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# The Chemistry of 5-Oxodihydroisoxazoles. XIII* Reactions of the Imino Carbene Derived from Photolysis of Ethyl 5-Oxo-2-phenyl-2,5-dihydroisoxazole-4-carboxylate

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*Abstract*

Photolysis of ethyl 5-oxo-2-phenyl-2,5-dihydroisoxazole-4-carboxylate at 300 nm in acetonitrile gives a carbene which is captured efficiently by bromide, chloride, acetate and cyanate, and less efficiently by iodide, thiocyanate, cyclohexene and tetrahydrofuran. No hydrogen abstraction or reaction with double bonds was evident.

## Introduction

We have recently shown that photolysis of isoxazol-5(2*H*)-ones (1) proceeds by a number of competing pathways.[1–5] Those substituted with alkyl or hydrogen at C 3 undergo photolysis either by loss of carbon dioxide to form an imino carbene (2), or by rapid reversible ring opening to a ketene (3). Both of these species are susceptible to reaction with nucleophiles, but we suspected that if the ketene (3) was formed in the presence of only weak nucleophiles, such as many anions, ring closure might occur to reform the isoxazolone. In particular, our observation that photolysis under acid conditions gives largely carbene (2) derived products,[5] appeared open to the interpretation that acid encouraged the ring closure of (5) to (1). This would effectively partition the photolysis in the direction of carbene-derived products (4) (Scheme 1). In this communication we report our observations which essentially confirm the above hypothesis, and extend our previous studies, in which the nucleophiles were confined to alcohols and amines, to a number of weaker nucleophiles.

## Discussion

In work to be published shortly, we will show that the group $R^3$ at C 4 is initially important to stabilize the carbene species (2). The presence of an ethoxycarbonyl group at C 4 has proved to be most satisfactory for obtaining carbene-derived products, and is used throughout the work reported herein. Photolysis of the

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[*] Part XI, *Aust. J. Chem.*, 1995, **48**, 217; Part XII, *Aust. J. Chem.*, 1995, **48**, 55.

[1] Singh, Y., and Prager, R. H., *Aust. J. Chem.*, 1992, **45**, 1811.
[2] Ang, K. H., and Prager, R. H., *Tetrahedron Lett.*, 1992, **33**, 2845.
[3] Ang, K. H., and Prager, R. H., *Tetrahedron*, 1992, **48**, 9073.
[4] Ang, K. H., and Prager, R. H., *Aust. J. Chem.*, 1993, **46**, 477.
[5] Prager, R. H., Singh, Y., and Weber, B., *Aust. J. Chem.*, 1994, **47**, 1249.

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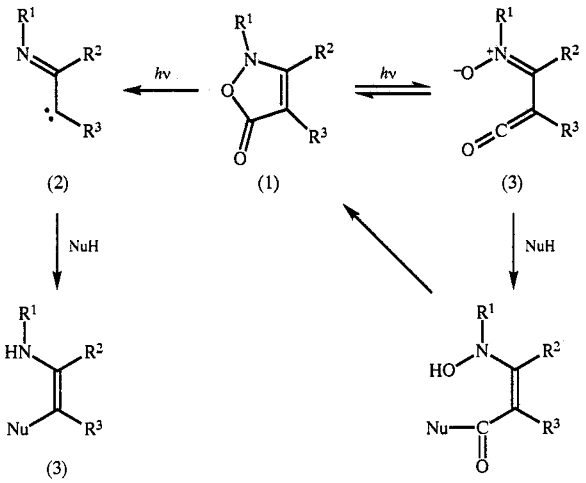
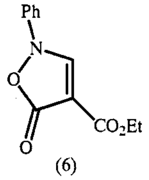
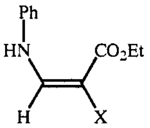


Scheme 1

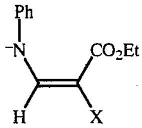
ester (6) in the presence of benzyltriethylammonium bromide, chosen for its solubility in organic solvents, gave complicated reaction mixtures in acetonitrile, with or without trifluoroacetic acid. However, when the bromide source was triethylamine hydrobromide, the vinyl bromide (7) was isolated in excellent yield (>95%). The product was largely the (*E*)-isomer (7), as expected by the effect of hydrogen bonding and predicted by molecular mechanics calculations ($\Delta H_{\mathrm{f}(E)-(Z)} = -18$ kJ mol$^{-1}$).



(6)



(7) X = Br (12) X = F
(9) X = Cl (14) X = OAc
(10) X = I (15) X = SCN



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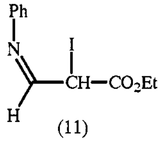
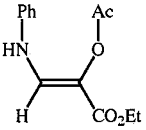


(11)

PhNHCOCH$_2$CO$_2$Et

(13)

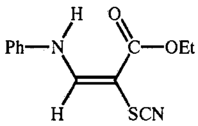


(14a)

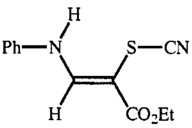
A similar yield was obtained when tetrabutylammonium bromide was used in the presence of 1 equiv. of acetic acid, suggesting the main role of the latter was to protonate the intermediate anion (8). In the same way, photolysis of (6) in the presence of triethylamine hydrochloride gave a mixture of (*E*)- and (*Z*)-propenoates (9) (95%). We also found that hydrochloric acid was a good source of chloride for the reaction (90%). Since we have previously shown[1] that even isoxazolones substituted on nitrogen with highly nucleophilic heterocycles will undergo such photochemically induced capture of chloride, this method represents a viable procedure for the synthesis of vinyl bromides and chlorides. Ethyl 2-iodo-3-phenylaminopropenoate (10) proved to be more difficult to obtain than the chloro or bromo enamines, partially because (10) tautomerized to (11), the C–I bond of which was then susceptible to photolysis. In this case, optimum yields of photolysis products came from the photolysis of tetraethylammonium iodide and acetic acid for 10 min, when the iodo compounds (10) and (11) were isolated in 21% yield (40 : 60). Attempts to synthesize the fluoro enamine (12) were unsuccessful. The use of tetrabutylammonium fluoride led to a multitude of products while hydrofluoric acid gave the malonamide (13) as the only characterizable product.

The acetoxy compound (14) was readily obtained by photolysis of (6) in acetic acid, whereupon it was obtained as a relatively stable crystalline solid. Only a single diastereoisomer was isolated, assumed to be the (*Z*)-isomer (14a), by contrast with the (*E*)-(7) obtained above. The assignment of (14a) rests on the extremely slow exchange of the NH proton with $D_2O$, slower than that seen with the halogen compounds (7), (9) and (10). In addition, a NOESY spectrum showed a strong n.O.e. between the methyl group of the acetoxy and the H 3′ of the aromatic ring. Such a correlation was even observable in the DQCOSY spectrum. Molecular mechanics calculations suggest that the (*Z*)-isomer is 2·31 kJ mol$^{-1}$ more stable than the (*E*)-isomer.

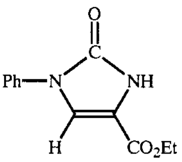
We next turned our attention to a number of ambident anions. Sodium thiocyanate was sufficiently soluble in acetonitrile to be usable. Ethyl (*E*)- and (*Z*)-3-phenylamino-2-thiocyanatopropenoate (15) were isolated in 20% yield, showing that this species preferred to attack the carbene through sulfur. Unlike the halogens, where the (*E*)-isomer predominated to a large extent, the (*E*)-to-(*Z*) ratio in (15) was only 2 : 1, indicating that hydrogen bonding between nitrogen and sulfur, as in (15b), was reasonably competitive with that between nitrogen and oxygen, as in (15a).



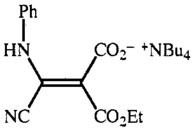
(15a)



(15b)



(16)



(17)

Photolysis in the presence of methyltrioctylammonium cyanate was synthetically more satisfactory. The product isolated was characterized as the imidazole (16) (70%). When the photolysis was carried out with a saturated aqueous solution of sodium cyanate and acetonitrile, the major product again was (16) (60%), accompanied by the malonamide (13). Since the latter has been obtained only when water is present, we believe its most likely origin is the ketene (3), addition of water to which, followed by rearrangement of the nitrone and decarboxylation,[3] would give (13). Alternatively, Wolf rearrangement of the imino carbene (2) would give a ketene, hydration of which would give (13). The use of sodium or lithium azide to trap the carbene was unsuccessful, leading to a gross mixture. O'Connor and Prout[6] have reported the photochemical decomposition of solid

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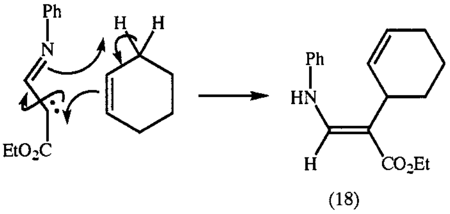
[6] O'Connor, C. T., and Prout, E. G., *S. Afr. J. Chem.*, 1981, **34**, 113 (*Chem. Abstr.*, 1981, **96**, 26802v).

lithium azide, but no indication of the nature of the products was given. Using ion chromatography, we have shown that azide ion, in methyltrioctylammonium azide, is essentially unaffected by irradiation at 300 nm for 30–60 min, under the normal conditions used. In the presence of isoxazolone (6), however, decomposition of azide was rapid, and appeared to be partially catalytic, as more than 1 equiv. was consumed, but consumption ceased when no further isoxazolone remained. We have been unable to characterize any pure products either from the reaction of azide with the imino carbene, or from the photochemical decomposition of azide.

The photolysis in the presence of tetrabutylammonium cyanide resulted in rapid consumption of the izoxazolone. The product was a pale yellow solid showing weak absorption around 2100 $cm^{-1}$, and was the same as that obtained at 20° in the dark. Structure (17) is suggested for this compound.

Photolysis of ester (6) in cyclohexene was investigated in the hope of obtaining cyclopropanes. We had previously observed that allyl alcohol reacted with the carbene exclusively through oxygen.[3] Consistent with this, no cyclopropanes were obtained, but a mixture of (*E*)- and (*Z*)-cyclohexenylpropenoates (18) was isolated (15%). This observation contrasts with that of methoxycarbonylcarbene,[7] which, although preferring to react with hydroxy or ethereal oxygen to double bonds, nevertheless did give cyclopropanes in the presence of alkenes. Product (18) could arise by insertion of the carbene into the allylic C–H bond or by an ene reaction (Scheme 2).* In view of the failure to note C–H insertion reactions with tetrahydrofuran (see below), we favour the latter. Radical reactivity of a triplet carbene has been ruled out by the addition of triplet quenchers, which failed to alter significantly the product composition.



(18)

Scheme 2

The major product isolated was (*E*)- and (*Z*)-*N*,*N*′-diphenylethene-1,2-diamine (19) whose origin is unclear, but which may arise from the ketene (20) as shown in Scheme 3. Some support for this hypothesis comes from the isolation of 3-(cyclohexen-3-yl)cyclohexene (21) (5%). The assignment of isomers of (19) was based on two-dimensional n.m.r. experiments and chemical reactivity. The n.m.r. assignments are shown in Fig. 1. The (*E*)-isomer was characterized by the rapid exchange of its NH proton with $D_2O$, and consequently the vinyl signal becoming a singlet. The (*Z*)-isomer underwent NH exchange only on addition of $DCl/D_2O$, owing to intramolecular hydrogen bonding. Separation of the isomers by radial chromatography was possible but re-equilibrium ($E/Z = 1/10$) occurred within 40 min. Irradiation of a mixture at 300 nm gave a 1 : 1 mixture.

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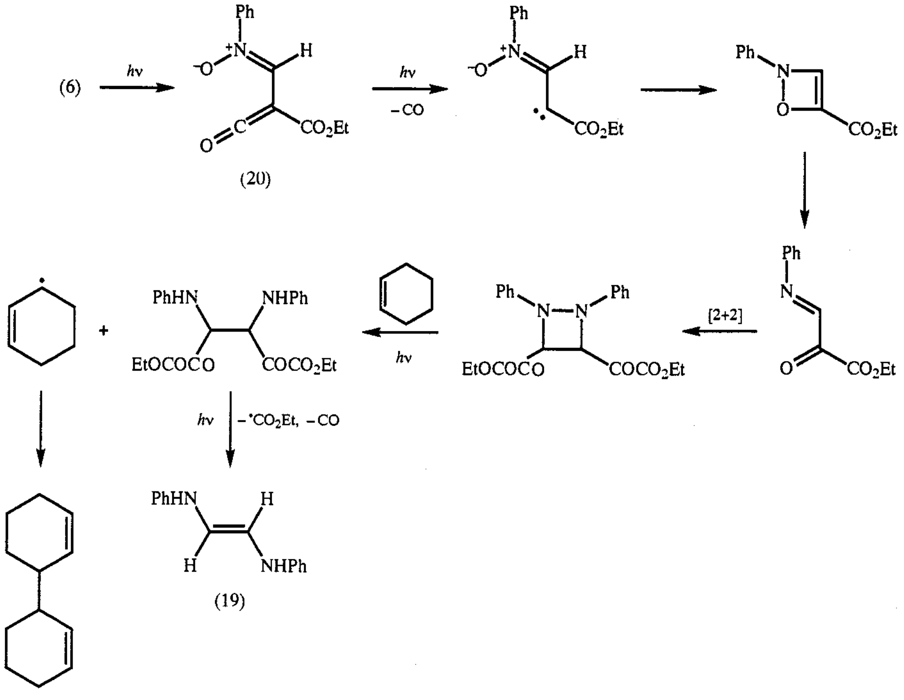
* We thank a referee for this suggestion.

[7] Wulfman, D. S., McGibboney, B. G., Steffen, E. K., Thinh, N. V., McDaniel, R. S., and Pearce, B. W., *Tetrahedron*, 1976, **32**, 1257.



Scheme 3

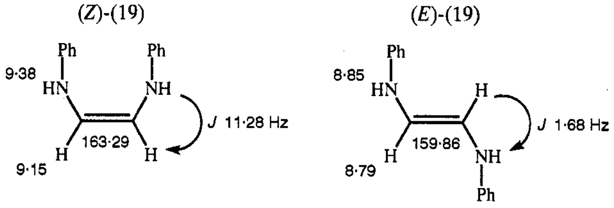
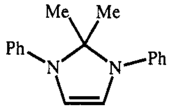
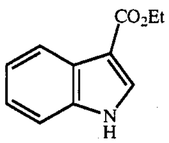


**Fig. 1.** $^1H$ and $^{13}C$ n.m.r. assignments for isomers of (19).

The above assignment was confirmed when the mixture of isomers was refluxed with acetone, which converted the (*Z*)-isomer into the dihydroimidazole (22), and left the (*E*)-isomer unchanged.



(22)

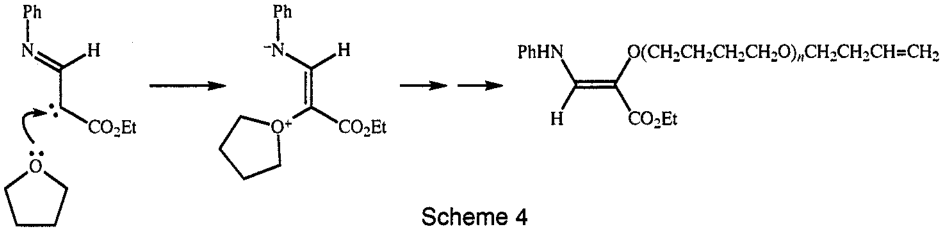


(23)

Finally, photolysis of (6) in tetrahydrofuran was informative in terms of mechanism. The occurrence of hydrogen atom abstraction in this solvent is generally viewed[8] as evidence for the formation of radical species derived from triplet carbenes. Although the photolysis was complex, and ethyl indole-3-carboxylate

[8] Patrick, T. B., and Wu, T. T., *J. Org. Chem.*, 1978, **43**, 1506.

(23) was the only pure characterized product, examination of the $^{1}H$ and $^{13}C$ n.m.r. spectra clearly showed the products were derived chiefly by attack of the oxygen at C 4, and no C–H insertion products[8] or C–O insertion[9] products were formed. The very polar products were consistent with polymer formation by a process similar to that shown in Scheme 4.



Scheme 4

In conclusion, photolysis of 4-ethoxycarbonylisoxazol-5(2*H*)-ones in mildly acidic media gives a carbene which is efficiently trapped by bromide, chloride, acetate, cyanate and, to a lesser extent, thiocyanate and iodide to give products not easily available by other procedures. The vinyl bromides, in particular, appear to be well set up for further elaboration by organometallic reagents.

## Experimental

General experimental procedures have been detailed previously.[1] Photolyses were carried out in Pyrex apparatus under nitrogen, by using a 450 W Hanovia high pressure quartz mercury vapour lamp.

### *Photolysis of Ethyl 5-Oxo-2-phenyl-2,5-dihydroisoxazole-4-carboxylate (6)*

(i) *With triethylammonium bromide.* The ester (6) (200 mg, 0·86 mmol) and triethylammonium bromide (469 mg, 2·58 mmol) were photolysed through Pyrex at 300 nm in anhydrous acetonitrile (200 ml) under $N_2$ at room temperature. Photolysis was followed by t.l.c. (ether) and was complete within 2 h. The solvent was removed under reduced pressure, and the residue was taken up into water and extracted with ethyl acetate (2×20 ml). After evaporation, the product was recrystallized from ether/light petroleum to give *ethyl* (E)- *and* (Z)-*2-bromo-3-phenylaminopropenoate* (7) as a colourless solid, in near quantitative yield, m.p. 69–70° (Found: C, 48·6; H, 4·4; N, 5·0. $C_{11}H_{12}BrNO_2$ requires C, 48·7; H, 4·5; N, 5·2%). $^{1}H$ n.m.r. $\delta$ 1·34, t, $J$ 6·67 Hz, 3H; 4·29, q, $J$ 6·67 Hz, 2H; 6·8–6·9, br d, $J$ 13·26 Hz, 1H, NH; 7·00–7·40, m, 5H; 8·25, d, $J$ 13·26 Hz, 1H. $^{13}C$ n.m.r. $\delta$ 14·52, $CH_3$; 61·47, $OCH_2$; 87·75, C 2; 115·84, C 2′; 123·44, C 4′; 129·88, C 3′; 138·29, C 3; 139·75, C 1′; 172·80, CO. $\nu_{max}$ 3319, 2979, 1703, 1504, 751, 692 $cm^{-1}$. Mass spectrum $m/z$ 269/271 (M), 225, 144, 117.

(ii) *With triethylammonium chloride.* Photolysis as in (i) above was complete in 2 h. The product, after removal of the salts as above, was recrysallized from ether/light petroleum to give *ethyl* (E)- *and* (Z)-*2-chloro-3-phenylaminopropenoate* (9) (95%) as off-white crystals, m.p. 80–81° (Found: C, 58·9; H, 5·4; N, 5·7. $C_{11}H_{12}ClNO_2$ requires C, 58·5; H, 5·4; N, 6·2%). $^{1}H$ n.m.r. $\delta$ 1·31, t, $J$ 7·12 Hz, 3H; 4·26, q, $J$ 7·12 Hz, 2H; 6·80–7·35, m, 6H, ArH, NH; 8·11, d, $J$ 13·26 Hz, 1H. $^{13}C$ n.m.r. $\delta$ 14·29, $CH_3$; 61·01, $OCH_2$; 97·37, C 2; 115·66, C 2′; 122·99, C 4′; 129·54, C 3′; 139·65, C 1′; 135·98, C 3; 163·86, CO. $\nu_{max}$ 1696, 1636, 1602, 1560, 1368, 1065 $cm^{-1}$. Mass spectrum $m/z$ 225/227 (M), 179, 144, 117, 104, 77.

(iii) *With hydrochloric acid.* The ester (6) (100 mg, 0·43 mmol) was photolysed in acetonitrile (100 ml) containing concentrated HCl (0·25 ml) as above. Photolysis was followed by t.l.c. (ether) until complete (*c.* 2 h). The excess acid was quenched with $Na_2CO_3$, before the solvent was removed. The crude mixture was extracted with ethyl acetate in

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[9] Frey, H. M., and Voisey, M. A., *J. Chem. Soc., Chem. Commun.*, 1966, 454.

the usual manner, to give after recrystallization (ether/light petroleum) ethyl (*E*)- and (*Z*)-2-chloro-3-phenylaminopropenoate (9) (90%), m.p. 80–81°.

(iv) *With tetraethylammonium iodide.* Ester (6) (100 mg, 0·43 mmol) was photolysed as above in the presence of tetraethylammonium iodide (270 mg, 1·29 mmol) and acetic acid (26 mg, 0·43 mmol). Photolysis was stopped after 10 min: further irradiation gave complex mixtures. Radial chromatography separated the products *ethyl* (E)- *and* (Z)-*2-iodo-3-phenylaminopropenoate* (10) and *ethyl 2-iodo-3-phenyliminopropanoate* (11) (21%) from unreacted (6), obtained as white platelets after recrystallization (dichloromethane/light petroleum), m.p. 119–120°, 126–127°. The analytical sample decomposed before analysis was possible. Ethyl 2-iodo-3-phenyliminopropanoate (11), $^1H$ n.m.r. $\delta$ 1·31, t, *J* 7·11 Hz, 3H; 4·18, q, *J* 7·11 Hz, 2H; 4·85, d, *J* 7·00 Hz, 1H; 6·80–7·40, m, 6H, ArH. Ethyl (*E*)- and (*Z*)-2-iodo-3-phenylaminopropenoate (10), $^1H$ n.m.r. $\delta$ 1·33, t, *J* 7·08 Hz, 3H, $CH_3$; 4·27, q, *J* 7·08 Hz, 2H, $OCH_2$; 6·80–7·40, m, 6H, ArH, NH; 8·07, d, *J* 13·44 Hz, 1H; 9·90, br d, NH. $^{13}C$ n.m.r. [of (10) and (11)] $\delta$ 14·51, $CH_3$; 30·05, CHI; 59·32, $OCH_2$; 61·76, $OCH_2$; 87·41, C2; 115·35, C=N; 116·36, C2′; 122·55, C4′; 123·57, C4′; 129·81, C3′; 139·67, C1′; 140·66, C1′; 143·22, C3; 164·39, CO; 170·39, CO. $\nu_{max}$ 3750, 1672, 1629, 1601, 1588, 1503 cm$^{-1}$. Mass spectrum *m/z* 317 (M), 271, 191.

(v) *With tetrabutylammonium fluoride.* Ester (6) was photolysed as above in the presence of tetrabutylammonium fluoride (3 equiv.) and acetic acid (1 equiv.). After removal of the salts, $^{19}F$ n.m.r. spectroscopy showed the absence of covalently bonded fluorine, and chromatography allowed the isolatation of ethyl *N*-phenylcarbamoylacetate (13) (50%), m.p. 38–40° (lit.[10] 38–39°), and a trace amount of ethyl (*Z*)-2-acetoxy-3-phenylaminopropenoate (14a). The use of aqueous hydrofluoric acid led to the formation of numerous products which were not identified.

(vi) *In acetic acid.* On completion of the photolysis (*c.* 60 min), the crude product was separated by radial chromatography on silica, dichloromethane/light petroleum (1 : 1) being used, to afford one major compound, ethyl (*Z*)-2-acetoxy-3-phenylaminopropenoate (14a). Further purification by a second radial chromatography on silica with dichloromethane/light petroleum (1 : 5) gave a yellow solid, which was recrystallized from tetrahydrofuran/cyclohexane as white cubic *crystals* (76%), m.p. 135–137° (Found: C, 62·9; H, 6·1; N, 5·6. $C_{13}H_{15}NO_4$ requires C, 62·6; H, 6·1; N, 5·6%). $^1H$ n.m.r. $\delta$ 1·25, t, *J* 7·54 Hz, 3H; 2·21, s, 3H; 4·25, q, *J* 7·54 Hz, 2H; 6·60, d, *J* 14·00 Hz, 1H, $D_2O$ exch; 6·60–7·40, m, 5H; 7·75, d, *J* 14·00 Hz, 1H. $^{13}C$ n.m.r. $\delta$ 14·26, $CH_3$; 20·31, $CH_3$; 60·41, $CH_2$; 115·23, C2′; 118·05, C2; 122·32, C4′; 129·26, C3; 129·48, C3′; 140·09, C1′; 164·23, C1; 169·24, CO. $\nu_{max}$ 3317, 1726, 1660, 1595 cm$^{-1}$. Mass spectrum *m/z* 249 (M), 231, 207, 177, 133.

(vii) *With sodium thiocyanate.* Ester (6) (100 mg, 0·43 mmol) was photolysed as above in the presence of sodium thiocyanate (104 mg, 1·29 mmol) and acetic acid (26 mg, 0·43 mmol). After 20 min the solid residue obtained was separated into its constituents by radial chromatography. Fractions of pure *ethyl* (E)- *and* (Z)-*3-phenylamino-2-thiocyanatopropenoate* (15) were obtained, but re-equilibration occurred within 30 min. The (*E*)-isomer had m.p. 108–109°, the (*Z*)-isomer 112–114°. The equilibrium mixture (2 : 1) (20%) was recrystallized from ether/light petroleum (Found: C, 57·9; H, 4·9; N, 11·3. $C_{12}H_{12}N_2O_2S$ requires C, 58·1; H, 4·9; N, 11·3%) $^1H$ n.m.r. $\delta$ 1·41, t, *J* 6·90 Hz, 3H; 4·33, q, *J* 6·90 Hz, 2H; 7·00–7·45, m, 6H, ArH, NH; 7·90, d, *J* 13·47 Hz, 1H; 8·45, d, *J* 13·5 Hz, 1H; 10·50, br d, 1H, HN. $^{13}C$ n.m.r. $\delta$ 14·34, $CH_3$; 61·49, $OCH_2$; 80·02, C2; 112·86, SCN; 116·88, C2′; 125·12, C4′; 129·97, C3′; 138·76, C1′; 152·47, C3; 167·78, CO. $\nu_{max}$ 3314, 2930, 2149, 1703, 1699, 1695, 1683, 1652, 1600, 1557, 1495, 1456 cm$^{-1}$. Mass spectrum *m/z* 248 (M), 220, 205, 174, 148, 117.

(viii) *With methyltrioctylammonium cyanate.* Ester (6) (100 mg, 0·43 mmol) was photolysed as above in acetonitrile (100 ml) containing the cyanate (528 mg, 1·29 mmol) and acetic acid (26 mg, 0·43 mmol). After 1·5 h the product was separated by radial chromatography (ether/light petroleum, 1 : 4). *Ethyl 2-oxo-3-phenyldihydro-1*H*-imidazole-5-carboxylate* (16) (70%) was isolated as colourless crystals, m.p. 212–214° after recrystallization from ethanol/water (Found: C, 62·3; H, 5·3; N, 11·9. $C_{12}H_{12}N_2O_3$ requires C, 62·1; H, 5·2; N, 12·1%). $^1H$ n.m.r. $\delta$ 1·36, t, *J* 7·12 Hz, 3H; 4·34, q, *J* 7·12 Hz, 2H; 7·20–7·65, m, 6H, ArH; 9·05, br

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[10] Rugheimer, L., and Hoffmann, R., *Ber. Dtsch. Chem. Ges.*, 1884, **17**, 741.

s, 1H, NH. $^{13}$C n.m.r. $\delta$ 14·29, CH$_3$; 61·23, OCH$_2$; 114·50, C2; 118·21, C4′; 122·43, C2′; 127·10, C3; 129·42, C3′; 136·07, C1′; 151·79, CONH; 159·18, CO. $\nu_{max}$ 1722, 1697, 1628, 1600, 1508, 1404 cm$^{-1}$. Mass spectrum *m/z* 232 (M), 186, 143.

The use of sodium cyanate (400 mg, 1·29 mmol) in acetonitrile (100 ml) and water (20 ml) allowed the isolation of the imidazole (16) (60%), and ethyl *N*-phenylcarbamoylacetate (13), m.p. 38° (lit.[10] 38–39°) (16%).

(ix) *In cyclohexene.* The isoxazolone (6) (580 mg, 2·5 mmol) was photolysed in benzene (450 ml) and cyclohexene (50 ml). On completion of the reaction (*c.* 60 min), the solvent was removed and the product separated by radial chromatography on silica, t-butyl methyl ether/light petroleum (3:2) being used as the eluent to afford ethyl 2-(cyclohexen-3-yl)-3-phenylaminopropenoate (18), 3-(3-cyclohexen-3-yl)cyclohexene (21) and *N,N′*-diphenylethene-1,2-diamine (19).

*Ethyl 2-(cyclohexen-3-yl)-3-phenylaminopropenoate* (18) was isolated as a yellow oil (15%), which rapidly decomposed on standing (*c.* 30 min) (Found: M$^{+\bullet}$ − PhNH (92), 179·1088. $C_{11}H_{15}O_2$ requires 179·1072). $^1$H n.m.r. $\delta$ 1·35, t, *J* 7·33 Hz, 3H; 1·40–1·76, m, 4H; 2·15, m, 2H; 3·76, m, 1H; 4·30, q, *J* 7·33 Hz, 2H; 5·40–5·58, m, 2H; 6·55, d, *J* 13·32 Hz, 1H, NH, D$_2$O exch; 6·71–7·45, m, 5H; 7·66, d, *J* 13·32 Hz, 1H. $^{13}$C n.m.r. $\delta$ 13·97, CH$_3$; 23·68, CH$_2$; 25·17, CH$_2$; 27·95, CH$_2$; 31·24, CH$_2$; 63·01, OCH$_2$; 115·38, 120·00, 121·03, 127·92, 127·99, 128·93, 129·00, 134·56, 142·14, 158·89. $\nu_{max}$ 3322, 1722, 1651, 1606 cm$^{-1}$. Mass spectrum *m/z* 179 (M−92), 150, 120.

3-(Cyclohexen-3-yl)cyclohexene (21) was isolated as a light yellow oil (5%)[11] (Found: M$^{+\bullet}$, 162·1428. Calc. for $C_{12}H_{18}$: M$^{+\bullet}$, 162·1408). $^1$H n.m.r. $\delta$ 1·01–2·35, m, 14H; 5·57–5·89, m, 4H. $\nu_{max}$ 3010, 1645 cm$^{-1}$. Mass spectrum *m/z* 161 (M), 97.

(E)-N,N′-*Diphenylethene-1,2-diamine* (19) was isolated as a yellow gum, which decomposed during attempted distillation or sublimation (125°/0·05 mm). The compound was purified by a second radial chromatography on silica, t-butyl methyl ether being used as the eluent. The yellow oil was partially transformed into (*Z*)-*N,N′*-diphenylethene-1,2-diamine over 30 min (Found: C, 79·9; H, 6·8; N, 13·4. $C_{14}H_{14}N_2$ requires C, 79·9; H, 6·7; N, 13·4%). $^1$H n.m.r. $\delta$ 7·01–7·64, m, 10H; 8·79, d, *J* 1·68 Hz, 1H; 8·54, d, *J* 1·68 Hz, 2H, NH, D$_2$O exch. $^{13}$C n.m.r. $\delta$ 118·84, C2′; 125·32, C4′; 129·78, C3′; 136·92, C1′; 159·86, HC=CH. $\nu_{max}$ 3260, 3051, 2881, 1679, 1599 cm$^{-1}$.

(Z)-N,N′-*Diphenylethene-1,2-diamine* (19) was isolated as a yellow gum, after a second radial chromatography on silica, t-butyl methyl ether being used as the eluent. It partially transformed into (*E*)-*N,N′*-diphenylethene-1,2-diamine (19) over 30 min (Found: C, 79·7; H, 6·6; N, 13·2. $C_{14}H_{14}N_2$ requires C, 79·9; H, 6·7; N, 13·4%). $^1$H n.m.r. $\delta$ 7·08–7·58, m, 10H; 9·15, d, *J* 11·28 Hz, 2H; 9·38, d, *J* 11·28 Hz, 2H, D$_2$O exch. $^{13}$C n.m.r. $\delta$ 120·27, C2′; 124·82, C4′; 129·78, C3′; 137·16, C1′; 163·29, HC=CH. $\nu_{max}$ 3261, 3046, 2882, 1682, 1600, 1538, 1441 cm$^{-1}$.

When a mixture of (*E*)- and (*Z*)-(19) was refluxed in acetone for 10 min, both the $^1$H and $^{13}$C n.m.r. spectra showed that the (*Z*)-isomer had been consumed, but the product was unstable.

(x) *In tetrahydrofuran.* Photolysis of (16) (580 mg, 2·5 mmol) in freshly distilled tetrahydrofuran (500 ml) was complete in 1 h. The crude product was separated by radial chromatography. Ether/light petroleum (3:2) eluted ethyl indole-3-carboxylate (23) (5%) as white needles, m.p. 118–120°, after recrystallization from aqueous ethanol (lit.[12] 118–119°). $^1$H n.m.r. $\delta$ 1·45, t, *J* 7·30 Hz, 3H; 4·45, q, *J* 7·30 Hz, 2H; 6·83–7·75, m, 5H; 9·20, br s, 1H, D$_2$O exch. $^{13}$C n.m.r. $\delta$ 14·31, CH$_3$; 63·01, CH$_2$; 108·62; 111·98; 120·65; 122·49; 123·55; 125·20; 127·42; 137·12; 162·47. Elution with methanol gave a polymeric oil.

### *Reaction of (6) with Tetrabutylammonium Cyanide*

Ester (6) (100 mg, 0·43 mmol) and tetrabutylammonium cyanide (346 mg, 1·29 mmol) in acetonitrile (100 ml) and acetic acid (26 mg, 0·43 mmol) were stirred under dry conditions in the dark at room temperature. T.l.c. (ethyl acetate/dichloromethane) showed that no

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[11] 'Beilsteins Handbuch der Organischen Chemie' Band 5(2), p. 342 (Springer–Verlag: Berlin 1943).

[12] Majima, R., *Ber. Dtsch. Chem. Ges.*, 1922, **55**, 3865.

starting material remained after 10 min. The solvent was removed under reduced pressure and the crude mixture was washed with water and extracted with ethyl acetate (2×20 ml) to give a yellow oil, which formed a pale yellow solid when subjected to high vacuum, but rapidly absorbed water when exposed to the atmosphere. *Tetrabutylammonium 3-cyano-2-ethoxycarbonyl-3-phenylaminopropenoate* (17) was isolated in near quantitative yield. $^1$H n.m.r. δ 0·7–1·9, m, 31H; 3·1, m, 8H; 4·2, q, *J* 7·2 Hz, 2H; 6·8–7·8, m, 5H; 11·7, s, 1H, NH. $^{13}$C n.m.r. δ 13·01, $CH_3$; 13·77, $CH_3$; 18·97, $CH_2$; 23·14, $CH_2$; 57·76, $CH_2$; 59·03, $OCH_2$; 102·27, C2; 117·88, CN; 118·93, C2′; 121·61, C3′; 128·05, C4′; 139·74, C3; 155·17, C1′; 164·75, CO; 168·04, C1. $\nu_{\max}$ 2236, 1707, 1655, 1592 cm$^{-1}$.

The same product was obtained when the above mixture was irradiated at 300 nm.

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