Melting points were determined on a Yanaco micromelting point apparatus and are uncorrected. The infrared spectra were

Scheme



taken on a JASCO A-102 spectrometer using potassium bromide pellets and ultraviolet spectra were recorded with a JASCO UVIDEK-505 in benzene solution. The nuclear magnetic resonance spectra were measured on a Varian XL-200 and Hitachi R-24A spectrometers in deuteriochloroform, using tetramethylsilane as the internal standard. Mass spectra were obtained with LC-Mass M 2000 or ESCO EMD-05B spectrometer. For column chromatography, silica gel (Kieselgel 60, Merck, 70-230 mesh ASTM) and for preparative layer chromatography, silica gel pre-coated plates (Kieselgel 60, Merck) were used. Elemental analyses were performed at Elemental Analysis Center in Kyoto University.

1,2-Diphenyl-3-(phenyliminomethyl)isoindole (**3a**).

An ether or benzene solution of 2.5 mmoles of **1** [4] was reacted with 25 mmoles of aniline at room temperature for 10 days. After concentrating the mixture under reduced pressure, the resulting yellow solid (280 mg, 30%) was recrystallized from benzene. Using methanol as the solvent, 5% of bis(2,3-diphenyl-1-isoindolyl)methane [5] was produced besides **3a**.

Compound **3a** had mp 196.0-197.0° (yellow needles); ir: 1620 (conjugated C=N) cm^{-1} ; uv: λ max, nm (log ϵ), 416 (4.48), 327 (sh), 286; ^1H nmr: δ 8.86 (m, 1H, 4-position of isoindole), 8.28 (s, 1H, iminomethyl), 7.78 (m, 1H, 7-position of isoindole), 7.52-7.08 (m, 17H); ms: m/e 372 (M^+).

Anal. Calcd. for $\text{C}_{27}\text{H}_{20}\text{N}_2$ (372.5): C, 87.07; H, 5.41; N, 7.52. Found: C, 87.10; H, 5.46; N, 7.38.

1,2-Bis(*p*-methoxyphenyl)-3-(*p*-methoxyphenyliminomethyl)isoindole (**3b**).

By treating 1 mmole of **1** with 10 mmoles of *p*-anisidine in a similar manner as for the preparation of **3a**, 176 mg (41%) of **3b** were obtained. This compound had mp 213.0-214.5° (yellow needles from benzene); ir: 1610 (conjugated C=N), 1241 and 1208 (=COC) cm^{-1} ; uv: λ max, nm (log ϵ), 423 (4.61), 284 (4.33); ^1H nmr: δ 8.76 (m, 1H, 4-position of isoindole), 8.27 (s, 1H, iminomethyl), 7.77 (m, 1H, 7-position of isoindole), 7.43-7.09 (m, 11H), 6.91 (m, 4H), 3.85 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3); ms: m/e 432 (M^+).

Anal. Calcd. for $\text{C}_{29}\text{H}_{24}\text{N}_2\text{O}_2$ (432.5): C, 80.53; H, 5.59; N, 6.48. Found: C, 80.60; H, 5.87; N, 6.44.

Yellow Products from *o*-Diacylbenzene (**2**) and Aniline.

To a benzene solution of **2** [6] (3 mmoles) 12 mmoles of aniline was added and allowed to stand at room temperature or 4° for 7 or 30 days. After evaporating the mixture under reduced pressure, the residue was chromatographed on silica gel column using benzene and benzene-ethyl acetate (30:1) as the eluent. From the first yellow fraction 1,3-bis(phenyliminomethyl)-2-phenylisoindole (**6a**) was isolated and from the second yellow fraction 1-methyl-2-phenyl-3-(phenyliminomethyl)isoindole (**4a**) as well as a small amount of 1-formyl-2-phenyl-3-(phenyliminomethyl)isoindole (**5a**) were obtained. The total yield of **4a**, **5a** and **6a** was 20-24%.

By further column chromatography for purification **4a** was gradually changed to **5a** and other decomposition products. Eluted **4a** was reacted with cerium(IV) ammonium nitrate in aqueous acetic acid [7] to afford **5a** in moderate yield.

Compound **5a** was also sensitive to oxidation and we were un-

successful in isolating it as a pure crystalline substance. Treating **5a** with aniline in benzene produced a certain amount of **6a**. Carrying out the reaction with a molar ratio of **2** and aniline by 1:1 and 1:10, the major part of yellow products were **4a** in 22% yield and **6a** in 20% yield were obtained respectively.

Compound **4a** had ir: 1600 (conjugated C=N) cm^{-1} ; uv: λ max, nm, 407, 377 (sh), 282; ^1H nmr: δ 8.67 (m, 1H), 8.16 (s, 1H, iminomethyl), 7.75-6.78 (m, >13H containing impurities), 2.44 (s, 3H, CH_3); ms: m/e 310 (M^+), 295 ($\text{M}-\text{CH}_3$) $^+$.

Compound **5a** had ir: 1642 (conjugated C=O), 1602 (conjugated C=N) cm^{-1} ; uv: λ max, nm, 410, 285; ^1H nmr: δ 9.75 and 9.65 (s and s, 1H, syn and anti CHO), 8.78 (m, 1H), 8.48 (m, 1H), 8.26 (s, 1H, iminomethyl), 7.98 (m, 1H), 7.71-6.94 (m, >11H containing impurities); ms: m/e 324 (M^+), 323 ($\text{M}-1$) $^+$.

Compound **6a** had mp 186.5-188.5° (from ethanol); ir: 1595 (conjugated C=N) cm^{-1} ; uv: λ max, nm (log ϵ), 447 (4.72), 357 (3.77), 298 (4.33); ^1H nmr: δ 8.80 (m, 2H, 4- and 7-positions of isoindole), 8.24 (s, 2H, iminomethyl), 7.68-7.12 (m, 17H); ms: m/e 399 (M^+).

Anal. Calcd. for $\text{C}_{28}\text{H}_{21}\text{N}_3$ (399.5): C, 84.18; H, 5.30; N, 10.52. Found: C, 83.93; H, 5.25; N, 10.41.

Yellow Products from **2** and *p*-Anisidine.

By treating of **2** and *p*-anisidine in a similar manner described above, 1-methyl-2-(*p*-methoxyphenyl)-3-(*p*-methoxyphenyliminomethyl)isoindole (**4b**), 1-formyl-2-(*p*-methoxyphenyl)-3-(*p*-methoxyphenyliminomethyl)isoindole (**5b**) and 1,3-bis(*p*-methoxyphenyliminomethyl)-2-(*p*-methoxyphenyl)isoindole (**6b**) were obtained. The total yield of **4b**, **5b** and **6b** was 27-30%.

Compound **4b** had ir: 1610 (conjugated C=N) cm^{-1} ; uv: λ max, 410 nm; ^1H nmr: δ 8.61 (m, 1H), 8.13 (s, 1H, iminomethyl), 7.95-6.67 (m, >11H containing impurities), 3.86 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 2.38 (s, 3H, CH_3); ms: m/e 370 (M^+).

Compound **5b** had ir: cm^{-1} , 1640 (conjugated C=O), 1602 (conjugated C=N), 1252 and 1025 (=COC); uv: λ max, nm, 446, 423; ^1H nmr: δ 9.61 (s, 1H, CHO), 8.74 (m, 1H), 8.39 (m, 1H), 8.24 (s, 1H, iminomethyl), 7.55-6.80 (m, 10H), 3.92 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3); ms: m/e 384 (M^+), 383 ($\text{M}-1$) $^+$.

Compound **6b** had mp 206.2-207.5° (from ethanol); ir: cm^{-1} , 1605 (conjugated C=N), 1248 and 1030 (=COC); uv: λ max, nm (log ϵ), 490 (sh), 462 (4.72), 365 (3.87), 299 (4.29); ^1H nmr: δ 8.72 (m, 2H, 4- and 7-positions of isoindole), 8.19 (s, 2H, iminomethyl), 7.48-6.78 (m, 14H), 3.88 (s, 3H, OCH_3), 3.76 (s, 6H, 2 x OCH_3); ms: m/e 489 (M^+).

Anal. Calcd. for $\text{C}_{31}\text{H}_{27}\text{N}_3\text{O}_3$ (489.6): C, 76.05; H, 5.56; N, 8.58. Found: C, 76.06; H, 5.46; N, 8.52.

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