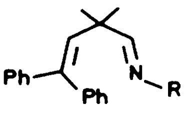
Photochemical Reactivity of Aldimines from 2,2-Dimethyl-3-oxo-3-phenylpropanal

Diego Armesto[a],* Ana Ramos[a], Rafael Perez-Ossorio[a], and William M. Horspool[b]
[a] *Departamento de Quimica Organica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040 Madrid, Spain*
[b] *Department of Chemistry, The University, Dundee, DD1 4HN, Scotland*

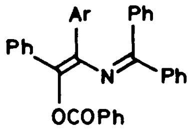
The syntheses of some thermally labile aldimines of 2,2-dimethyl-3-oxo-3-phenylpropanal are described. The aldimines (**7a**—**c**) are photochemically reactive and undergo fission mainly into isopropyl phenyl ketone. Several other minor products are also formed. One aldimine, from aniline, (**7d**) is photochemically inert. The mechanism of the reaction is discussed in terms of fission of the α, β-bond perhaps involving an electron transfer process.

The photochemistry of molecules containing the imine group has been a subject of study for many years. Many diverse reactions, such as isomerization, rearrangement, cycloaddition, photoreduction, and photoalkylation, have been reported and only in the last 15 years or so have attempts been made to classify the reactions.[1,2]

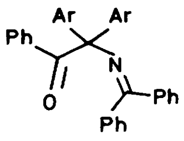
Our interest in this area has arisen from our observations of the photochemical transformations of imines (**1**), (**2**), and (**3**). It is clear from the rearrangements into (**4**),[3] (**5**),[4] and (**6**)[5] respectively that the incorporation of nitrogen into the system has a profound effect on the course of the reaction. The behaviour of these systems is substantially different from the reactions of β, γ-unsaturated enones to which the imines are closely related.[6]



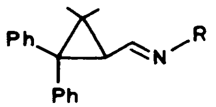
(**1**)



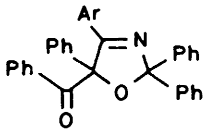
(**2**)



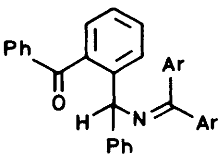
(**3**)



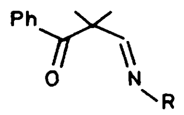
(**4**)



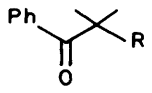
(**5**)



(**6**)



(**7**)
a; R = CH$_2$Ph
b; R = Pr^i
c; R = Bu^t
d; R = Ph



(**8**)
a; R = CHO
b; R = H

We now report the photochemical behaviour of the simpler imines of 2,2-dimethyl-3-oxo-3-phenylpropanal.

Results and Discussion

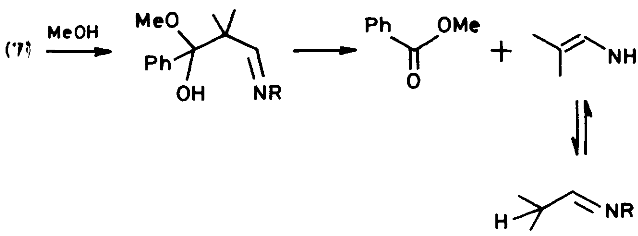
The imines (**7**) chosen for the study were synthesized by reaction of the ketoaldehyde (**8a**) with the appropriate amine under nitrogen in dry ether with added anhydrous magnesium sulphate. The imines (**7a**—**d**) were obtained as pale yellow oils after conventional work-up.

(*Note:* All these imines must be stored and handled under nitrogen since they decompose very readily in the presence of moisture to give the benzoate of the corresponding amine.)

The imines were identified by their spectral properties. In particular, all showed absorption at 1 640—1 650 cm^{-1} in their i.r. spectra characteristic of the imine functional group[7] and also a band at 1 680 cm^{-1} characteristic of the carbonyl group. All the ^{1}H n.m.r. spectra show resonances attributable to the alkyl groups on the nitrogen as well as the standard aromatic resonances. The aldimine proton is also present in the δ 7.6—8.1 region, but the assignment of the actual position is complicated by the lowfield aromatic resonances.

The imine (**7a**) gave acceptable microanalytical results and the less stable imines (**7b**) and (**7c**) showed mass spectral fragmentations compatible with the proposed structures. Principally fragmentation on electron bombardment follows the path where the molecular ion fragments to a PhCO ion. Subsidiary fragmentation paths involving loss of methyl and CO from the parent ion can also be identified. More importantly a path can be identified where the molecular ion fragments to the radical cation of isopropyl phenyl ketone. The *N*-phenylimine (**7d**) also fits into this pattern.

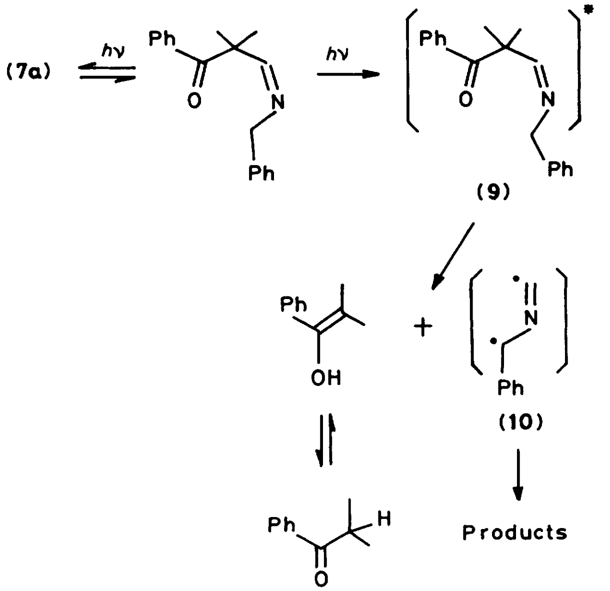
Further proof that the imines are as represented in (**7**) comes from the thermal ene-type fragmentation, the details of which have been published elsewhere.[8] Scheme 1 summarises these results and clearly establishes the manner of concatenation within the imines.



Scheme 1.

The u.v./visible spectra of the imines (**7**) showed strong absorptions in the 240—280 nm region and weaker absorptions around 350 nm tailing into the yellow at 400 nm. The imines were thus all irradiated under an atmosphere of nitrogen through a Pyrex filter into the long wavelength edge of the 280 nm band and above. By this approach it is likely that the carbonyl group is excited. The imine group normally absorbs in the 240 nm region and consequently will not be excited directly through a Pyrex filter. Brief exposure brought about the transformation of the imine (**7a**) into principally isopropyl phenyl ketone, benzyl isonitrile, and several minor products formed in < 2 or 3% yields.

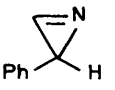
The formation of the ketone (**8b**) could arise by a path analogous to the not uncommon Norrish type II process involving δ-hydrogen abstraction.[9] Prior to this reaction the imine, shown in (**7**) as the *anti*-isomer, has to undergo *anti-syn*-isomerization to yield (**9**). In this conformation the carbonyl group is suitably disposed for the hydrogen abstraction (Scheme 2). Such a route adequately explains the formation of the ketone (**8b**) but also affords a species (**10**), related to the azirine (**11**), which might not be thermally stable. Furthermore the biradical (**10**) or the azirine (**11**)[10] would not undergo secondary photolysis under the conditions used, since the absorption of such species is at wavelengths < 280 nm.



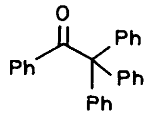
Scheme 2.

Doubt can be cast on the proposal of Norrish type II reactivity since recovered starting material gives no evidence for the formation of the *syn*-isomer (**9**). However, it is likely that such an isomer is consumed rapidly by the photochemical reaction or else the *syn*-isomer could be immediately transformed to the *anti*-isomer (**7**) on work-up*. There is evidence in the literature for such thermal instability.[11] Confirmation of the non-applicability of this reaction mode comes from the irradiation of the imine (**7c**) which under the same conditions as the above also affords the ketone (**8b**). The imine (**7b**) is also photoreactive and yields the same ketone (**8b**) as the principal product.

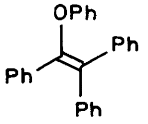
It thus seems likely that an alternative path is operative such as the fission of the α, β bond in (**7**). Such reactions are not common in aryl ketone photolysis but one example, that of ketone (**12**), serves to illustrate the reaction.[12] Irradiation of ketone (**12**) yields the enol ether (**13**) by a 1,3-migration. Thus, by analogy, we could interpret the principal reaction of imines (**7**) as one involving the formation of an imino radical. The formation of imino radicals is not without precedent in the photochemistry of such systems. Ohta and Tokumaru[13] have shown that imino radical can be formed by hydrogen abstraction from benzaldimines by photoexcited benzophenone and in a later publication they[14] also demonstrated that the imine (**14**) undergoes C–C fission to liberate a benzyl radical and the radical (**15**). The implication of such a path in our system could account for the formation of both principal products, namely the ketone (**8b**) and the isonitrile (**16**). The presence of the isonitrile (**16**) is detected not only by its obnoxious odour but also by g.l.c./mass spec. Indeed all the imines (**7a**—**c**) yield the corresponding isonitriles. The behaviour of this imine system is in direct contrast to that of the all carbon system, enone (**17**), which undergoes *cis–trans*-isomerization as well as an oxa-di-π-methane reaction.[15]



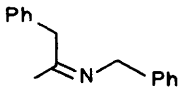
(11)



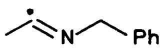
(12)



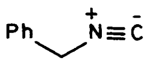
(13)



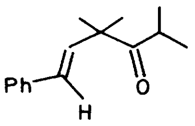
(14)



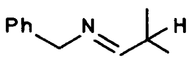
(15)



(16)

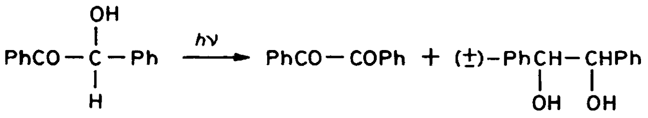


(17)



(18)

Earlier we alluded to the formation of minor products. Some of these, from the irradiation of imine (**7a**), have been identified by g.l.c./mass spec and shown to be deoxybenzoin, 1,2-diphenylethane, and the imine (**18**). It is clear that fragmentation by a path other than the α, β-path proposed above could also be operative. Thus a Norrish type I route could yield compounds containing a benzyl group or yield *N*-benzyl-2-methylpropanimine (**18**). Norrish type I behaviour of simple aryl alkyl ketones such as acetophenone is not known. However, benzoin derivatives have been reported[16] to yield the products shown in Scheme 3.



$$\mathrm{PhCO-\underset{H}{\overset{OH}{C}}-Ph} \xrightarrow{h\nu} \mathrm{PhCO-COPh} + (\pm)\text{-}\mathrm{Ph\underset{OH}{CH}-\underset{OH}{CH}Ph}$$

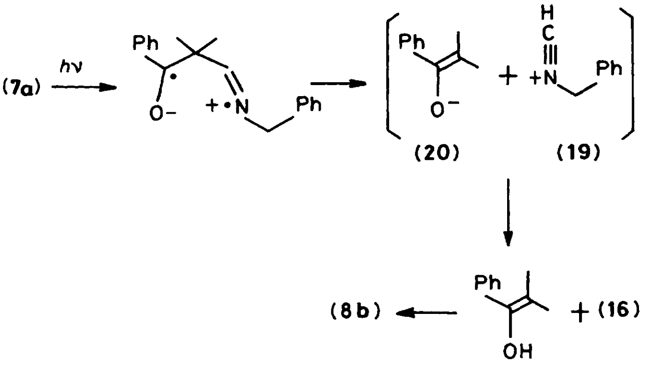
Scheme 3.

---

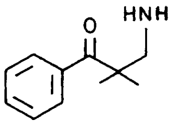
* Unlike the oximes where *syn*,*anti*-isomers are isolable it appears that, in general, only the *anti*-isomers of imines are stable. There is no spectral evidence for the imines (**7a**—**d**) to show the presence of the *syn*-isomer. Wettermark *et al.*[11] have also demonstrated that the *syn*,*anti*-isomerization of *N*-benzylideneanilines can be induced photochemically but the thermal reversion, even at 25 °C, is extremely rapid with a half-life of *ca.* 1 s.

Finally, under irradiation the imine (**7d**) failed to react under conditions identical with those for the other imines and was recovered intact.

The above rationalisation involving the fission of the α,β-bond of the imine can account for the formation of the principal products, *i.e.* the ketone and the isonitrile. The event which is most worrysome in this process is the hydrogen abstraction step, a disproportionation. The reaction can be made more reasonable by the incorporation of an electron transfer prior to the bond fission. This is outlined in Scheme 4. When the bond fission occurs, the disproportionation is replaced by the abstraction of an acidic proton from intermediate (**19**) by the enolate anion (**20**). This then yields the observed products. The incorporation of an intramolecular electron transfer from the nitrogen to the carbonyl function has ample precedence in the literature where recent years have seen the report of many examples of such a process.[17] It is interesting to note that a similar interpretation could be used to account for the reported fragmentation of the amino ketone (**21**)[18] although a Norrish Type II process appears to be more likely in this instance. The behaviour of (**21**) is very susceptible to changes in substitution and with the ketones (**22**) irradiation leads to a new pathway yielding cyclopropanols by abstraction of hydrogen from carbon.[19] Our reaction is also prone to substitution changes as can be seen by the failure of imine (**7d**) to react. The only major structural difference between (**7d**) and the other imines (**7a**—**c**) is that the phenyl group is attached directly to nitrogen while in the others a saturated carbon occupies this site. It is not clear why this should have such a profound effect on the process.

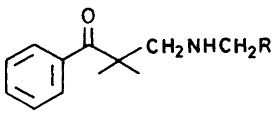


Scheme 4.



(21)

R = Me, Ph



(22)

R = Ph, CH$_2$Ph

We are currently investigating this phenomenon and are also seeking more concrete evidence for the involvement of the electron transfer path.

Experimental

I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Band positions are reported in wave numbers (cm^{-1}). ^{1}H N.m.r. spectra were recorded on a Varian T-60A spectrometer and line positions are recorded in p.p.m. downfield from internal SiMe$_4$. The mass spectra were determined on a Varian MAT-711 spectrometer. Elemental analyses were performed by the Consejo Superior de Investigacions Cientificas de Madrid.

Synthesis of the Imines (**7a,b,d**).—The synthesis of the imines was carried out by reaction of the ketoaldehyde, 2,2-dimethyl-3-oxo-3-phenylpropanal (3 g, 17 mmol) with an equimolar amount of the corresponding amine in anhydrous diethyl ether (150 ml) under nitrogen and with anhydrous magnesium sulphate as an added dehydrant. The mixture was stirred for 1 h at room temperature. The solution was filtered to remove drying agent and the solvent was removed under reduced pressure. The i.r. and ^{1}H n.m.r. spectra for the crude mixture showed that the transformation into the imine was quantitative in all cases. The products were purified by vacuum distillation. The results shown are yields after purification.

2-*Benzoyl*-2-*methyl*-N-*phenylpropanimine* (**7d**). Aniline (1.55 ml, 17 mmol) yielded the imine (**7d**) (3.54 g, 78%), b.p. 120 °C/1.0 mmHg; δ(CCl$_4$) 1.6 (6 H, s, 2 Me), 6.8—7.5 (8 H, m, ArH), and 7.8—8.1 (3 H, m, Ar plus CH=N); $\nu_{max.}$ (liq. film) 3 050, 2 980, 2 930, 2 860, 1 680 (C=O), 1 640 (C=N), 1 595, 1 450, 1 260, 770, 720, and 700 cm^{-1}; $\lambda_{max.}$(EtOH) (log ε) 244 (4.2) and 280 (3.6); *m*/*z* (rel. intensity) 251(5) *M*$^+$, 236(5), 223(2), 180(13), 148(3), 105(100), and 77(38).

2-*Benzoyl*-N-*benzyl*-2-*methylpropanimine* (**7a**). Benzylamine (1.86 ml, 17 mmol) yielded imine (**7a**), (3.34 g, 75%), b.p. 125 °C/0.1 mmHg; δ(CCl$_4$) 1.5 (6 H, s, 2 Me), 4.6 (2 H, br s, CH), 7.0—7.4 (8 H, m, ArH), and 7.6—7.9 (3 H, m, Ar and CH=N); $\nu_{max.}$ (liq. film) 3 060, 3 030, 2 980, 2 930, 2 840, 1 680 (C=O), 1 650 (C=N), 1 595, 1 575, 1 490, 1 450, 1 445, 1 260, 715, and 700 cm^{-1} $\lambda_{max.}$(EtOH) (log ε) 245 (4.0) and 280 (3.1); *m*/*z* (rel. intensity) 250 (4) *M*$^+$ – 15, 237 (14), 148 (10), 105 (100), 91 (35), and 77 (37) (Found: C, 81.55; H, 7.5; N, 5.25. Calc. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28%).

2-*Benzoyl*-N-*isopropyl*-2-*methylpropanimine* (**7b**). The general procedure was followed but the ratio of aldehyde : amine and the temperature were modified. Thus the aldehyde (3.0 g, 17 mmol) and isopropylamine (2.9 ml, 34 mmol) were refluxed for 3 h in diethyl ether. The solvent and the excess of amine were removed under reduced pressure and the residual oil was purified by vacuum distillation to give the imine (**7b**) (2.48 g, 67%), b.p. 62 °C/0.1 mmHg; δ(CDCl$_3$) 1.2 (6 H, d, isopropyl methyls), 1.5 (6 H, s, 2 Me), 3.4 (1 H, m, CH), 7.3—7.6 (3 H, m, ArH), and 7.7—8.1 (3 H, m, Ar and CH=N); $\nu_{max.}$ (liq. film) 3 060, 2 960, 2 930, 2 860, 1 680 (C=O), 1 650 (C=N), 1 595, 1 575, 1 460, 1 440, 1 260, 715, and 700 cm^{-1}; $\lambda_{max.}$(EtOH) (log ε) 243 (4.0) and 280 (3.1); *m*/*z* (relative intensity) 189 (9) *M*$^+$ – 28, 148(16), 133(8), 106(9), 105(100), and 77(33).

Synthesis of 2-*Benzoyl*-N-t-*butyl*-2-*methylpropanimine* (**7c**).—When the standard procedure was followed in this example only 50% yield was obtained even after increasing the reaction time to 70 h. The monoimine (**7c**) was obtained in quantitative yield by carrying out the reaction in benzene at reflux. The method was as follows. A solution of 2,2-dimethyl-3-oxo-3-phenylpropanal (3.0 g, 17 mmol) and t-butylamine (7.2 ml, 68 mmol) was refluxed in benzene (100 ml) for 4 h under nitrogen. The analysis of the crude reaction mixture by g.l.c. showed that the transformation into the imine was quantitative. Conventional work-up gave after vacuum distillation the imine (**7c**) as an oil (3.12 g, 79%), b.p. 73—75 °C/0.1 mmHg; δ(CCl$_4$) 1.13 (9 H, s, Me), 1.43 (6 H, s, Me), 7.20—7.50 (3 H, m, ArH), and 7.60—8.00 (3 H, m, Ar and CH=N); $\nu_{max.}$ (liq film) 2 970, 2 930, 2 870, 1 680 (C=O), 1 640 (C=N), 1 590, 1 570, 1 460, 1 440, 1 260, 1 220, 950, and 715 cm^{-1}; $\lambda_{max.}$(EtOH) (log ε) 242(3.98) and 280(3.03); *m*/*z* (rel. intensity) 231(0.3) M^+, 216(0.8), 203(12), 175(5), 148(46), 133(12), 105(100), 77(33), and 57(43).

General Procedure for Photolysis of Imines (**7**).—The photolyses were carried out in an immersion well apparatus. Irradiation was effected by a 400 W medium-pressure Hg arc lamp. The solutions of the imines (6.8 mmol) in t-butyl alcohol were purged with nitrogen prior to photolysis. Analysis of the photolysates was carried out using g.l.c. The isopropyl phenyl ketone was isolated in all cases by column chromatography on silica gel.

Irradiation of the Imine (**7a**).—This imine was irradiated for 105 min. The solvent was removed under reduced pressure and the photolysate was analysed by g.l.c./mass spec. and the following compounds were identified. Benzyl isonitrile; *m/z* (relative intensity) 117(100) M^+, 116(47), 91(55), 90(63), 89(39), 85(12), and 83(13). Isopropyl phenyl ketone; *m/z* 148(15) M^+, 105(100), and 77(29). *N*-Benzyl-2-methylpropanimine; *m/z* 161(12) M^+, 146(9), 132(6), 92(18), 91(100), and 77(5). Bibenzyl; *m/z* 182(4) M^+, 92(15), and 91(100). Deoxybenzoin: *m/z* 196(2) M^+, 105(100), 91(8), and 77(35). The i.r. spectrum of the crude mixture showed an intense band for the $R-N\equiv C$ of the isonitrile at 2 150 cm^{-1}. During the photolysis aliquots were withdrawn after 15, 30, 45, and 105 min. These were analysed directly by g.l.c. and the isopropyl phenyl ketone: imine (**7a**) ratio was determined. The isonitrile was isolated from the reaction mixture by vacuum distillation and was identified by comparison with an authentic sample prepared by reaction of benzylamine with dichlorocarbene.[20]

Irradiation of the Imine (**7b**).—This imine was irradiated and analysed as above for imine (**7a**). The isonitrile in this case was not isolated because its b.p. was too close to that of t-butyl alcohol. The presence of the isonitrile was confirmed by i.r. spectroscopy[21] which showed a strong absorption at 2 150 cm^{-1}.

Irradiation of the Imine (**7c**).—This imine was irradiated and analysed under conditions identical with the above. The presence of the isonitrile was demonstrated by i.r. spectroscopy.

Irradiation of the Imine (**7d**).—This imine was irradiated for 12 h under the general conditions described above. After this time work-up yielded the unchanged imine.

Acknowledgements

We thank the British Council and the Ministerio de Educacion y Ciencia for financial assistance.

References

1 A. Padwa, *Chem. Rev.*, 1977, **77**, 37; A. C. Pratt, *Chem. Soc. Rev.*, 1977, **6**, 63.

2 G. Wettermark in 'The Chemistry of the Carbon-Nitrogen Double Bond,' ed. S. Patai, Interscience, New York, 1969, p. 565; P. Beak and W. R. Messer, 'Organic Photochemistry,' vol. 2, ed. O. L. Chapman, Marcel Dekker, New York, 1969.

3 D. Armesto, J. A. F. Martin, R. Perez-Ossorio, and W. M. Horspool, *Tetrahedron Lett.*, 1982, **23**, 2149.

4 D. Armesto, M. J. Ortiz, R. Perez-Ossorio, and W. M. Horspool, *Tetrahedron Lett.*, 1983, **24**, 1197.

5 D. Armesto, M. G. Gallego, R. Perez-Ossorio, and W. M. Horspool, *Tetrahedron Lett.*, 1983, **24**, 1089.

6 S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531; K. N. Houk, *Chem. Rev.*, 1976, **76**, 1.

7 L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Chapman and Hall, London, 1975, pp. 299 and 296.

8 D. Armesto, A. Ramos, and R. Perez-Ossorio, *Tetrahedron Lett.*, 1982, **23**, 5195.

9 A. G. Schultz, C. D. De Boer, W. G. Herkstroeter, and R. H. Schlessinger, *J. Am. Chem. Soc.*, 1970, **92**, 6086.

10 A. Padwa, J. K. Rasmussen, and A. Tremper, *J. Am. Chem. Soc.*, 1976, **98**, 2065.

11 G. Wettermark and L. Dogliotte, *J. Chem. Phys.*, 1964, **40**, 1486; D. G. Anderson and G. Wettermark, *J. Am. Chem. Soc.*, 1965, **87**, 1433.

12 H. G. Heine, *Tetrahedron Lett.*, 1971, **12**, 1473.

13 H Ohta and K. Tokumaru, *Chem. Ind.* (*London*), 1971, 1301.

14 H. Ohta and K. Tokumaru, *Chem. Lett.*, 1974, 1403.

15 W. G. Dauben, M. S. Kellog, J. I. Seeman, and W. A. Spitzer, *J. Am. Chem. Soc.*, 1970, **92**, 1786; see also W. Adam, A. Berkessel, and S. Krimm, *Tetrahedron Lett.*, 1985, **26**, 619 where it is argued that this reaction type should correctly be an oxo-di-π-methane process.

16 H. G. Heine, W. Hartmann, D. R. Kory, J. G. Magyar, C. E. Hoyle, J. K. McVey, and F. D. Lewis, *J. Org. Chem.*, 1974, **39**, 691.

17 See chapters by P. S. Mariano, J. L. Stavinoha, and J. D. Coyle, in 'Synthetic Organic Photochemistry,' ed. W. M. Horspool, Plenum Press, New York and London, 1984, for references to intra- and intermolecular electron transfer processes.

18 F. Rotter, A. Abdul-Baki, T. Schrauth, and H. J. Roth, *Arch. Pharm.*, 1978, **311**, 346 (*Chem. Abstr.*, 1978, **89**, 42623).

19 A. Abdul-Baki, F. Rotter, T. Schrauth, and H. J. Roth, *Arch. Pharm.*, 1978, **311**, 341 (*Chem. Abstr.*, 1978, **89**, 23896).

20 G. W. Gokel, R. P. Widera, and W. P. Weber, *Org. Synth.*, 1976, **55**, 96.

21 L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' Chapman and Hall, London, 1975.

Received 22nd April, 1985; *Paper* 5/670