

Use of Tertiary Amino-groups as Substituents to Stabilise Compounds Towards Attack by Singlet Oxygen

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An alkene, a dihydropyran, a furan, and an anthracene, each having a tertiary amino-substituent insulated from the olefinic system, have been shown to be particularly stable towards singlet oxygen generated by irradiation of methanolic solutions of Methylene Blue. The stability is attributed to the amino-group quenching the singlet oxygen. Addition of triethylamine or 1,4-diazabicyclo[2.2.2]octane to solutions of 2-methylfuran and anthracene also reduces the rate of oxidation of the latter compounds but much less efficiently.

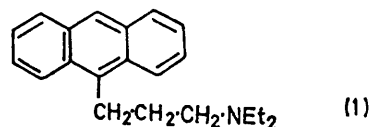
SINCE the finding that 1,4-diazabicyclo[2.2.2]octane (DABCO) acts as a physical quencher of singlet oxygen,¹ there have been a number of studies in which rate constants for the quenching of singlet oxygen by amines have been determined.^{2a-f} The rate constants increase as the ionisation potential of the amine decreases and thus it appears that some type of charge-transfer mechanism is responsible for the quenching. However, as yet, the exact nature of the mechanism has not been defined. Recently, several other good electron donors have been shown to be efficient quenchers of singlet oxygen, e.g. sulphides,³ phenols,^{2e} and azides.⁴

Another problem associated with the interaction of singlet oxygen with amines is whether any chemical reaction results. There have been claims for⁵ and against⁶ the proposal. In the majority of rate constant determinations, the singlet oxygen was generated by a microwave discharge, and since, therefore, interaction of oxygen with the amine takes place in the vapour phase, there will be relatively few collisions between the singlet oxygen and amine molecules.^{2a-c} Usually in solution phase work, the singlet oxygen is generated by use of a sensitising dye, and because this process is continuous many more collisions between singlet oxygen and amine molecules are possible than in the vapour phase. Thus if chemical reaction is possible, albeit relatively inefficient, it should be more readily detectable in solution phase experiments.

RESULTS AND DISCUSSION

We have recently reported that the anthracene compound (1) exhibits intramolecular exciplex formation.⁷ Another interesting property of this compound is its stability to irradiation for prolonged periods in oxygenated solutions. This is in contrast to the well known and documented⁸ fact that anthracene and

9-alkylanthracenes readily undergo oxidation on irradiation in oxygenated solutions. Since irradiation of (1)



does lead to efficient population of its triplet state,⁹ it cannot be argued that its stability is due to its inability to sensitise the formation of singlet oxygen. From the previously discussed findings that tertiary amines efficiently quench singlet oxygen it seemed likely that (1) owes its stability to the amino-group. This suggestion seems sensible on the grounds that the rate constants for quenching of singlet oxygen by triethylamine (k_q 2.1×10^6 l mol⁻¹ s⁻¹)^{2e} is five times greater than that for oxidation of such a reactive compound as 2,5-dimethylfuran ($k_r = 4 \times 10^5$ l mol⁻¹ s⁻¹).^{2c}

In order to assess the effectiveness of tertiary amine substituents in protecting compounds towards attack by singlet oxygen, the amines (2)–(6) were prepared. These compounds were chosen because they would allow an assessment of the capability of the amino-group to protect compounds to the three main types of photo-oxygenation reactions, i.e. hydroperoxide formation (i), endo-peroxide formation (ii), and carbonyl compound formation¹⁰ (iii).

Oxidation of compounds (2)–(6) was studied by measuring the amount of material consumed on irradiation in methanolic solution containing Methylene Blue as sensitiser. A comparison of the amounts of aminated compounds (2)–(6) consumed with the corresponding consumption of their non-aminated counterparts (7)–(10) was made (Table 1). The rate of consumption of compounds (7)–(10) was found to be constant until

³ R. A. Ackerman, J. Rosenthal, and J. N. Pitts, *J. Chem. Phys.*, 1971, **54**, 4960.

⁴ C. S. Foote, T. T. Fujimoto, and Y. C. Chang, *Tetrahedron Letters*, 1972, 45; N. Hasty, P. M. Merkel, P. Radlick, and D. R. Kearns, *Tetrahedron Letters*, 1972, 49.

⁵ M. H. Fisch, J. C. Gramain, and J. A. Olesen, *Chem. Comm.*, 1970, 13; 1971, 663; W. F. Smith, *J. Amer. Chem. Soc.*, 1972, **94**, 186; J. H. E. Lindner, H. J. Kuhn, and K. Gollnick, *Tetrahedron Letters*, 1972, 1705.

⁶ R. F. Bartholomew and R. S. Davidson, *Chem. Comm.*, 1970, 1174; *J. Chem. Soc. (C)*, 1971, 2347.

⁷ D. R. G. Brimage and R. S. Davidson, *Chem. Comm.*, 1971, 1385.

⁸ K. Gollnick, *Adv. Photochem.*, 1968, **6**, 111.

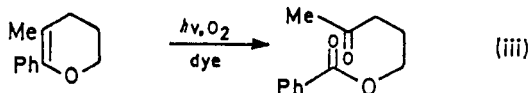
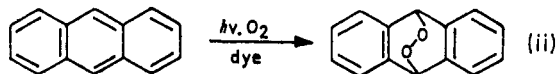
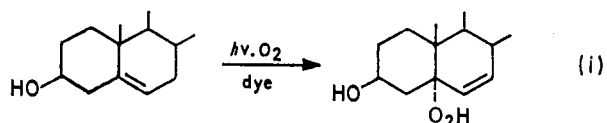
⁹ D. R. G. Brimage and R. S. Davidson, unpublished results.

¹⁰ R. S. Atkinson, *J. Chem. Soc. (C)*, 1971, 784.

¹ C. Ouannes and T. Wilson, *J. Amer. Chem. Soc.*, 1969, **90**, 6527.

² (a) K. Furukawa and E. A. Ogryzlo, *Chem. Phys. Letters*, 1971, **12**, 370; (b) E. A. Ogryzlo and C. W. Tang, *J. Amer. Chem. Soc.*, 1970, **92**, 5034; K. Furukawa, E. W. Gray, and E. A. Ogryzlo, *Ann. New York Acad. Sci.*, 1970, **171**, 175; (c) I. B. C. Matheson and J. Lee, *Chem. Phys. Letters*, 1970, **7**, 475; G. A. Hollinden and R. B. Timmons, *J. Amer. Chem. Soc.*, 1970, **92**, 4181; (d) W. S. Gleason, A. D. Broadbent, E. Whittle, and J. N. Pitts, *J. Amer. Chem. Soc.*, 1970, **92**, 2068; (e) I. B. C. Matheson and J. Lee, *J. Amer. Chem. Soc.*, 1972, **94**, 3310; *Chem. Phys. Letters*, 1972, **14**, 350; (f) C. S. Foote, R. W. Denney, L. Weaver, G. Chan, and J. Peters, *Ann. New York Acad. Sci.*, 1970, **171**, 139; R. H. Young and R. L. Martin, *J. Amer. Chem. Soc.*, 1972, **94**, 5183.

relatively large amounts of the compounds had been utilised. Table 1 shows that the protective action of the



amino-group is extremely efficient. In fact, the efficiency is much greater than one would anticipate from

and 1,4-diazabicyclo[2,2,2]octane in protecting compounds (7), (9), and (10) towards photo-oxidation, with the protective action of the amino-groups in compounds (2), (4), and (6). The results (Table 2) show that the intramolecular quenching is more effective than intermolecular quenching.

The question remains as to why intramolecular quenching is so effective. One possible explanation is that the amino-compounds quench the triplet state of the sensitizers and consequently inhibit singlet oxygen production. Table 2 shows that this cannot be an important contributing process, since hydrocarbons such as anthracene, and compounds (7)—(9), still suffer appreciable oxidation when either triethylamine or 1,4-diazabicyclo[2,2,2]octane is present. Since these amines were present in the same concentration as the amino-compounds (2)—(6), they should have led to as much quenching of singlet oxygen production as compounds (2)—(6) and therefore should have afforded much greater protection than was observed. It therefore seems that

TABLE 1

Comparison of the rates of photo-oxidation (sensitised by Methylene Blue) of some amines with those of related compounds which lack an amino-substituent

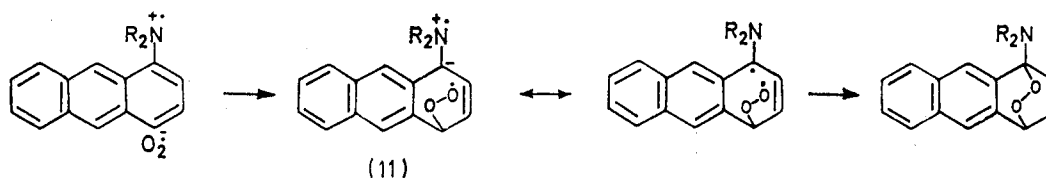
Amine	Control	Irradiation time (h)	Amount amine used (%)	Amount control used (%)
(2)	(7)	16	11	68
(3)	(8)	3	ca. 0	ca. 100
(4)	(9)	0.25	ca. 0	ca. 100
(5)	(9)	3	56	
(6)	(10)	3	36	
		2	ca. 0	ca. 100

a consideration of the relevant rate constants. The relative efficiency of inter- and intra-molecular quenching of singlet oxygen by amino-groups was therefore assessed by comparing the effectiveness of triethylamine

the amino-groups in compounds (2)—(6) are acting as quenchers of singlet oxygen and in doing so protect the olefinic systems from oxidation. Their effectiveness must be due to their proximity to the olefinic systems.

It is possible that the amino-groups can interact with the singlet oxygen even when attack on the olefinic system is under way. If this were not the case, one would have expected the protective action to be related to the rate constants for reaction of the amines and olefinic systems with singlet oxygen.

That the amino-groups in compounds (2)—(6) act as protecting groups apparently contradicts the previous finding that 1-aminoanthracenes¹¹ and enamines¹² are very reactive towards singlet oxygen. The reactivity of



these systems may well be due either to the amino-group enhancing the susceptibility of the olefinic system towards electrophilic attack by means of the mesomeric effect or to the amino-group undergoing some charge-transfer reaction with the oxygen which ultimately leads to reaction. The interaction may be visualised as occurring *via* an intermediate such as (11). When there is an insulating methylene group between the amino-group and the olefinic system, smooth electron flow

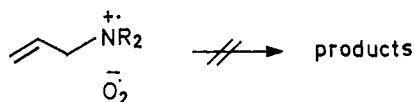
TABLE 2

Comparison of the effectiveness of tertiary amino-groups in stabilising compounds towards photo-oxidation, by inter- and intra-molecular quenching of singlet oxygen

Amine	Hydrocarbon or substituted hydrocarbon	Irradiation time (h)	Amount of hydrocarbon or substituted hydrocarbon used (%)
Triethylamine	Anthracene	4	73
DABCO	Anthracene	4	65
	(6)	4	0
Triethylamine	2-Methylfuran	1	90
DABCO	2-Methylfuran	1	85
	(4)	1	~10
Triethylamine	3,7-Dimethyloct-6-en-1-ol	5	78
DABCO	3,7-Dimethyloct-6-en-1-ol	5	70
	(2)	5	5
(4)	2-Methylfuran	0.16	80
	2-Methylfuran	0.16	85

[Sensitiser (Methylene Blue)] = $5 \times 10^{-4}M$; [hydrocarbon] and [amine quencher] $5 \times 10^{-2}M$.

which leads to product formation cannot take place and consequently quenching occurs.



¹¹ J. Rigaudy, A. Defoin, and N. K. Cuong, *Compt. rend.*, 1970, **271C**, 1258.

¹² C. S. Foote and J. W. Lin, *Tetrahedron Letters*, 1968, 3267; J. E. Huber, *ibid.*, p. 3271; K. Pfoertner and K. Bernauer, *Helv. Chim. Acta*, 1968, **51**, 1787.

From previous reports,^{5,6} it was anticipated that the amino-groups in compounds (2)—(6) would suffer oxidation on prolonged irradiation. In the case of compounds (2)—(4) and (6) the expected oxidation product, acetaldehyde, was not detected. We attribute the stability of the amino-groups to the concentration of the amines being kept relatively low ($\sim 5 \times 10^{-2} \text{ mol l}^{-1}$), and also to the fact that the rate constants for reactions of triplet thionine dyes with amines fall in the range 10^8 — $10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.¹³

The amines (1)—(6) were prepared by the following reaction sequences:

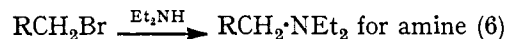
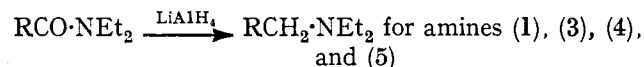


Photo-oxidation of the alcohol (8) was found to give the ester (12).



EXPERIMENTAL

Spectra.—¹H N.m.r. spectra were recorded for solutions in deuteriochloroform (with tetramethylsilane as internal standard) with a Varian T60 spectrometer. Mass spectra were determined with an A.E.I. MS9 instrument. I.r. spectra, for samples in Nujol, were obtained with a Perkin-Elmer 257 spectrophotometer.

G.l.c. Analysis.—Analyses were carried out with a Pye-Unicam series 104 gas chromatograph equipped with a flame ionisation detector. The detector gave a linear response over the whole range of concentrations used. Quantitative estimation of materials was carried out by comparing the area of the elution peak for the material with that for a solution, of known concentration, of the same material. Reproducibility was within $\pm 5\%$. 2-Methylfuran, *NN*-dimethylfurfurylamine, *N*-phenylfurfurylamine, 3,7-dimethyloct-6-en-1-ol, and *NN*-diethyl-3,7-dimethyloct-6-enylamine were determined by use of a glass column (5 ft \times $\frac{1}{4}$ in) containing 10% Apiezon L on 100—120 mesh acid-washed Diatomite C at 55, 120, 150, 200, and 200°, respectively.

3-(Anthracen-9-yl)-*NN*-diethylpropylamine (1).—A mix-

¹³ R. Bonneau and J. Jousot-Dubien, Lecture given at the International Symposium on the Organic Chemistry of the Excited State, Reading, 1972.

ture of 9-anthraldehyde (6 g), malonic acid (3.8 g), pyridine (15 ml), and piperidine (0.1 ml) was heated at 100° for 3 h, then at 180—190° for 30 min. The cool mixture was poured, with vigorous stirring, into cold 2*N*-hydrochloric acid (100 ml). The product crystallised out and was filtered off to give 3-(anthracen-9-yl)acrylic acid (yellow needles) (3.0 g), m.p. 244—245° (lit.,¹⁴ 246—247°).

A solution of this acid (3.0 g) in ethanol (100 ml) containing palladium-charcoal (10%; 1.0 g) was stirred under hydrogen for 3 h (uptake 1 mol. equiv.). Filtration and evaporation left a white solid, 3-(anthracen-9-yl)propionic acid (2.5 g), m.p. 192—193° (from ethanol) (lit.,¹⁵ 191—192°). The acid (2.5 g) was heated under reflux with benzene (20 ml) containing thionyl chloride (5 ml). Removal of the solvent and excess of thionyl chloride by evaporation under reduced pressure gave the crude acid chloride (2.6 g), ν_{\max} 1785 cm⁻¹. To a solution of the acid chloride (2.6 g) in benzene (10 ml), diethylamine (5 ml) was added with stirring. After 20 h the solution was extracted with 2*N*-sulphuric acid (2 × 25 ml) and water (1 × 25 ml). The benzene solution was dried (Na₂SO₄) and evaporated to give 3-(anthracen-9-yl)-*NN*-diethylpropionamide, m.p. 252—254° (from benzene), ν_{\max} 1645 cm⁻¹, τ 2.0 (9H, m, aromatic), 6.0 (4H, m), 7.2 (4H, q, CH₂·CH₃), and 9.1 (6H, t, CH₂·CH₃).

To a stirred ethereal (100 ml) suspension of lithium aluminium hydride (0.3 g) was slowly added the amide (2.0 g) dissolved in ether (50 ml). After stirring at 20° for 2 h, water was cautiously added to destroy the excess of hydride. The ethereal layer was separated and washed with water (2 × 20 ml), dried, and evaporated. The crude amine was distilled (b.p. 93—97° at 0.001 mmHg) to give a pale yellow oil (1.5 g), τ 2.6 (9H, m, aromatic), 3.2 (4H, m), 7.7 (4H, q, CH₂·CH₃), 8.3 (2H, m), and 9.2 (6H, t, CH₂·CH₃); *methiodide*, m.p. 192—193° (aqueous ethanol) (Found: C, 60.7; H, 6.5; N, 3.35. C₂₂H₂₈N requires C, 60.95; H, 6.45; 3.25%).

NN-Diethyl-3,7-dimethyloct-6-enylamine (3).—To a stirred solution of 3,7-dimethyloct-6-en-1-ol (citronellol) (10.7 g) in benzene (100 ml) was added pyridine (5.94 g), followed by toluene-*p*-sulphonyl chloride (14.3 g). The mixture, under nitrogen was stirred at 15° for 15 h, during which time a white precipitate formed. The mixture was cooled to 0° and water (10 ml) was added slowly. The benzene layer was separated, washed with 2*N*-hydrochloric acid (2 × 15 ml) and water (1 × 15 ml), dried (Na₂SO₄), and evaporated to give the crude tosylate (12.0 g) ν_{\max} (film) 1170 and 1190 cm⁻¹, τ 2.1 (2H, m), 2.6 (2H, m), 6.2 (2H, t), 7.6 (3H, s), 8.15 (6H, d), and 9.0 (3H, d).

A solution of the crude tosylate (6 g) in diethylamine (20 ml) was heated, under nitrogen, under reflux for 15 h. A yellow precipitate was formed. The excess of diethylamine was removed by evaporation under reduced pressure. Ether (25 ml) was added and the ethereal solution was washed with 2*N*-hydrochloric acid (1 × 10, 1 × 5 ml). The acid washings were made basic with 2*N*-sodium hydroxide and extracted with ether (2 × 25 ml). The ethereal layer was washed with water (1 × 10 ml), dried (Na₂SO₄), and evaporated to give the crude amine (3.2 g), which was distilled to give pure material, b.p. 58° at 0.5 mmHg (Found: C, 79.75; H, 13.65; N, 6.7. C₁₄H₂₈N

requires C, 79.75; H, 13.75; N, 6.65%), τ 4.8 (t, *J* 8 Hz, olefinic H), and 7.4 (q, *J* 8 Hz, CH₂Me), 8.34 (s) and 8.38 (s) (Me₂C=C), and 8.95 (t, *J* 8 Hz, CH₂Me) all superimposed on a broad multiplet; *m/e* 211 (M⁺), 196, 126, and 86.

5-Diethylaminomethyl-3,4-dihydro-6-phenyl-2*H*-pyran (3).—3,4-Dihydro-6-phenyl-2*H*-pyran-5-carboxylic acid (500 mg) was heated under reflux with oxalyl chloride (600 mg) and benzene (2 ml) for 1.5 h. All volatile material was removed under vacuum at room temperature and the residue was dissolved in ether (5 ml) and treated dropwise with diethylamine (3 ml). After stirring for 30 min at room temperature, the mixture was diluted with ether, washed successively with cold hydrochloric acid (2*N*), sodium hydroxide (2*N*), and water, dried, and evaporated. The crude product was chromatographed over Kieselgel (benzene-ethyl acetate, 1:1) to give the diethylamide (385 mg, 60%) as a viscous oil, ν_{\max} 1642 and 1614 cm⁻¹, τ (CDCl₃) 9.24 and 9.04 (2 × CH₃·CH₂, 2 overlapping t, *J* 7 Hz), 8.25—7.75 (2 × H-3, m), 7.54 (2 × H-4, t, *J* 6 Hz), 6.88 and 6.64 (2 × CH₃·CH₂, 2 overlapping q, *J* 7 Hz), 5.75 (2 × H-2, t, *J* 5 Hz), and 2.75—2.13 (5 × ArH, m).

The oily amide (350 mg) was reduced with excess of lithium aluminium hydride in ether under reflux for 3 h. After distillation (bulb-tube; b.p. 157—165° at 1 mmHg), the amine (3) was obtained as a mobile oil (249 mg, 75%) (Found: C, 78.0; H, 9.1; N, 6.0. C₁₆H₂₃N requires C, 78.3; H, 9.45; N, 5.7%), ν_{\max} (film) 1656 cm⁻¹, τ (CCl₄) 9.12 (2 × CH₃·CH₂, t, *J* 7 Hz), 8.3—7.35 (2 × H-3, 2 × H-4, 2 × CH₃·CH₂, m), 7.03 (Et₂N·CH₂, s), 5.95 (2 × H-2, t, *J* 6 Hz), and 2.74 (5 × ArH, s).

NN-Diethylfurfurylamine (4).—A mixture of 2-furoic acid (9 g) and thionyl chloride (18 ml) was heated under reflux for 2 h. Excess of thionyl chloride was evaporated off under reduced pressure to give crude 2-furoyl chloride (11.1 g), ν_{\max} 1780 cm⁻¹. Diethylamine (20 ml) was added drop by drop to the crude acid chloride and the mixture so obtained was stirred at 15° for 14 h. The excess of amine was distilled off and the residue extracted with ether (2 × 25 ml). The extract was washed with 2*N*-hydrochloric acid (2 × 25 ml) and water (1 × 25 ml), dried (Na₂SO₄), and evaporated to give the crude *NN*-diethyl-2-furamide as an oil,¹⁶ ν_{\max} 1620 cm⁻¹, τ 2.42 (1H, d), 2.9 (1H, d), 3.45 (1H, dd), 6.4 (4H, q), and 8.7 (6H, t).

The crude amide (6.2 g) in ether (50 ml) was slowly added to a stirred ethereal solution (100 ml) of lithium aluminium hydride (2.5 g). The mixture was stirred for 2 h at 15° and then water was cautiously added to destroy the excess of hydride. The ether layer was separated, dried (Na₂SO₄), and evaporated to give the crude *NN*-diethylfurfurylamine (4.5 g). Redistillation (b.p. 70—72° at 0.5 mmHg) gave a clear liquid, τ 2.65 (1H, d), 3.65 (1H, dd), 3.80 (1H, d), 6.3 (2H, s), 7.45 (4H, q), and 8.95 (6H, t); *methiodide*, m.p. 118—119° (aqueous ethanol) (Found: C, 40.6; H, 6.15; N, 4.75. C₁₀H₁₈INO requires C, 40.7; H, 6.1; N, 4.75%).

N-Phenylfurfurylamine (5).—*N*-Methylaniline (10 ml) was added drop by drop to crude 2-furoyl chloride (5 g); the mixture was stirred at 15° for 14 h, then extracted with ether (50 ml). The extract was washed with 2*N*-sulphuric acid (2 × 50 ml) and water and evaporated to give the crude amide as an oil, ν_{\max} 1618 cm⁻¹, τ 2.5 (7H, m), 5.32 (1H, dd), and 5.9br (1H, s, collapsed on addition of D₂O). The crude amide (4 g) was reduced with lithium aluminium

¹⁴ C. H. Davis and M. Carmack, *J. Org. Chem.*, 1947, **12**, 76.

¹⁵ J. W. Cook and R. S. Ludwuzak, *J. Chem. Soc.*, 1950, 1112.

¹⁶ J. R. Willard and C. S. Hamilton, *J. Amer. Chem. Soc.*, 1951, **73**, 4805.

hydride (1.2 g) in the usual way to give *N*-phenyl-2-furfurylamine as a liquid, b.p. 85–88° at 0.5 mmHg (lit.,¹⁷ 152–156° at 16 mmHg), τ 3.0 (6H, m), 3.8 (2H, m), 5.7 (2H, s), and 6.3br (1H, s, collapsed on addition of D₂O).

NN-Diethylantracene-9-ylmethylamine (6).—A mixture of 9-methylantracene (0.5 g) and *N*-bromosuccinimide (0.4 g) in carbon tetrachloride (50 ml) was heated under reflux for 30 min, then cooled. The precipitated succinimide was filtered off and the filtrate was evaporated to leave crude 9-bromomethylantracene (0.5 g). To the crude bromo-compound, diethylamine (5 ml) was added. The mixture was heated under reflux for 14 h. Excess of diethylamine was evaporated off and the residue was dissolved in 2*N*-sulphuric acid (50 ml) and extracted with ether (2 × 50 ml). The acidic solution was made basic with 2*N*-sodium hydroxide and then extracted with ether (2 × 25 ml). The ethereal extracts were dried (Na₂SO₄) and evaporated to give the crude amine, purified by distillation under reduced pressure (b.p. 75–80° at 0.001 mmHg) to give a pale yellow solid, m.p. 101–102°, τ 2.0 (9H, m, aromatic), 4.55 (2H, s, benzylic CH₂), 7.4 (4H, q, CH₂·CH₃), and 9.0 (6H, t, CH₂·CH₃); *methiodide*, m.p. 172–173° (aqueous ethanol) (Found: C, 59.0; H, 5.9; N, 5.45. C₂₀H₂₄IN requires C, 59.25; H, 5.95; N, 5.4%).

3,4-Dihydro-5-hydroxymethyl-6-phenyl-2H-pyran (8).—Ethyl 3,4-dihydro-6-phenyl-2*H*-pyran-5-carboxylate was prepared¹⁸ from ethyl benzoylacetate (43 g) and dibromopropane (45 g) in only 11% yield after crystallisation from ether. After evaporation of ether, the residue was heated under reflux for 3 h with excess of sodium hydroxide (2*N*) containing ethanol (5%). The basic solution was cooled and extracted with ether (the extract was discarded) and then acidified. Crystallisation of the solid obtained gave 3,4-dihydro-6-phenyl-2*H*-pyran-5-carboxylic acid (12) (13 g, 29%), m.p. 138–140° (lit.,¹⁸ 142–144°).

Reduction of either the acid or the foregoing ester with excess of lithium aluminium hydride in ether under reflux for 3 h gave the dihydroxyran as an acid-sensitive oil. It decomposed upon attempted distillation. Traces of a polar impurity visible on t.l.c. (alumina) were removed by chromatography over alumina but the i.r. spectrum remained unchanged: ν_{\max} (film) 3330br and 1656m cm⁻¹, τ (CCl₄) 8.4–7.6 (2 × H-3, 2 × H-4, m), 6.53 (OH, s), 6.3–5.9 (2 × H-2, m), 6.06 (CH₂·OH, s), and 2.9–2.5 (5 × ArH, m).

Photo-oxidation of 3,4-Dihydro-5-hydroxymethyl-6-phenyl-2H-pyran (8).—The dihydroxyran (300 mg) was dissolved in methanol (40 ml) together with Methylene Blue (4 mg) and photo-oxidised by use of a tungsten bulb (150 W) at 0.5 cm from a 20 × 3 cm test-tube equipped with oxygen

bubbler (sintered disc), internal cooling coil, and magnetic stirrer. The reaction was monitored by observing the disappearance of the i.r. band at 1656 cm⁻¹ in withdrawn samples. After 5.5 h the solvent was evaporated off and the residue chromatographed over Kieselgel (benzene–ethyl acetate, 1 : 1). Combination of those fractions showing a single spot at *R_F* 0.3 (t.l.c. silica; benzene–ethyl acetate, 3 : 1) gave *5-hydroxy-4-oxopentyl benzoate* (12) (175 mg, 50%) as needles (from chloroform–light petroleum), m.p. 53–54° (Found: C, 64.95; H, 6.2. C₁₂H₁₄O₄ requires C, 64.85; H, 6.35%), ν_{\max} (Nujol) 3430, 3385, and 1718br cm⁻¹, τ (CDCl₃) 8.0–7.2 (2 × H-3, 2 × H-4, m), 6.82br (OH, s), 5.70 (CH₂·OH, s), 5.61 (2 × H-2, t, *J* 7 Hz), and 2.7–2.3 and 2.0–1.8 (5 × ArH, m).

Irradiation Procedure.—In all cases the volume of methanolic solutions irradiated was 25 ml and all solutions were 5 × 10⁻²M in the substrate and 5 × 10⁻⁴M in Methylene Blue. The solutions were contained in 1 cm diam. Pyrex tubes and were continually flushed by a stream of oxygen throughout the irradiation period. Irradiation was carried out by means of eight 25 W 'daylight' fluorescent lamps which were arranged in a circular bank around the solution. In the case of the reactions reported in Table 1, irradiation of the amine and the control was carried out simultaneously. Duplicate runs were made and the results were reproducible. For the comparison runs shown in Table 2, the reaction mixture containing triethylamine and the hydrocarbon, the one containing 1,4-diazabicyclo[2,2,2]octane and the hydrocarbon, and the one containing the amine were irradiated simultaneously. Under these conditions, duplicate runs gave consistent results.

Analysis of Reaction Mixtures.—The amounts of the amines (2) and (4) and compounds (7) and (9) utilised in reactions were estimated by g.l.c. analysis. In the case of the amine (3) and the alcohol (8) the amount of material oxidised could be estimated by i.r. spectroscopy since the oxidation products had a band at 1650 cm⁻¹. As a further check, in the case of the amine, the reaction mixture was chromatographed and the amine isolated. The amounts of anthracene compounds (6) and (10) utilised were determined by u.v. spectroscopy.

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