The Photoreaction of Naphthalene with Pyrrole; Products and Reaction Mechanism

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Irradiation of naphthalene and pyrrole by u.v. light through Pyrex or at 310 nm affords 2-(1,4-dihydro-1-naphthyl)-pyrrole (II) and 2-(1,2-dihydro-2-naphthyl)pyrrole (III). These products together comprise 85% of the mixture, the remainder consisting of two 3-(dihydronaphthyl)pyrroles. Products (II) and (III) were characterized by n.m.r. spectra, and by conversion into the stable, crystalline 5-ethoxycarbonyl derivatives. The mechanism of this addition was studied by use of fluorescence quenching, solvent effects, and a labelling experiment. Pyrrole quenches naphthalene fluorescence at a rate close to the diffusion limit in benzene, acetonitrile, and ethanol. The quenching is similar to that of amines, which is used as model for the pyrrole case. *N*-Methylpyrrole also quenches naphthalene fluorescence, but does not react. Use of *N*-deuteriopyrrole as the addendum showed that the deuterium is retained in the methylene groups of compounds (II) and (III). The pyrrole–naphthalene addition does not occur on triplet sensitization, implying that the first excited singlet state of naphthalene is reacting. The ratio of products (II) and (III) is solvent-dependent, and changes in a manner which resembles that observed for certain ground-state, ionic processes. A mechanism is discussed in the light of our results and those in the literature.

We have been studying photoadditions of indene and naphthalene derivatives, from the viewpoint of the structures of the products and the reaction mechanism.[1-3] The report by Bryce-Smith and his co-workers of the reaction of benzene with pyrrole[4,5] to afford the dihydrophenylpyrrole (I) prompted us to investigate the photolysis of naphthalene and pyrrole.[6] The question of multiplicity is easier to answer for the

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[1] J. J. McCullough and C. W. Huang, *Canad. J. Chem.*, 1969, **47**, 757.

[2] R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, *J. Amer. Chem. Soc.*, 1970, **92**, 4106.

[3] R. M. Bowman and J. J. McCullough, *Chem. Comm.*, 1970, 948.

[4] M. Bellas, D. Bryce-Smith, and A. Gilbert, *Chem. Comm.*, 1967, 263.

[5] D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 147.

[6] J. J. McCullough, C. W. Huang, and W. S. Wu, *Chem. Comm.*, 1970, 1368. A preliminary report of our results is given there.

reactions of naphthalene than of benzene, and it seemed that the structural similarity between pyrrole and amines might enable us to use the considerable body of photochemical work with the latter substances[7-19] to formulate a mechanism for the reactions of pyrrole. Amines interact with excited states, singlets, and triplets of many molecules, including aromatic hydrocarbons[7-14] and ketones.[15-19] This interaction is believed to be of the charge- or electron-transfer type,[7-12] which always results in deactivation[7-13] of the excited states, and often in photochemical changes.

RESULTS AND DISCUSSION

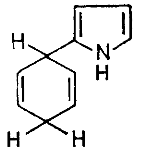
Irradiation of naphthalene and pyrrole in ethanol, acetonitrile, benzene, or hexane with light of wavelength >300 nm, resulted in the formation of four 1 : 1 adducts. Their proportions were solvent-dependent (see Table 1), but the two major products were 2-(1,4-dihydro-1-naphthyl)pyrrole (II) and 2-(1,2-dihydro-2-naphthyl)pyrrole (III).[6] The progress of the reaction and the ratios of products were monitored by g.l.c., and compounds (II) and (III) were isolated by chromatography on silica gel and characterized by spectroscopic methods [both showed m/e 195 (M^+)]. The n.m.r. spectrum[20] of the isomer (II) had resonances at δ 6·97 (4H, benzenoid), 6·29 (1H, 5-H), 5·88 (4H, 3-, 4-, 2′-, and 3′-H), 4·50 (1H, 1′-H), and 3·30 (2H, 4′-H$_2$) p.p.m. The last two peaks were multiplets, consistent with an ABX system. Irradiation of the resonance at δ 4·50 p.p.m. caused the methylene signal at δ 3·30 p.p.m. to simplify by the elimination of a coupling with J 6·2 Hz, thus pointing to a 1,4-dihydronaphthalene structure.[4,21] In the n.m.r. spectrum of (III), resonances appeared at δ 6·95 (4H, benzenoid), 6·26 (2H, 5- and 3′(4′)-H), 5·87 [3H, 3-, 4-, and 4′(3′)-H], 3·57 (1H, 2′-H), and 2·91 (2H, 1′-H$_2$). The u.v. spectra of compounds (II) and (III) were also consistent with these structures.

TABLE 1

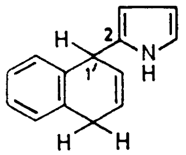
Solvent effects on the naphthalene–pyrrole reaction

Solvent	Dielectric constant (D) [a]	Fraction [c] (%) of (II)	Relative reaction rates
Hexane	1·9	82	
Benzene	2·3	74	1·45
Dichloromethane	9·1	66	1·08
95% Ethanol [b]	24·3	60	1·04
Acetonitrile	37·5	62	1·00
Methanol [b]	32·6	52	0·89
80% Methanol [b]	32·6	49	0·59

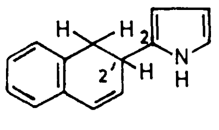
[a] A. A. Maryott and E. R. Smith, 'Table of Dielectric Constants of Pure Liquids,' National Bureau of Standards, Circular 514, Washington, 1951. [b] The effects of these solvents are probably due in part to their hydrogen bonding properties. [c] Given by [(II)/(II) + (III)] × 100; minor products were present in all runs, total 14%.



(I)



(II)



(III)

The products resemble pyrrole in rapidly becoming coloured in air, and although the isomer (II) was obtained as a solid, it was not sharp melting and satisfactory analytical figures were not obtained. Both adducts were characterized by treatment with carbonyl chloride, followed by ethanol,[22] to afford the 5-ethoxycarbonyl derivatives, which were stable, crystalline compounds. Their n.m.r. spectra were consistent with the assigned structures.[23] Thus, the ester protons of the compound (II) derivative gave signals at δ 1·12 (t) and 4·39 (q, J 7·0 Hz) p.p.m.[23] Also, two protons assigned to the pyrrole nucleus gave signals at δ 6·0 and 6·72 p.p.m. These are at different chemical shifts but are both attributed to the β-protons, and are both shifted downfield relative to the analogous signals from compound (II).[23] Similarly, the ester from compound (III) showed signals at δ 1·62 (t) and 4·53 (q) p.p.m., respectively. The pyrrole protons (β-H) resonated at δ 6·34 and 7·10 p.p.m. The methine proton and the methylene group comprised an ABX system, and the methylene group gave a doublet at δ 3·50 p.p.m., in contrast to the corresponding signal for the isomer (III) which was a multiplet. The spectrum apparently belongs to the 'deceptively simple' type[24] for the ester of the isomer (III), meaning that the protons of the methylene group have almost the same chemical shift.

Dehydrogenation of compounds (II) and (III) gave different 2-(naphthyl)pyrroles in agreement with the structures assigned.

One of the minor adducts was isolated by column

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[7] H. Leonhardt and A. Weller, *Z. phys. Chem. (Frankfurt)*, 1961, **29**, 277; *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 791.

[8] D. Rehm and A. Weller, *Israel J. Chem.*, 1970, **8**, 259.

[9] T. Miwa and M. Koizumi, *Bull. Chem. Soc. Japan*, 1966, **39**, 2588; K. Kaneta and M. Koizumi, *ibid.*, 1967, **40**, 2254.

[10] H. Yamashita, H. Kokubun, and M. Koizumi, *Bull. Chem. Soc. Japan*, 1968, **41**, 2312.

[11] N. Mataga and K. Ezumi, *Bull. Chem. Soc. Japan*, 1967, **40**, 1355; Y. Nakato, N. Yamamoto, and H. Tsubomura, *ibid.*, p. 2480.

[12] W. R. Ware and H. P. Richter, *J. Chem. Phys.*, 1968, **48**, 1595.

[13] M. G. Kuzmin and L. N. Guseva, *Chem. Phys. Letters*, 1969, **3**, 71.

[14] (*a*) R. S. Davidson, *Chem. Comm.*, 1969, 1450; (*b*) C. Pac and H. Sakurai, *Tetrahedron Letters*, 1969, 3829.

[15] R. C. Cookson, S. M. de B. Costa, and J. Hudec, *Chem. Comm.*, 1969, 753.

[16] S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, 1968, **90**. 165; S. G. Cohen and B. Green, *ibid.*, 1969, **91**, 6824.

[17] R. A. Caldwell, *Tetrahedron Letters*, 1969, 2121.

[18] C. Pac, H. Sakurai, and T. Tosa, *Chem. Comm.*, 1970, 1311.

[19] R. S. Davidson and P. F. Lambeth, *Chem. Comm.*, 1969, 1098.

[20] *Cf.* the spectrum of 2-methylpyrrole, R. L. Hinman and S. Theodoropulos, *J. Org. Chem.*, 1963, **28**, 3052.

[21] S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.

[22] M. W. Roomi and S. F. MacDonald, *Canad. J. Chem.*, 1970, **48**, 139.

[23] M. W. Roomi and H. Dugas, *Canad. J. Chem.*, 1970, **48**, 2303.

[24] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1965, vol. 1, p. 363.

chromatography, and although it was not characterized completely, the n.m.r. spectrum suggested that it was a 3-substituted pyrrole.

Reaction Multiplicity.—The two excited states of naphthalene most likely to be involved in this reaction are the lowest singlet (S_1) and triplet (T_1) states. Although reactions of the naphthalene system have been attributed to a higher triplet state,[25] to our knowledge no bimolecular processes have been shown to involve states other than S_1 and T_1 of this compound, in fluid media.

Since the energy of T_1 of naphthalene is 61 kcal mol^{-1},[26] benzophenone (E_t 68),[26] acetophenone (E_t 73),[26] and Michler's ketone (E_t 61 kcal mol^{-1})[26] were employed as sensitizers, but the products (II) and (III) were not found, even after long irradiation times. This strongly suggests that T_1 of naphthalene is not the reactive species.

Evidence supporting S_1 as the reactive state has been obtained from fluorescence quenching studies. The fluorescence of naphthalene is strongly quenched by pyrrole and *N*-methylpyrrole in benzene, acetonitrile, and ethyl alcohol. The quenching was studied as a function of pyrrole concentration, and if the quenching is a bimolecular process involving pyrrole, the relation (1)[27] should hold; Φ is the quantum yield for fluorescence,

$$\Phi_0/\Phi = 1 + k_q\tau[\text{pyrrole}] \qquad (1)$$

Φ_0 the value at zero pyrrole concentration, k_q is the rate constant of the bimolecular quenching process, and τ the lifetime of the state being quenched, in this case S_1. The Stern–Volmer plots of Φ_0/Φ *versus* [pyrrole] are linear in all three solvents and are shown in Figures 1 and 2. It is clear that a bimolecular quenching process is operating. Further, it is a simple matter to derive the rate constants for this process, from the lifetimes of S_1 and the slopes of the Stern–Volmer plots for each solvent, and these are all shown in Table 2.

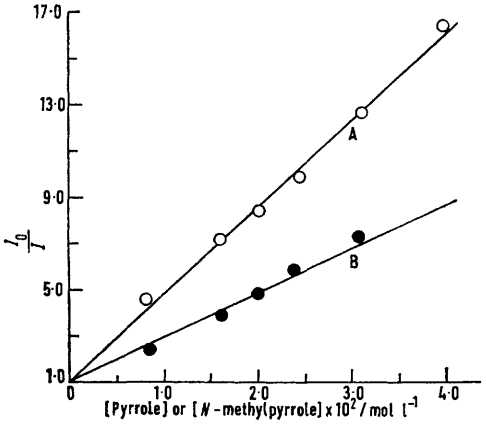

FIGURE 1 Stern–Volmer plots for quenching of naphthalene fluorescence by pyrrole A and *N*-methylpyrrole B in deoxygenated acetonitrile. Slopes, A, $3{\cdot}85 \times 10^2$ and B, $1{\cdot}95 \times 10^2$ l mol^{-1}

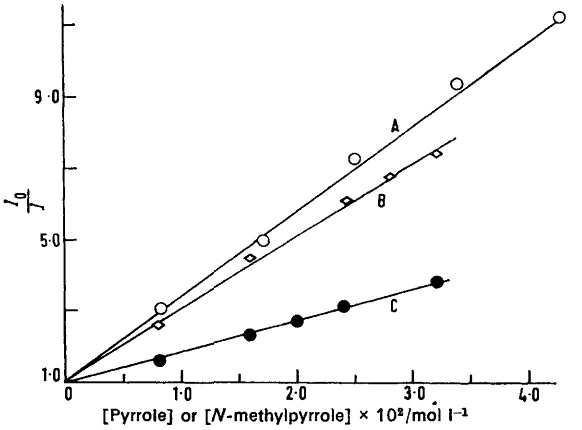

FIGURE 2 Stern–Volmer plots for quenching of naphthalene fluorescence by pyrrole in benzene A and in ethanol B, and by *N*-methylpyrrole in ethanol C. Slopes, A, $2{\cdot}43 \times 10^2$, B, $2{\cdot}07 \times 10^2$, and C, $0{\cdot}86 \times 10^2$ l mol^{-1}

The diffusion-limited rate constants are also given in this Table.

TABLE 2

Quenching of naphthalene fluorescence by pyrroles

Solvent	Quencher	k^{a}_{diff} $\times 10^{-9}$/ l mol^{-1} s^{-1}	Fluorescence lifetime (ns)	Slope $\times 10^{-2}$ (l mol^{-1})	$k_q \times 10^{-9}$/ l mol^{-1} s^{-1}
Ethanol	Pyrrole	8·5	85 [b]	2·07	2·43
	N-Methylpyrrole			0·86	1·01
Acetonitrile	Pyrrole	10·0	118 [c]	3·85	3·26
	N-Methylpyrrole			1·95	1·65
Benzene	Pyrrole	5·0	96 [b]	2·43	2·53

[a] Ref. 34. [b] D. Schulte-Frohlinde and R. Pfefferkorn, *Ber. Bunsengesellschaft Phys. Chem.*, 1968, **72**, 330. [c] N. Mataga, M. Tamura, and H. Nishimura, *Mol. Phys.*, 1965, **9**, 367.

The high values of k_q preclude T_1 of naphthalene as the reactive species. Thus, if we calculate the maximum quantum yield for reaction from T_1 using the values of k_q in Table 1, and the intersystem crossing rate[28] of 1·5—4·4 × 10^6 s^{-1} we arrive at a value of *ca.* 10^{-2}, for 0·1M-pyrrole. The quantum yield for the reaction in ethanol is found to be 0·24, indicating that S_1 is the reactive state, a conclusion in agreement with the sensitization experiments.

Since the work of Bryce-Smith on benzene and maleic anhydride[29] had shown that the latter react if the charge-transfer complex is irradiated at the frequency of its absorption band, we examined the u.v. spectra of pyrrole–naphthalene mixtures in ethanol and in hexane, to determine whether a charge-transfer complex was

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[25] J. Michl and J. Kolc, *J. Amer. Chem. Soc.*, 1970, **92**, 4128; also footnote 12 of this reference.

[26] J. G. Calvert and J. N. Pitts, 'Photochemistry,' Wiley, New York, 1966, p. 297.

[27] N. J. Turro, 'Molecular Photochemistry,' Benjamin, New York, 1965, pp. 93—95.

[28] T. D. S. Hamilton and J. P. Ray, *Photochem. and Photobiol.*, 1965, **4**, 269.

[29] D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 1962, **2675**.

formed. The absorption spectra were the sums of naphthalene and pyrrole absorption, in both solvents, indicating that charge-transfer interaction in the ground state is absent or weak.

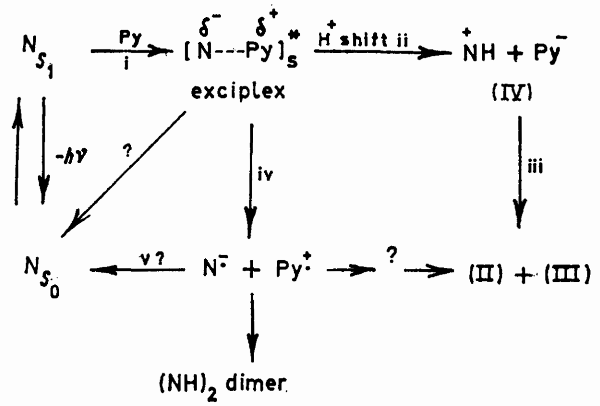
Photolysis with N-*Methylpyrrole and* N-*Deuteriopyrrole.*—Although *N*-methylpyrrole quenches naphthalene fluorescence almost as effectively as pyrrole, we found that it does not undergo the 1,2- and 1,4-additions to naphthalene. The same effect was noted by Bryce-Smith in the corresponding reaction of benzene.[4] This suggested that, while the N–H group is not necessary for the quenching process, its presence is vital for the addition to occur. We therefore conducted a photoaddition with *N*-deuteriopyrrole, in acetonitrile as solvent, and found that the deuterium is retained in the adducts (II) and (III) (by mass spectrometry). The adducts had m/e 196 (M^+, $C_{14}H_{12}DN$). The deuterium label was shown to be in the methylene groups of compound (II) and (III) by n.m.r. Hence, the N–H group of pyrrole is involved in the addition in a fundamental way.

Solvent Effects on Product Distribution.—Medium effects in solution photochemistry have led to a number of important conclusions regarding certain reactions.[30–34] We have studied solvent effects on the rates and product distributions of the naphthalene–pyrrole addition, and the results are given in Table 1.

The product distribution appears to be analogous to that observed in some ground-state, ionic reactions under kinetic control and involving an intermediate carbonium ion. For example, in the silver ion-catalysed solvolysis of allyl halides to generate allyl carbonium ions, the product of kinetic control is often the major one, and is decreased in amount by the effect of more polar media.[35] Also, in the ionic addition of bromine to 1,3-dienes, the more stable 1,4-dibromide is favoured over the 1,2-dibromide in polar media.[36] Since compound (III) is the more stable isomer,[37] the parallel between our photoaddition and the ground-state examples may indicate an ionic mechanism in the former reaction.

Mechanism.—In the Scheme, the various processes of naphthalene and pyrrole are summarized, and we will now consider the nature of the steps i—iv, and their relative importance in the formation of adducts (II) and (III).

After excitation of naphthalene to S_1, it is captured by pyrrole in a bimolecular process, which results in quenching of the naphthalene fluorescence. The latter can hardly be attributed to energy transfer, since S_1 of pyrrole is 24 kcal mol^{-1} higher in energy than S_1 of naphthalene (from absorption spectra). The quenching must be due to chemical interaction, and is represented in step i of the Scheme as formation of a charge-transfer exciplex, but may involve other singlet exciplexes or ion-pairs.



SCHEME Probable processes in the naphthalene–pyrrole photoaddition; N = naphthalene, Py = pyrrole

Leonhardt and Weller [7] first suggested these species to account for quenching by amines, and there is now ample evidence supporting their existence and their charge-transfer nature.[7–13] The similarity of pyrrole and amines in structure and ionization potential (8·0—9·0 eV) makes it reasonable to interpret the pyrrole quenching in a similar way. In an exciplex with the polarity shown the relatively acidic *N*-proton of pyrrole should become even more acidic, and step ii, which involves a shift of this proton from pyrrole to naphthalene, giving the ion-pair (IV), is reasonable.

This suggestion is supported by our deuterium-labelling experiment, and by the inertness of *N*-methylpyrrole. A similar proton shift in an exciplex was proposed by Cohen *et al.* to account for the rapid photoreduction of ketones by amines.[16] Step ii has already been discussed, and it is subject to solvent effects, and the observed effects favour the ionic process, as described above.

In view of the results for benzene and pyrrole,[4,5] for the reactions of anthracene with amines,[14] and for those of naphthalene with amines,[14] the electron-transfer process iv has been included in the Scheme. This process was suggested [4,5,14] to account for reductive dimerization of benzene,[4,5] anthracene,[14] and naphthalene in the presence of amino-compounds. In the irradiation of naphthalene with pyrrole, dimers of dihydronaphthalene do appear to be formed, but the amount is very small. These are undoubtedly formed *via* an electron-transfer process, such as step iv, but it is not certain that products (II) and (III) are also formed through this step.

We have found that the quantum yield for formation

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[30] G. Porter and P. Suppan, *Trans. Faraday Soc.*, 1966, **62**, 3375.

[31] I. M. Hartmann, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, 1967, **100**, 3146.

[32] B. D. Challand and P. de Mayo, *Chem. Comm.*, 1968, 982.

[33] F. Plummer and R. A. Hall, *Chem. Comm.*, 1970, 44.

[34] P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, 1969, **91**, 3085.

[35] For examples, including the cinnamyl cation, see R. H. De Wolfe and W. G. Young, *Chem. Rev.*, 1956, **56**, 753.

[36] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Bell, London, 1953, p. 673.

[37] A. J. Birch, *Quart. Rev.*, 1950, **4**, 69, and references therein. See also D. J. Cram, 'Fundamentals of Carbonium Chemistry,' Academic Press, New York, 1965, ch. V.

of compounds (II) and (III) is 0·31 in benzene and 0·24 in 95% ethanol (see Table 3). The fact that the quantum yield is appreciably less than unity, even though essentially all naphthalene singlets will be captured by pyrrole, demands that energy-wasting processes occur from the suggested exciplexes, the radical–ion-pair, or the ion-pair. Such processes could involve separation of charged species, and therefore would be sensitive to solvent polarity. The suggested mechanism might be tested by correlating the quenching properties of heterocyclic compounds with ionization potential, and by n.m.r. experiments.

EXPERIMENTAL

Materials.—All reagents and solvents were reagent grade and were crystallized or distilled. Naphthalene (Fisher Scientific Co.) had m.p. 78·5—80° (from ethanol). Benzophenone (Eastern Chemical Corp.) had m.p. 47·5—48°; *p*-bromobenzophenone (Eastern Chemical Corp.) had m.p. 78—80° (from ether–light petroleum). Acetophenone, b.p. 52° at 0·5 mmHg was supplied by the Eastern Chemical Corp. Pyrrole (Baker or Aldrich Chemical Co.) had b.p. 104° at 20 mmHg and was used when freshly distilled, as were *N*-methylpyrrole (Columbia Organic Chemicals) and *N*-deuteriopyrrole.[38] Silica gel (Davison Chemical Co.) was 100—200 mesh. For t.l.c., Eastman plastic sheet, precoated with silica gel was used. Celite (type Celaton F-W 80) was obtained from the Eagle–Picher Co. Carbonyl chloride was supplied by Matheson of Canada Ltd.

Instruments.—G.l.c. was performed on a Varian Aerograph 204B two column instrument, with flame-ionization detectors. The column (150 × 0·30 cm) was packed with 5% QF-1 (from Varian) on 60—80 mesh Chromosorb W, and was used with a helium flow rate of 31 ml min^{-1} at 153°. I.r. spectra were recorded on a Beckman IR-5 instrument and u.v. spectra on a Cary 14 recording spectrophotometer. Fluorescence measurements were performed on an Aminco–Bowman spectrofluorimeter. Quantum yields were measured on an optical bench by use of a Bausch and Lomb high-intensity monochromator, and ferrioxalate actinometry.[39] The details of this equipment and procedure will be described elsewhere.[40] N.m.r. spectra were measured in carbon tetrachloride or deuteriochloroform on a Varian HA100 instrument. Chemical shifts are given in δ values (p.p.m. downfield from tetramethylsilane). M.p.s were determined on a Kofler hot-stage apparatus and are corrected. Microanalyses were performed by the Spang Microanalytical Laboratories, Ann Arbor, Michigan. All pyrrole derivatives gave positive colour reactions with *p*-dimethylaminobenzaldehyde in acid.

Photolysis of Naphthalene and Pyrrole.—Naphthalene (12·0 g, 0·0938 mol) and pyrrole (14·0 g, 0·177 mol) in 95% ethanol were irradiated (Pyrex filter) under nitrogen with stirring with a Hanovia type L 450 W lamp, in a water-cooled immersion apparatus fitted with a means of withdrawing portions by a syringe. The progress of the reaction was followed by analysis of portions by g.l.c. Two major peaks appeared at R_t 3·5 (50%) and 3·9 min (35%), and minor products had R_t 5·2 and 5·9 min (total 15%). The photolysis was continued for 16 h. The solvent, unchanged pyrrole, and some naphthalene were then removed under vacuum at 40°. The residue was chromatographed on silica-gel (benzene–hexane 1 : 1), and fractions (200 ml) were collected. When all the naphthalene had been recovered (*ca.* 8·0 g) (fractions 1—4), elution with 5% methanol in ether (500 ml) afforded a mixture of adducts (6·519 g). This was separated by liquid–liquid chromatography (dimethylformamide–water–ethyl acetate as the stationary phase on Celite support, with cyclohexane as the mobile phase).[41] Fractions (200 ml) were collected and monitored by g.l.c. Fractions 19 and 20 contained compound (II) (1·16 g), 21—24 contained compounds (II) and (III) in roughly equal amounts (total 3·00 g), and 25 contained compound (III) and the minor products (total 0·44 g). The last fraction was chromatographed on silica gel (benzene–hexane) to afford the component (0·21 g) with R_t 5·9 min, found in fractions 17—21. The n.m.r. spectrum of this substance (IV) is described below. Fractions 21—24 were combined and chromatographed again on the same column. Fractions 10—12 contained compound (II) (0·68 g), 12—15 gave mixtures, and 16 contained compound (III) (0·43 g).

Compound (II) had m.p. 149—154°, $\nu_{\max.}$ 3484 cm^{-1}, (NH), $\lambda_{\max.}$ (EtOH) 211, 265, and 274 nm (ref. 42) (log ε 4·44, 3·59, and 3·51).

Compound (III) was an oil, $\nu_{\max.}$ 3484 cm^{-1} (NH), $\lambda_{\max.}$ (EtOH) 209 and 270 nm (ref. 42) (log ε 5·39 and 3·80).

Compound (IV) had R_t 5·9 min and constituted *ca.* 5% of the adduct mixture; $\nu_{\max.}$ 3517 cm^{-1} (NH), δ 6·95 (m, aromatic), 6·30 (2H, m, 2- and 5-H), 5·84 [2H, m, 4- and 2′(3′)-H], 4·43br (1H, m, 1′-H), and 3·34 (2H, m, 4′-H_2), and was tentatively identified as 3-(1,2-dihydro-1-naphthyl)-pyrrole.

Dehydrogenation of Compounds (II) *and* (III).—The adduct (II) or (III) (0·5 g) and 10% palladium–charcoal (0·45 g) (Matheson, Coleman, and Bell) were heated under reflux in *p*-xylene (15 ml). The solution was filtered and evaporated, and the unstable oil was examined by g.l.c. (1·5 m × 30 mm; 5% SE-30; 180°) and by n.m.r. The two adducts gave rise to naphthalene derivatives, which had different R_t values and n.m.r. spectra, but both were α-substituted pyrroles. This indicates that the pyrrole substituent is at different positions in the adducts (II) and (III), in agreement with the assigned structures. The dehydrogenations proceed at different rates, compound (II) requiring 2 days, but the isomer (III) only 3 h.

Conversion of Compound (II) *into the Ester Derivative.*[22]—Carbonyl chloride was passed into dry toluene (20 ml) cooled in ice until 1·0 g had been absorbed. Freshly distilled *NN*-dimethylaniline (1·5 g) was added, followed by compound (II) (1·16 g) in toluene (10 ml). After stirring for 12 h, further *NN*-dimethylaniline (1·5 g) was added, followed by absolute ethanol (10 ml). The mixture was heated under reflux for 2 h and the solvents were evaporated off. The mixture was chromatographed on silica gel, eluting with benzene–hexane (1 : 1) (1·75 l), and benzene–hexane–methanol (75 : 24 : 1) (1 l). Fractions (250 ml) were collected. Fraction 8 showed a single spot on t.l.c. This fraction was washed with 5% HCl (2 × 50

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[38] F. A. Miller, *J. Amer. Chem. Soc.*, 1942, **64**, 1543.

[39] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, *A*, **235**, 518.

[40] R. M. Bowman and J. J. McCullough, to be published.

[41] H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, 1961, **83**, 4486.

[42] *Cf.* the spectra of the dihydronaphthalenes, W. Hückel, E. Vevera, and W. Wörfel, *Chem. Ber.*, 1957, **90**, 901.

ml) and water (3×50 ml), dried (Na_2SO_4), and evaporated. The residue was washed with cold ether to afford *ethyl* 5-(1,4-*dihydro*-1-*naphthyl*)*pyrrole*-2-*carboxylate* (326 mg, 23%), m.p. 160·5—162·5° [from ethanol (charcoal)], $\nu_{max.}$ ($CHCl_3$) 3430 (NH) and 1690 cm^{-1} (C=O) (Found: C, 76·2; H, 6·4; N, 5·05. $C_{17}H_{17}NO_2$ requires C, 76·4; H, 6·4; N, 5·25%).

Conversion of Compound (III) *to the Ester Derivative*.[22]—Photoadduct (III) (868 mg) was treated with carbonyl chloride (600 mg) in toluene and then with ethanol as described above. The residue obtained by evaporation of the toluene, was chromatographed on silica gel, eluting with benzene–hexane (1 : 1) (4·5 l) and then with benzene–hexane–methanol (74 : 25 : 1) (1·8 l). Fractions (450 ml) were collected. Fractions 11—14 showed one spot on t.l.c. Monitoring by n.m.r. showed that these fractions contained the ester, but the residue did not crystallize. It was rechromatographed on silica gel eluting with benzene–hexane (3 : 1) (9 l). Fractions 18—20 contained the ester (350 mg, 30%). The product was first crystallized from hexane at low temperature and then from ethanol–water. *Ethyl* 5-(1,2-*dihydro*-2-*naphthyl*)*pyrrole*-2-*carboxylate* had m.p. 84—85°, $\nu_{max.}$ (CCl_4) 3310 (NH) and 1680 cm^{-1} (C=O) (Found: C, 76·2; H, 6·4; N, 5·55%).

Photolysis of Naphthalene and N-*Deuteriopyrrole*.—Naphthalene (6·0 g) and *N*-deuteriopyrrole[38] (3·0 g) in acetonitrile [distilled from phosphorus(V) oxide] were irradiated (Pyrex) with the 450 W Hanovia lamp for 5 h. The adducts (II) and (III) were isolated as before. In the n.m.r. spectra, the incorporation of deuterium in the methylene groups was shown by the 50% reduction in the areas of the peaks at δ 3·30 and 2·91, respectively. Also the mass spectra showed that one deuterium atom had been incorporated into the adducts.

Quantum Yield Measurements.—The details will be published elsewhere.[40] Solutions (26 ml) of naphthalene ($5{\cdot}8 \times 10^{-2}$ mol l^{-1}) and pyrrole (0·11 mol l^{-1}) in 95% ethanol and in benzene were deoxygenated by purging with argon, and irradiated at 313 nm for 4 h using a high intensity monochromator and a high pressure mercury lamp. The quantum yield for formation of the major adducts [(II) and (III)] was measured by g.l.c. using *p*-bromobenzophenone as internal standard. The results are in Table 3.

Table 3

Solvent	Quantum yield Run 1	 Run 2
Benzene	0·30	0·32
95% Ethanol	0·23	0·25

Solvent Effects.—Solutions containing naphthalene (0·0237 mol l^{-1}) and pyrrole (0·346 mol l^{-1}) in each of the solvents listed in Table 1 were placed in Pyrex tubes ($11 \times 3{\cdot}5$ cm). The samples were degassed by the freeze–pump–thaw method, and sealed. The tubes were irradiated for 2½ h in a Rayonet Photochemical Reactor (Southern New England Ultraviolet Company) using 16 RPR 300 nm lamps, and a ' merry-go-round ' turntable to ' average ' the light intensity. The relative rates in each of the solvents were estimated by g.l.c., using *p*-bromobenzophenone as internal standard. The product ratios were also measured, and results are given in Table 1.

Attempted Sensitization of the Naphthalene–Pyrrole Reaction.—Irradiation of the following solutions of naphthalene, pyrrole, and sensitizer for 2·5 or 25 h with the Hanovia 450 W lamp (Pyrex filter) gave no measurable yield of adducts (II) or (III) (g.l.c. monitoring): solution (i), naphthalene (0·0235M), pyrrole (0·0448M), and benzophenone (0·033M); solution (ii), naphthalene (0·0235M), pyrrole (0·0448M), and acetophenone (0·0416M).

Attempted Reaction of Naphthalene with N-*Methylpyrrole*.—Irradiation of naphthalene and *N*-methylpyrrole in the same way as described for naphthalene and pyrrole gave no detectable amounts of the adducts (II) and (III) (g.l.c. monitoring), after short (2·5 h) or long (25 h) irradiation times.

Quenching of Naphthalene Fluorescence by Pyrrole.—Measurements were made on an Aminco–Bowman spectrofluorimeter. Irradiation was carried out at 322 and monitoring at 343 nm. Naphthalene concentration was $1{\cdot}48 \times 10^{-2}$ mol l^{-1}. Sample solutions were deoxygenated by purging with argon. The results are given in Table 4 and Figures 1 and 2. I_0/I is the ratio of fluorescence intensities with and without pyrrole present.

Table 4

Solvent							
Ethanol	Pyrrole (M $\times 10^{-2}$)	0·00	0·80	1·60	2·39	2·79	3·19
	I_0/I	1·00	2·59	4·44	6·03	6·66	7·45
	N-Methylpyrrole (M $\times 10^{-2}$)	0·00	0·80	1·60	2·00	2·40	3·20
	I_0/I	1·00	1·63	2·30	2·66	3·09	3·83
Acetonitrile	Pyrrole (M $\times 10^{-2}$)	0·00	0·80	1·60	2·00	2·40	3·20
	I_0/I	1·00	4·49	7·09	8·47	9·84	12·71
	N-Methylpyrrole (M $\times 10^{-2}$)	0·00	0·80	1·60	2·00	2·40	3·20
	I_0/I	1·00	2·39	3·93	4·86	5·80	7·34
Benzene	Pyrrole (M $\times 10^{-2}$)	0·00	0·85	1·70	2·55	3·40	4·26
	I_0/I	1·00	3·05	4·85	7·28	9·36	11·29

Investigation of Charge-transfer Interactions by Ultraviolet Absorption.—Solutions of naphthalene ($5{\cdot}33 \times 10^{-3}$ mol l^{-1}) and pyrrole ($1{\cdot}23 \times 10^{-2}$ mol l^{-1}) in ethanol and of naphthalene ($5{\cdot}12 \times 10^{-3}$ mol l^{-1}) and pyrrole ($2{\cdot}12 \times 10^{-2}$ mol l^{-1}) in hexane were found to have u.v. absorption equal to the sum of the absorbances of the separate constituents. The path length was 0·1 mm. No evidence for charge-transfer interactions was found.

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