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PHOTOCHEMICAL REACTION OF 2,5-DIPHENYL-1,3,4-OXADIAZOLE WITH INDENE*

Otohiko Tsuge, Masashi Tashiro and Kōji Oe
Research Institute of Industrial Science, Kyushu University
Hakozaki, Fukuoka, Japan

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Current interest in the photochemistry of heterocyclic compounds prompts us to report our findings on the photochemical reaction of 2,5-diphenyl-1,3,4-oxadiazole (I) with indene (II). The irradiation of a solution of I and II has been investigated under various conditions.

In a typical run, a benzene solution (400 ml) of I (1×10^{-2} mol/l) and II (4×10^{-2} mol/l), stirred by a stream of nitrogen, was irradiated by 300W high-pressure mercury lamp with a Pyrex filter at room temperature for 12 hr. Evaporation of the reaction mixture in vacuo and chromatography of the residue on active alumina afforded 100 mg of yellow needles (III), m.p. 284-285°C, besides I (120 mg), II (310 mg) and a resinous material.

The compound III agreed with the formula $C_{32}H_{26}N_2$ (m/e M^+=438), which was equivalent to the compound derived from an 1:2 adduct of I and II under the elimination of oxygen. UV λ_{max}^{EtOH} mμ (log ε): 246 (3.68 sh), 435 (3.73).

When a similar benzene solution of I and II was irradiated under the influence of iodine (5 mol%) for 24 hr, 180 mg of III and 90 mg of colorless prisms (IV), m.p. 196.5-197°C. The compound IV was in agreement with the formula $C_{23}H_{18}ON_2$ (m/e M^+=338), which was equivalent to an 1:1 adduct of I and II. IR:

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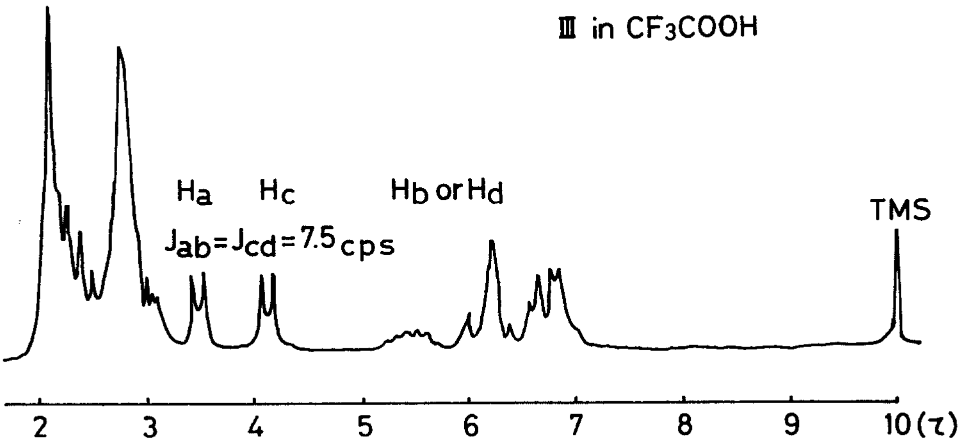
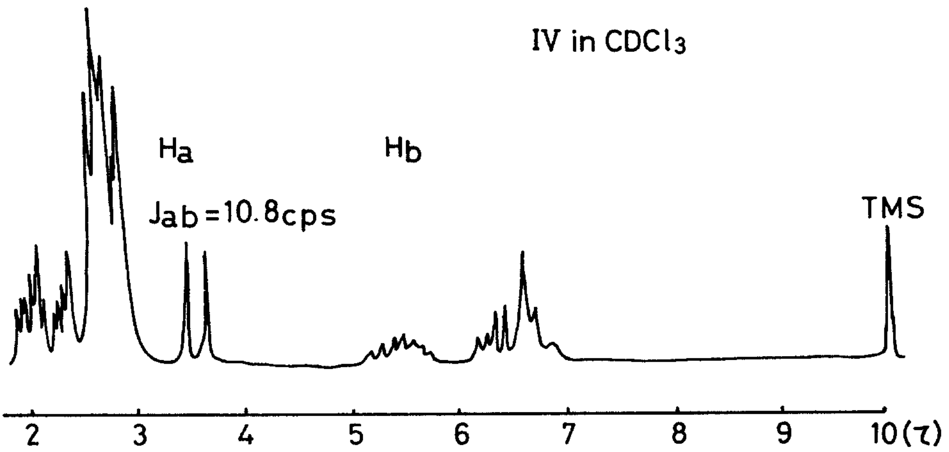
1630 cm^{-1} (C=N). UV $\lambda_{max}^{CHCl_3}$ mμ(log ε): 260 (3.36), 268 (3.45), 274 (3.53), 306 (3.83). As is illustrated in Fig. 1, the NMR spectrum of IV in $CDCl_3$ shows signals at τ 6.55 (2H, CH_2), 5.55 (1H, CH), 3.55 (1H, CH) and 1.8-2.9 (14H, aromatic protons).

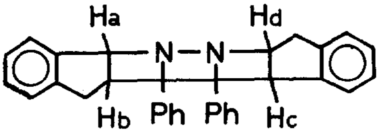
Although two structures for IV are possible, the above observations are in agreement with the structure of 3a,3b,8a,8b-tetrahydro-2,8b-diphenylindeno-[2,3-c]azetidino[2,1-b]-1,3,4-oxadiazole (IV) rather than the isomer IV'.



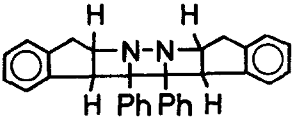


As is also shown in Fig. 1, the NMR spectrum of III exhibits signals at τ 5.9-6.8 (5H, 2 CH_2 and CH), 5.43 (1H, CH), 4.18 (1H, CH), 3.59 (1H, CH) and 2-3 (18H, aromatic protons). From comparison of the spectra of III and IV, the methine-proton signals at τ 3.59 and 4.18 in III may be ascribed to the Ha- and Hc-protons respectively: the difference of chemical shifts could be understood in term of the shielding effect of the phenyl group.

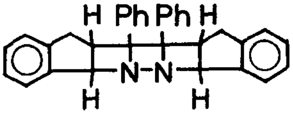
On the basis of the above data, the compound III is assumed to be 4b,4e-9b,9e-tetrahydro-4c,4d-diphenylindeno[3,2-c]azetidino[1,2-b]diazetidino[1,4-a]-azetidino[3,4-b]indene rather than the isomers III′ and III″. However, the stereochemistry is uncertain as yet, which is under investigation.



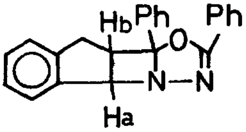
III



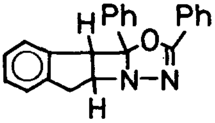
III′



III″



IV



IV′

The mass-spectral evidences support the suggested structures III and IV.
The fragmentation of III on electron impact (m/e):

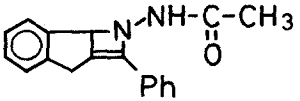
$$\begin{tikzcd}
M^{+}/2(219) \arrow[rr, "-PhC\equiv NH"] & & C_9H_7^{+}(115) & & (202) & & Ph^{+}(77) \\
M^{+}(438) \arrow[r, "-2H"] & (436) \arrow[r, "-N_2"] & (408) \arrow[r, "-Ph"] & (331) \arrow[r, "-PhC\equiv C"] \arrow[ur, "-C_{10}H_9"] & (230), & PhCN^{+}(103) \arrow[ur, "-CN"] & \text{base peak}
\end{tikzcd}$$

The fragmentation of IV on electron impact (m/e):

$$\begin{tikzcd}
M^+(338) \arrow[r, "-PhCN", "(163.3)^{**}"'] \arrow[dr, "-C_9H_8"'] & (235) \arrow[r, "-NO", "(183.0)^{**}"'] & (205) \arrow[r, "-Ph"] \arrow[drr, "-C_7H_8"] & (128) & \\
& C_{14}H_{10}ON_2^+\ (222) \arrow[r, "-PhCN"] \arrow[d, "-N_2"'] & (119) & & C_9H_7^+\ (115) \\
& (194) \arrow[r, "-C_7H_5"] & PhCO^+\ (105) \arrow[r, "-CO", "(56.5)^{**}"'] & Ph^+\ (77),\ \text{base peak} &
\end{tikzcd}$$

Furthermore, the treatment of III with zinc dust in boiling acetic acid for 10 hr afforded colorless needles (V), m.p. 216-217°C, in 40% yield.

The compound V was determined to be 7b-hydro-1-acetamido-2-phenylazeto-[3,4-b]indene by the following evidences.



V

Molecular formula: $C_{18}H_{16}ON_2$ (m/e M^+=276). UVλ_{max}^{EtOH} mμ(log ε): 260 (3.44), 267 (3.61), 274 (3.74), 288 (3.84). IR cm : 3280 (NH), 1655 (CO). NMR in $CDCl_3$: τ 7.65 (3H, CH_3), 6.43 (2H, CH_2), 4.83 (1H, CH), 2-3 (10H, aromatic and NH protons). The fragmentation on electron impact:

$$\begin{tikzcd}
& (233) & (219) \arrow[r, "-PhCN"] & (116) & \\
M^+(276) \arrow[ur, "-COCH_3"] \arrow[urr, "-NCOCH_3"] \arrow[r, "-C_2H_2O"] \arrow[dr, "-C_9H_7"'] & (234),\ \text{base peak} \arrow[r, "-PhC\equiv NH"] & (130) \arrow[r, "-NH"] & C_9H_7^+\ (115) & \\
& (161) \arrow[r, "-COCH_3"] & (118) \arrow[r, "-NH"] & PhCN^+(103) \arrow[r, "-CN"] & Ph^+\ (77)
\end{tikzcd}$$

Detailed mechanism of the photochemical reaction is uncertain at the present stage. Work is in progress and the results will be reported elsewhere.

** Observed metastable ion peaks.