36. Photolysis and Pyrolysis of *N*-Methyl Isoindole[1])

by **Wolfgang Rettig**[2]) and **Jakob Wirz**

Physikalisch-chemisches Institut der Universität,
Klingelbergstrasse 80, CH-4056 Basel

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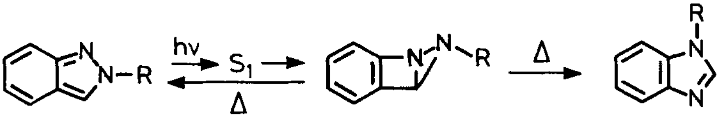
Summary

Near UV. irradiation of *N*-methyl isoindole (**1**) in deaerated solution has yielded two constitutionally isomeric $[{}_{\pi}4_s + {}_{\pi}4_s]$ dimers **3** and **4** *(Scheme 2)*. No transient or stable photoisomers of **1** were detected. The photodimers were reconverted to **1** both by pyrolysis and photolysis. The photocleavage of dimer **3** proceeds (predominantly) by a nonadiabatic pathway yielding **1** in its electronic ground state. Prolonged pyrolysis of **1** afforded 11*H*-indeno[1,2-*c*]-isoquinoline (**5**) as a major product.

The photoisomerization of 2-alkyl indazoles to 1-alkyl benzimidazoles *(Scheme 1)*, discovered ten years ago by *Schmid et al.* [1], has been subjected to considerable scrutinity [2]. While this work has provided convincing evidence for the basic mechanism shown below, it was found that such a simple Scheme is insufficient to account for the complexity of the observed reaction kinetics.

Scheme 1



We speculated that the isoelectronic "parent" heterocycle, *N*-methyl isoindole (**1**) might provide a related, but simpler photochemical system for study. Indeed, the spectroscopic (UV., NMR., MS.) and microanalytical data of the main product, isolated after an exploratory UV. irradiation of **1**, were quite compatible with the expected tricyclic isomer **2**. However, further work reported herein showed that this product is a dimer of **1** and that, in all probability, **2** is not formed as a stable or transient photoproduct of **1**.

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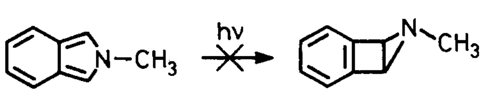
[1]) Taken from the Ph. D. thesis of *W. R.*, University of Basel 1975.

[2]) Present address: *Iwan-N.-Stranski*-Institut für Physikalische und Theoretische Chemie, Technische Universität, Strasse des 17.Juni 112, D-1 Berlin 12.



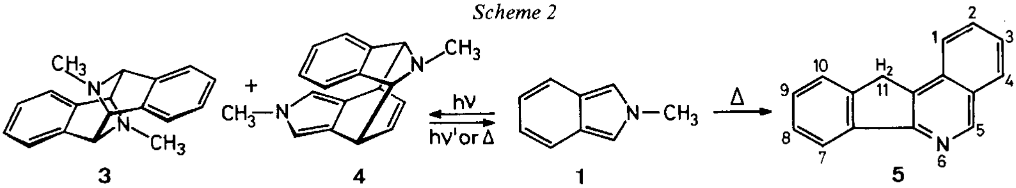
1 2

Results and Discussion. - UV.-irradiation of degassed, $\geqslant 10^{-2}$ M solutions of **1** through *Pyrex* yielded two isomeric photodimers **3** and **4** in a ratio of *ca.* 10:1 which did not depend on the extent of photoconversion. Their structures were tentatively assigned on the basis of the spectroscopic data given in the Preparative Part. Though the mass spectra of both **3** and **4** were virtually identical with that of **1** and did not exhibit any significant signals above *m/e* 131, the dimeric nature of these products became evident from their low volatility and solubility and was established by molecular weight determinations. As expected, the photodimerization was efficient only in concentrated solutions (quantum yield estimated near unity), rapidly decreasing in rate at concentrations of **1** below 10^{-2} M. Slow photochemical decomposition yielding an insoluble green polymer took place in highly dilute, deaerated solutions upon direct, but not upon sensitized excitation. These results are in accord with a dimerization mechanism involving the lowest excited singlet state of **1**, the lifetime of which was determined as 12 ns in dilute hexane [3]. No red-shifted excimer emission was detected in concentrated solutions. Each of the constitutional isomers **3** and **4** was obtained as a single stereoisomer. While the assignment of the molecular constitution of **3** and **4** from their respective NMR. spectra was straight-forward, their configuration is uncertain, based solely on the comparison of chemical shifts with suitable reference compounds [4].

The question arose, whether the photodimers **3** and **4** or their stereoisomers would form upon pyrolysis of **1**. We were encouraged by a note of *Schönberg et al.* [5] reporting on the related photochemical and thermal dimerization of 1,3-diphenyl-isobenzofuran and by the known reactivity of **1** as a diene in *Diels-Alder* additions [6] whereby the *o*-quinonoid π-system is converted to a benzenoid structure. Pyrolysis of neat **1** in the absence of air oxygen at 230° for 1 h afforded a brown oil from which 11*H*-indeno[1,2-*c*]isoquinoline (**5**) [7] was obtained in *ca.* 45 percent yield as the only isolable product apart from some volatile amines.

The structure of **5** was identified from its spectroscopic characteristics and confirmed by a comparison of its IR. spectrum with that of an authentic sample[3]. Intermittent NMR. analysis indicated that **5** is formed by a complex sequence of reactions; an attempt to isolate intermediate products failed. Addition of hydro-

Scheme 2



3 4 1 5

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[3] We wish to thank Prof. *Wawzonek*, University of Iowa, for supplying us with a copy of his IR. spectrum of **5** [7].

quinone or dibenzoylperoxide had no obvious effect on the course of the reaction. The apparent absence of simple dimers of **1** in the pyrolysate was explained by the subsequent finding that a brief heating of **3** to 120° was sufficient to reconvert it to **1**.

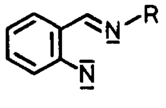
Dissociation of the dimers **3** and **4** to the starting material **1** also occurred upon short-wavelength irradiation at 254 nm. A quantum yield of 0.7 ± 0.1 for the photocleavage of **3** was determined spectrophotometrically for conversions of less than ten percent on a split-beam apparatus described earlier [8]. The reaction rate was not affected by the presence of air oxygen, but degassing was mandatory to prevent the subsequent photooxidation of **1**. Interestingly, the fluorescence spectrum of **3** was found to be identical with that of **1** [3], while the fluorescence excitation spectrum of unirradiated samples corresponded to the absorption spectrum of **3**. This suggested that the photocleavage of **3** proceeds adiabatically yielding one of the product molecules in its fluorescent excited singlet state S_1 (**1**). *Menter & Förster* [9] have reported excited state product formation, albeit in very small yield, in the related photodissociation of the 9-methyl-anthracene dimer. However, a careful analysis [10] of our experimental conditions revealed that the observed luminescence could be accounted for by the unavoidable biphotonic process (1). The data obtained with the conventional fluorescence instrumentation used (*Zeiss* PMQ II) allowed but to estimate an upper limit of 0.01 for the quantum efficiency of the adiabatic process (2).

$$\mathbf{3} \xrightarrow{h\nu} \mathbf{1} + \mathbf{1} \xrightarrow{h\nu} S_1(\mathbf{1}) + \mathbf{1} \tag{1}$$

$$\mathbf{3} \xrightarrow{h\nu} S_1(\mathbf{1}) + \mathbf{1} \tag{2}$$

We have previously reported [3] that the quantum yields of fluorescence and intersystem crossing of **1** in dilute, degassed solution at room temperature add up to approximately unity. All present attempts to provide evidence for the transitory or permanent formation of valence isomer **2** have failed. Thus **1** was found to be highly photostable in rigid glassy solutions (hydrocarbon mixture 77 °K, 9:1 mixture of 2- and 1-propanol 133 °K) in which the photodimerization was prohibited. Flash photolysis of highly dilute (10^{-5} M) solutions of **1** at room temperature did not give rise to a detectable transient photobleaching of the 320 nm absorption. No consumption of **1** was evident after prolonged 365 nm irradiation of chrysene in a degassed, 10^{-4} M solution of **1** in benzene; previous flash photolytic work has shown [3] that the lowest triplet state of **1** is efficiently populated by energy transfer under such conditions.

Labhart and *Heinzelmann* have shown that the efficient, light-induced valence isomerization of the isoelectronic 2-alkyl indazoles is not a simple pericyclic reaction, but proceeds *via* at least two metastable intermediates (**Z'** [2a], **X*** and **Y** [2c]). It is tempting to associate these with different electronic states of the tritopic [11], biradicaloid species **6** which could explain the contrasting behaviour of **1**. PPP SCF CI calculations indeed suggest [3] that the 1,2-bond, which is broken in **6**, is considerably weakened by excitation of these chromophores to the S_1 state.



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Preparative Part. - *General remarks.* 100 MHz ^{1}H-NMR. and 22.63 MHz ^{13}C-NMR. spectra are quoted in ppm relative to internal TMS., coupling constants in Hz. Strong ^{13}C peaks due to carbon atoms bound to a hydrogen atom are printed in italics. UV. spectral maxima are given in nm (log ε), IR. spectra in cm^{-1}. Mass spectral peaks exceeding 5 percent intensity of the base peak are given in *m/e* (relative intensity). Molecular weights were determined by the isopiestic method. Melting points are uncorrected.

Photodimerization of **1**. A degassed solution of **1** (100 mg) in moist hexane (25 ml) was irradiated for 35 hours with *Pyrex*-filtered light from a 200 W high pressure mercury arc. The sparingly soluble photoproducts crystallized from the solution and were purified by fractionating sublimation *in vacuo* yielding 35 mg of the dimer **3** (60% relative to consumed **1**), m.p. 259-261° (dec.), and 4 mg of the dimer **4** (7%), m.p. 129-131° (dec.). Molecular weights: **3** 262 ± 12, **4** 230 ± 35. - UV. (**3**, hexane): 284.5 (3.89); 280.5 (3.65). - UV. (**4**, hexane): 289.5 (3.13); 282.5 (3.17). - IR. (**3**): 3080, 1470, 1435, 1343, 1128, 975, 790, 680, 460. - IR. (**4**): 3040, 1455, 1370, 1140, 823, 772, 690, 597. - ^{1}H-NMR. (**3**, $CDCl_3$): 7.21 (*s*, 8 H); 3.64 (*s*, 4 H); 1.93 (*s*, 6 H). - ^{1}H-NMR. (**3**, $CDCl_3$ with CF_3COOD): 7.66 (*s*, 8 H); 5.41 (*s*, 4H); 2.66 (*s*, 6H). - ^{1}H-NMR. (**4**, C_6D_6): 6.85 (*s*, 4H); 6.64 (*m*, 2H); 5.64 (*s*, 2H); 3.56 (*m*, 4H); 2.71 (*s*, 3H); 2.30 (*s*, 3H). - MS. (**3**): 131 (100), 130 (18), 116 (8), 90 (7), 89 (9). - MS. (**4**): 131 (100), 130 (13), 116 (10), 90 (9), 89 (10).

$C_{18}H_{18}N_2$ **3** (262.36) Calc. C 82.40 H 6.92 N 10.68% Found C 82.26 H 7.14 N 10.89%

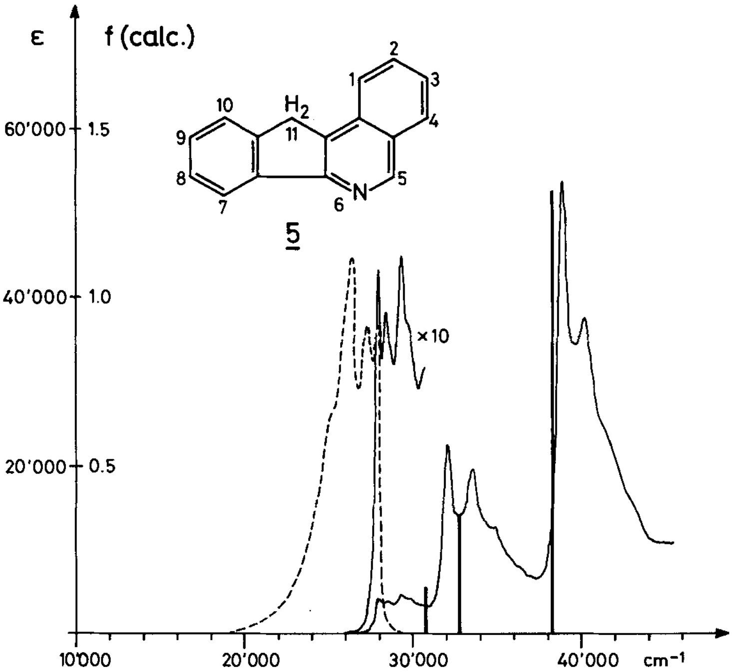

Fig. *UV.* (———) *and corrected fluorescence spectrum* (- - - -, relative quanta) *of* **5** *in hexane.* Vertical bars indicate calculated oscillator strengths f.

Pyrolysis of **1**. Neat **1** (500 mg) was heated in an evacuated and sealed tube (*ca.* 5 ml) to 230° for 1 h. The resulting brown oil was vacuum distilled at 120° and the solid product **5** recrystallized from petroleum ether/benzene yielding colourless needles (225 mg), m.p. 162-163° (163-164° [7]). Molecular weight 228±20. The UV. and fluorescence spectra are shown in *Figure 1*, together with the predictions from a PPP SCF CI calculation using standard parameters [12]. - ^{1}H-NMR. ($CDCl_3$): 9.20 (*s*, 1H); 8.14-8.06 (*m*, 1H); 8.0-7.23 (*m*, *ca.* 7H); 4.00 (*s*, 2H). Addition of $Eu(fod)_3$ shift reagent allowed a first-order interpretation of the individual aromatic proton signals. The S-values were measured in $CDCl_3$ according to *Cockerill et al.* [13] and should have, on the basis of the pseudocontact interaction model, a linear relationship to the calculated R_μ-values [14]. The position of Eu in the complex was optimized to satisfy such a relationship (found: $R(N \cdots Eu) = 4.65$ Å, α(Eu–N-ring center) = 18° for regular polygons and $R(C-C) = R(C-N) = 1.38$ Å, $R(C-H) = 1.08$ Å), yielding the tentative assignment of the measured S-values given in *Table 1*. A double resonance experiment showed that the multiplet at 8.1 ppm (8.5 ppm in C_6D_6) is due to H–C(7) ($^3J_{78} = 7$). - ^{13}C-NMR. ($CDCl_3$, broadband H-decoupling) 154.3, *152.6*, 142.8, 142.2, 133.64, 131.2, *130.8*, *128.9*, *127.55*, *127.33*, *126.25*, *125.01*, *123.12*, *120.37*, *33.29*. - MS. 218 (19), 217 (100), 189 (12), 180.5 (28), 94.5 (17), 85 (14), 83 (20), 63 (7), 44 (17).

$C_{16}H_{11}N$ (217.27) Calc. C 88.45 H 5.10 N 6.45% Found C 88.21 H 5.14 N 6.59%

Pyrolysis of **3**. A small sample of **3** (3 mg) was heated to 120° for 10 min. in an evacuated tube. The contents were then identified as **1** (1.5 mg) and remaining **3** (1.5 mg).

Table 1. *Assignment of the S-values of* **5**

	H–C(5)	H–C(7)	H–C(11)	H–C(4)	H–C(2)	H–C(1)[a]	H–C(3)[a]	H–C(10)[a]	H–C(9)	H–C(8)
S	10.4	6.74	2.8	2.41	1.37	1.15	1.15	0.94	0.63	0.18
$R_\mu \cdot 10^2$ [Å^{-3}]	1.366	0.884	0.300	0.327	0.235	0.156	0.156	0.159	0.082	0.041

[a]) Assignment ambiguous.

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