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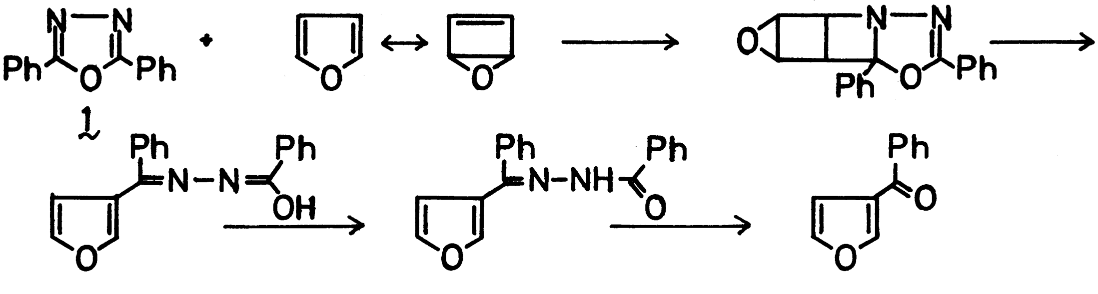
THE PHOTOCHEMICAL REACTION OF 2,5-DIPHENYL-1,3,4-OXADIAZOLE WITH INDAZOLES[1]

Kōji OE, Masashi TASHIRO, and Otohiko TSUGE*

Research Institute of Industrial Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

The novel photo-induced reaction of 2,5-diphenyl-1,3,4-oxadiazole (**1**) with indazoles (**2a**-**2d**), which gave the benzoylhydrazones of benzoylindazoles, is described.

The photochemical reaction of 2,5-diphenyl-1,3,4-oxadiazole (**1**) with furan with or without benzophenone as a sensitizer affords the 1:1 cycloadduct, while in the presence of iodine 3-benzoylfuran and its benzoylhydrazone are formed.[2] We also suggested that the reaction pathway of this novel photo-induced benzoylation may proceed via a cyclic intermediate which corresponds to the 1:1 cycloadduct of oxadiazole **1** to the valence tautomer of furan, cyclobutadiene oxide, as depicted in Scheme 1. We now wish to report the photochemical reaction of oxadiazole **1** with indazole (**2a**) and methylindazoles (**2b**-**2d**) without iodine which gave the benzoylhydrazones of benzoylindazoles.



Scheme 1

In a typical run, a solution of oxadiazole **1** (2 x 10^{-2} mol/l) and indazole **2** (4 x 10^{-2} mol/l) in 250 ml of diethyl ether, stirred by a stream of nitrogen, was irradiated by 300W high-pressure mercury lamp with a Pyrex filter under cooling with running water for 20 hr. Evaporation of the reaction mixture in vacuo and the residue was extracted with two 50 ml of hot petroleum ether (bp 60-80°C) to remove the corresponding o-aminobenzonitrile (yield was trace in each run) and unchanged starting materials. Chromatography of the insoluble residue on silicagel using chloroform as an eluent gave the corresponding 1:1 adduct **3**.

3a: yield 6%; mp 282-283°C; ir 3200 (NH), 1655 cm^{-1} (C=O); mass m/e 340 (M^+), 263 (M^+ - Ph), 235 (M^+ - PhCO), 219 (M^+ - $PhCONH_2$), 151, 105, 77. **3b**: yield 3%; mp 233-235°C; ir 3240 (NH), 1660 cm^{-1}

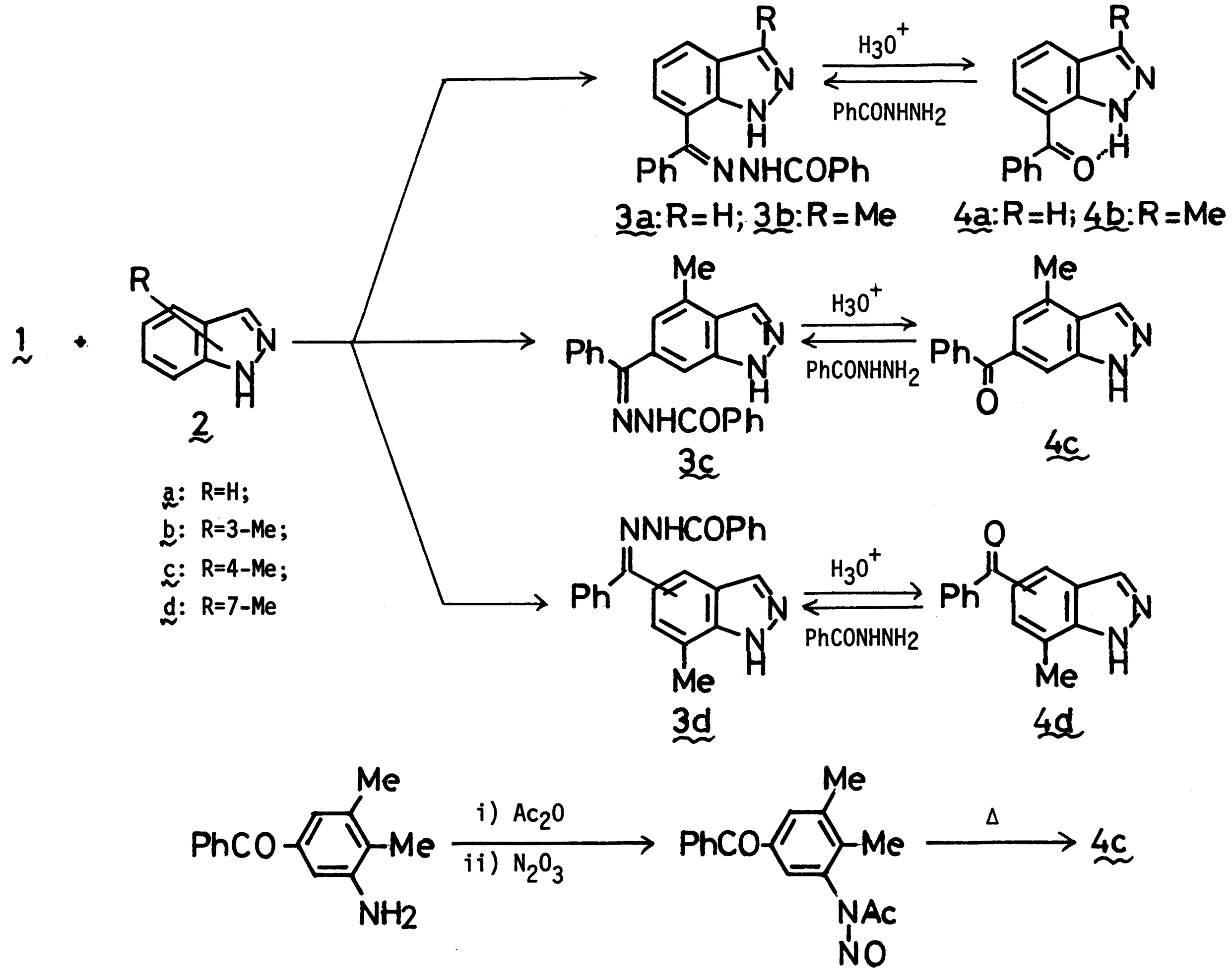
(C=O); mass m/e 354 (M^+), 277 (M^+ - Ph), 249 (M^+ - PhCO), 233 (M^+ - $PhCONH_2$), 219, 189, 152, 119, 105, 77. **3c**: yield 20%; mp 210-211°C; ir 3260 (NH), 1670 cm^{-1} (C=O); mass m/e 354 (M^+), 277, 249, 233, 221, 219, 189, 165, 119, 105, 77. **3d**: yield 22%; mp 309-310°C; ir 3200 (NH), 1660 cm^{-1} (C=O); mass m/e 354 (M^+), 277, 249, 233, 219, 189, 165, 119, 105, 77.[3]

The above spectral data indicate that the products **3** are benzoylhydrazone derivatives. It is known that indazoles undergo photochemical isomerization into the benzimidazoles and o-aminobenzonitriles.[4, 5] However, the corresponding benzimidazole was undetectable in each run. In addition, the photochemical reaction of oxadiazole **1** with benzimidazole did not occur under the similar conditions with the above. Thus, benzoylhydrazones of the benzimidazoles can be excluded from the potential structures for **3**.

On the basis of the result of hydrolysis, the products **3** were confirmed to be benzoylhydrazones of C-benzoylated indazoles. Hydrolysis of **3c** with hydrochloric acid in methanol at room temperature gave benzoic acid and 6-benzoyl-4-methylindazole (**4c**) in 28 and 64% yields respectively. The structure of **4c** was confirmed by the identification with an authentic sample prepared from 3-amino-4,5-dimethylbenzophenone by application of Huisgen' method for the preparation of indazole (Scheme 2).[6] **4c**: mp 148-149°C; ir 3280 (NH), 1640 cm^{-1} (C=O); nmr ($CDCl_3$) δ 2.6 (3H, s, $C\underline{H}_3$), 7.0-8.0 (8H, m, aromatic protons), 8.2-9.3 (1H, br, $N\underline{H}$); mass m/e 236 (M^+), 221 (M^+ - Me), 159 (M^+ - Ph), 131 (M^+ - PhCO), 105, 104, 77. On treatment with benzoylhydrazine **4c** was readily reverted to **3c**. Thus, **3c** is 6-benzoyl-4-methylindazole benzoylhydrazone.

Similarly, hydrolysis of **3a**, **3b** and **3d** produced the corresponding benzoylindazoles **4a**, **4b** and **4d** which on treatment with benzoylhydrazine were converted into the original compounds, in 44, 75 and 70% yields respectively. **4a**: mp 173-174°C; ir 3250 (NH), 1600 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.0-8.0 (9H, m, aromatic protons), 8.5-9.5 (1H, br, $N\underline{H}$); mass m/e 222 (M^+), 205, 196 (M^+ - CN), 165, 145 (M^+ - Ph), 117 (M^+ - PhCO), 105, 77. **4b**: mp 190-192°C; ir 3280 (NH), 1600 cm^{-1} (C=O); nmr ($CDCl_3$) δ 2.65 (3H, s, $C\underline{H}_3$), 7.0-8.0 (8H, m, aromatic protons), 8.4-9.5 (1H, br, $N\underline{H}$); mass m/e 236 (M^+), 221, 159, 131, 105, 104, 77. **4d**: mp 170-172°C; ir 3180 (NH), 1650 cm^{-1} (C=O); nmr ($CDCl_3$) δ 2.62 (3H, s, $C\underline{H}_3$), 7.0-8.0 (8H, m, aromatic protons), 8.4-9.5 (1H, br, $N\underline{H}$); mass m/e 236 (M^+), 221, 207, 159, 131, 105, 104, 77.

On the basis of the above spectral data, it is clear that **4a**, **4b** and **4d** are indazoles in which benzoyl groups are on the benzene rings. It is noteworthy that in the ir spectra the carbonyl absorption bands of **4a** and **4b** appeared at 1600 cm^{-1}, while those in **4c** and **4d** were revealed at ordinary regions (1640-1650 cm^{-1}). These facts indicate that there is an interaction between the benzoyl and NH groups in **4a** and **4b** (Scheme 2). Thus, **4a** and **4b** were deduced to be the corresponding 7-benzoylindazoles, and then 7-benzoylindazole and 7-benzoyl-3-methylindazole benzoylhydrazone were assigned for the structures of **3a** and **3b** respectively. However, the position of benzoyl group in **4d** could not



Scheme 2

be determined, although 4-, 5- or 6-benzoylindazole is thought possible for the structure of **4d**.

The photochemical reaction was greatly affected by the nature of solvents. As mentioned above, irradiation of oxadiazole **1** with **2c** in diethyl ether afforded **3c** in 20% yield. However, in benzene the yield of **3c** was only 1%, and no **3c** was formed in methylene chloride, tetrahydrofuran and glyme. On the other hand, in a diethyl ether solution with benzophenone as a sensitizer **3c** was obtained in 10% yield; thus the reaction seems to start with a singlet state.

Under the same conditions, the photochemical reaction of oxadiazole **1** with benzimidazole which can not have o-quinoid structure, did not take place. It seems that the 2H-indazole is involved in this novel photo-induced reaction, since it is known that there is an equilibrium between 1H-indazole and 2H-indazole.[7, 8] However, the mechanism of the present reaction is not clear, and under study.

References and Notes

* To whom all correspondences should be addressed.

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