Reduction of Nitro- and Nitroso-compounds by Tervalent Phosphorus Reagents. Part X.[1] Ring Expansion to give 2-Diethylamino-3*H*-azepines

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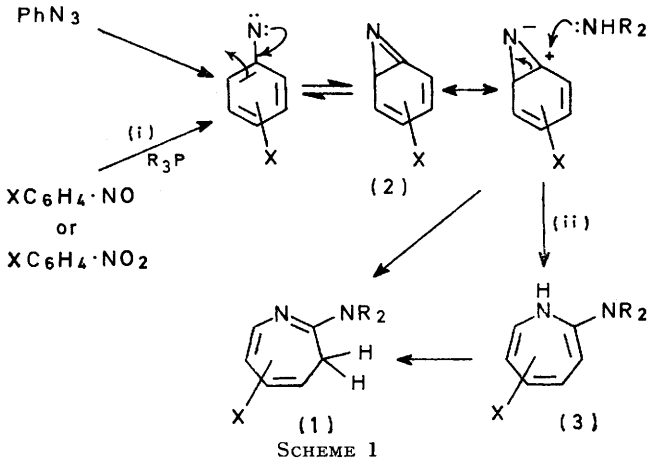
Reactions of tervalent phosphorus reagents [$(EtO)_2PMe$, Ph_2POEt] with nitroarenes ($XC_6H_4{\cdot}NO_2$; X = H, *o*-, *m*-, or *p*-Me, *m*- or *p*-CO_2Et, *m*- or *p*-Cl, *m*- or *p*-Br, *m*-MeO, or 2.4.6-Me_3) in diethylamine give 2-diethylamino-3*H*-azepines in 36—78% yields, together with smaller amounts of the corresponding anilines. *m*-Nitroarenes give mixtures of 4- and 6-substituted 2-diethylamino-3*H*-azepines, the isomeric compositions of which are identical, within experimental error, with those obtained by photolysis, in Pyrex, of the corresponding *m*-substituted aryl azides in diethylamine, thus providing strong confirmatory evidence for the existence of a common intermediate, the 7-azabicyclo[4.1.0]heptatriene (2), in equilibrium with the arylnitrene, in these reactions. In the above reactions of diethyl methylphosphonite with nitroarenes, the ratio of 3*H*-azepine to aniline produced varies with substituent. Reactions of *m*- and *p*-chloronitrobenzenes with tris(diethylamino)phosphine in t-butyl alcohol gave the corresponding 2-diethylamino-3*H*-azepines.

In the photoconversion of aryl azides into 3*H*-azepines, benzophenone enhances the formation of anilines, the triplet-derived products, but pyrene does not exhibit noticeable singlet sensitiser behaviour, in contrast to previously reported results obtained from related systems.

THE ring expansion which occurs on thermolysis or photolysis of aryl azides in amines to give 2-amino-3*H*-azepines (1) is well known,[2-4] and is generally believed to occur *via* nucleophilic attack on an intermediate 7-azabicyclo[4.1.0]heptatriene (2) (Scheme 1), assumed

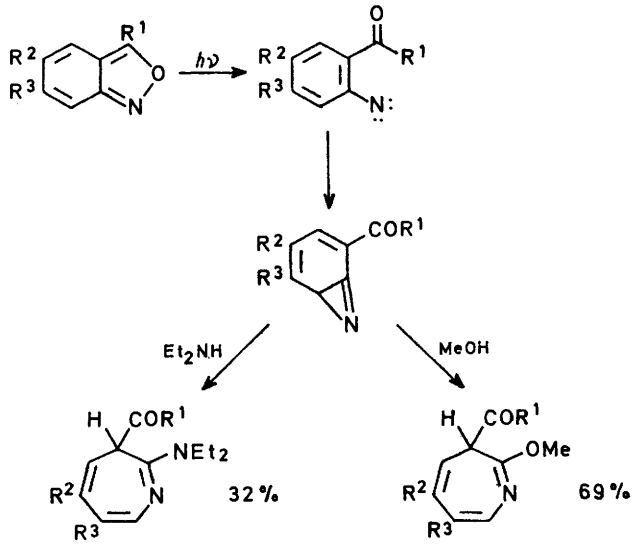


SCHEME 1

to be in equilibrium with a first-formed arylnitrene.[2,3] Using this concept elegantly, Odum and Brenner [5] took the isolation of 2-dialkylamino-3*H*-azepines from reactions of nitrosobenzene with triphenylphosphine in dialkylamines [Scheme 1, reaction (i)] to support the postulate [6] that phenylnitrene was an intermediate in the deoxygenation of nitrosobenzene by triphenylphosphine. Soon after,[7] deoxygenation of nitrobenzene and 2-nitrobiphenyl in diethylamine by diethyl methylphosphonite, which was sufficiently reactive at the boiling point of the amine, was shown to give the corresponding 2-diethylamino-3*H*-azepines.

A refinement of mechanism was later introduced by Sundberg *et al.*[8] who produced good evidence for the intermediacy of a 1*H*-azepine (3; X = 3-alkyl) as a precursor to the ultimately obtained 3*H*-azepine in photolysis of *o*-azides in the presence of diethylamine [Scheme 1, reaction (ii)].

Few reports of ring-expansion reactions under the influence of other nucleophiles have been reported: thermolysis of phenyl azide in the presence of hydrogen sulphide gave a small amount only of the 3*H*-azepine



SCHEME 2

(5%),[3] and photolysis of anthranils in methanol gave 3-acyl-2-methoxy-3*H*-azepines (Scheme 2).[9] Photolysis

[1] Part IX, J. I. G. Cadogan and S. Kulik, *J. Chem. Soc.* (*C*), 1971, 2621.

[2] R. Huisgen, D. Vossins, and M. Appl, (*a*) *Angew. Chem.*, 1955, **23**, 756; (*b*) *Ber.*, 1958, **91**, 1; (*c*) R. Huisgen and M. Appl, *ibid.*, 1958, **91**, 12.

[3] R. A. Odum and W. von Doering, *Tetrahedron*, 1966 **22**, 81.

[4] R. A. Odum and A. M. Aaronson, *J. Amer. Chem. Soc.*, 1969, **91**, 5680.

[5] R. A. Odum and M. Brenner, *J. Amer. Chem. Soc.*, 1966, **88**, 2074.

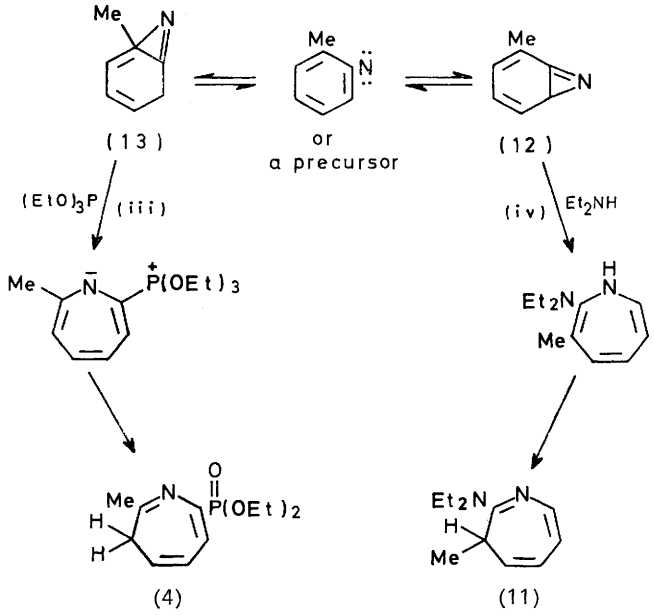
[6] P. J. Bunyan and J. I. G. Cadogan, *Proc. Chem. Soc.*, 1962, 78.

[7] J. I. G. Cadogan and M. J. Todd, *Chem. Comm.*, 1967, 178; *J. Chem. Soc.* (*C*), 1969, 2808.

[8] R. J. Sundberg, S. R. Suter, and M. Brenner, *J. Amer. Chem. Soc.*, 1972, **94**, 513.

[9] M. Ogata, H. Kano, and H. Matsumoto, *Chem. Comm.*, 1968, 397; M. Ogata and H. Matsumoto, *Tetrahedron*, 1969, **25**, 5205.

of phenyl azide in methanol similarly gave 2-methoxy-3*H*-azepine (11%).[10] In contrast, the reaction of nitroarenes, such as *o*-nitrotoluene with an excess of triethyl phosphite led to a different pattern of nucleophilic substitution, giving, for example, diethyl 2-methyl-3*H*-azepin-7-ylphosphonate (4) [Scheme 3, reaction (iii)].[11]



SCHEME 3

In an attempt to explain these anomalies and to gain greater insight into the mechanism of such ring expansion reactions, we carried out an investigation of effects of differing aryl substituents on the distribution of products from deoxygenation of nitroarenes and from photolysis of the corresponding aryl azides. After this work was completed a complementary report of deoxygenation of a series of nitroarenes in the presence of amines was published.[12]

DISCUSSION

Deoxygenation of Nitroarenes by Tervalent Phosphorus Reagents (3—6 *mol. equiv.*) *in the Presence of Diethylamine* (ca. 70 *mol. equiv.*) *at* 56°.—(i) Products of these reactions are summarised in Table 1. In general, the major products were 2-diethylamino-3*H*-azepines, which were isolated by chromatography and distillation; their purity was checked by g.l.c., mass spectra, and elemental analysis, and their structures were determined by n.m.r. spectroscopy (see Experimental section). In addition, various amounts of the corresponding anilines were formed.

(ii) *The question of nitrene participation. Reactions with* m-*nitroarenes.* Since the ring expansion of aryl azides to 3*H*-azepines by thermolysis in diethylamine is generally held to involve arylnitrenes, in equilibrium with azabicycloheptatrienes, the isolation of such 3*H*-azepines from deoxygenation of nitro-compounds by tervalent phosphorus reagents in diethylamine has been assumed to point to nitrene participation.[5,7] We now present what we believe to be the strongest evidence yet that the intermediates produced from *m*-substituted azido- or nitro-arenes based on identity of the isomeric composition of pairs of 3*H*-azepines, are the same.

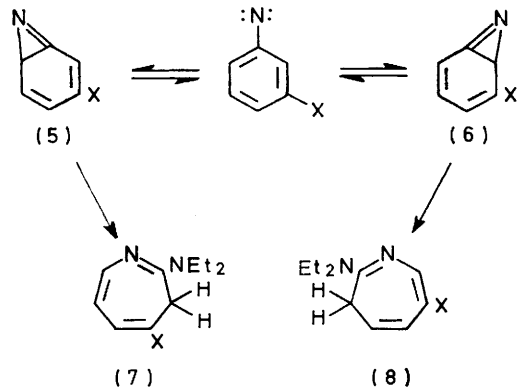
TABLE 1

2-Diethylamino-3*H*-azepines from $XC_6H_4{\cdot}NO_2$ + $(EtO)_2PMe$ + Et_2NH *

	2-Diethylamino-3*H*-azepines (%)			
X	4-X	6-X	5-X	3-X
H †	79			
o-Me †				35·5
m-Me	38·5	31·5		
m-Me †	46	27		
m-MeO	73	13		
m-Cl	18	56		
m-Br	7	37		
m-CO_2Et	17	55		
p-Me			74	
p-Cl			78	
p-Br			35·5	
p-CO_2Et			67	

* When X = *o*-Cl, *o*-CN, or *p*-CN, no azepines were detected. When X = 2,4,6-Me_3, 2-diethylamino-3,5,7-trimethyl-3*H*-azepine (60%) was obtained. † $EtOPPh_2$ was used.

In theory *m*-substituted aryl nitrenes may ring close in either of two directions to give two isomeric azabicycloheptatrienes, (5) and (6) (Scheme 4), each of



SCHEME 4

which may react with diethylamine to give 4- and 6-substituted 2-diethylamine-3*H*-azepines, (7) and (8). In the presence of pyrene, which it has been suggested is a singlet sensitiser,[13] photolysis at 56·5° of *m*-chloro-, *m*-bromo-, *m*-methoxy-, and *m*-methyl-phenyl azides, with a Pyrex filter, led to good yields of mixtures of both 3*H*-azepines (7) and (8), isomeric compositions of which are given in Table 2. Thermal deoxygenations of the corresponding nitro-compounds at 56·5° in

[10] R. J. Sundberg and R. H. Smith, *J. Org. Chem.*, 1971, **36**, 295.

[11] J. I. G. Cadogan, R. K. Mackie, and M. J. Todd, *Chem. Comm.*, 1968, 736; J. I. G. Cadogan, D. J. Sears, D. M. Smith, and M. J. Todd, *J. Chem. Soc.* (*C*), 1969, 2813.

[12] F. R. Atherton and R. W. Lambert, *J.C.S. Perkin I*, 1973, 1079.

[13] J. S. Swenton, *Tetrahedron Letters*, 1968, 3421; J. S. Swenton, T. J. Ikeler, and B. H. Williams, *J. Amer. Chem. Soc.*, 1970, **92**, 3103.

diethylamine also gave good yields of the same mixtures of 3*H*-azepines (7) and (8), the isomeric compositions of which (Table 2) are identical, within experimental error, with those obtained from photolysis of aryl azides. The ratios of isomers were obtained by quantitative g.l.c. analysis and differ quantitatively, but not qualitatively, from those recently obtained from a similar system by a more qualitative method based on crystallisation of oxalate derivatives.[12]

The observed ratios of isomers (Table 2) show that

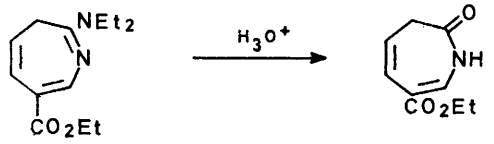
TABLE 2

Isomer ratios of 3*H*-azepines from (A) *m*-$XC_6H_4{\cdot}N_3$ photolysis, (B) *m*-$XC_6H_4{\cdot}NO_2$–$(EtO)_2PMe$

	4-X		6-X	
X	(A)	(B)	(A)	(B)
Cl	30	24	70	70
Br	10	10	90	90
Me	52	55	48	45
MeO	81	84	19	16
CO_2Et		24		76

electron-withdrawing *m*-substituents (Cl, Br, or CO_2Et) favour intramolecular cyclisation of the nitrene at the *ortho*-position to give, ultimately, (8) *via* (6), while *m*-methyl is almost indiscriminate in its effect and the strongly electron-repelling *m*-methoxy-group favours cyclisation at the *para*-position [*i.e.* to give (7) *via* (5)]. Clearly the ratios cannot be explained in terms of the polarity of the substituents alone, indicating that other competing factors in this complex equilibrating system are involved.

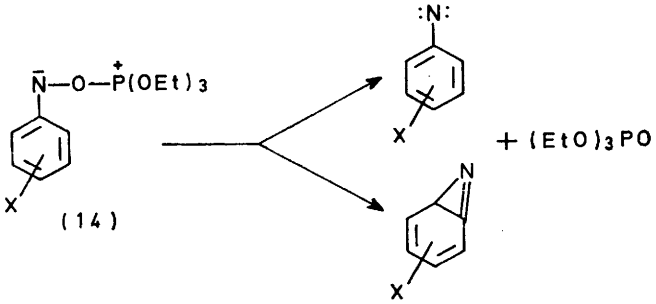
The 3*H*-azepines produced in this investigation were stable on alumina under the conditions used, with the exception of ethyl 2-diethylamino-3*H*-azepine-6-carboxylate (9) isolated from the reaction of ethyl *m*-nitrobenzoate. This was hydrolysed, on prolonged treatment with alumina, to give the 1,3-dihydroazepin-2-one (10), recalling the previously reported conversions of 3*H*-azepines into 1,3-dihydroazepin-2-ones on prolonged hydrolysis.[9,12]



(9) (10)

These results, summarised in Table 2, strongly support the concept that deoxygenation of these simple nitrocompounds by phosphonite in diethylamine leads to intermediates identical with those produced by photolysis of the corresponding azides, also in diethylamine. As a result of what is known about the latter reaction, this intermediate is considered to be the azabicycloheptatriene (2), in equilibrium with free nitrene. These experiments do not tell us anything about the nature of the original deoxygenation; this could proceed *via* a nitrenoid species (14) (Scheme 5) which could then decompose to give a free nitrene or, in a concerted fashion, to give the azabicycloheptatriene partner of the nitrene.

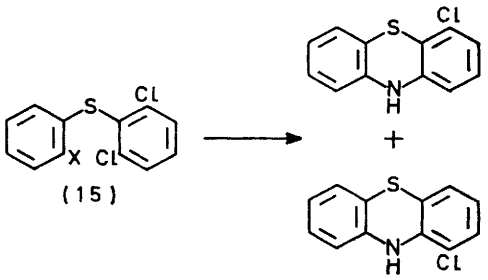
In general the choice between reaction *via* a nitrene or *via* a nitrenoid species (14) would be expected to



(14)

SCHEME 5

depend very much on molecular circumstances, particularly if the possibility exists of intramolecular reaction with an adjacent grouping or ring. In the case of certain diaryl sulphides (Scheme 6), decomposition of the



(15)

SCHEME 6

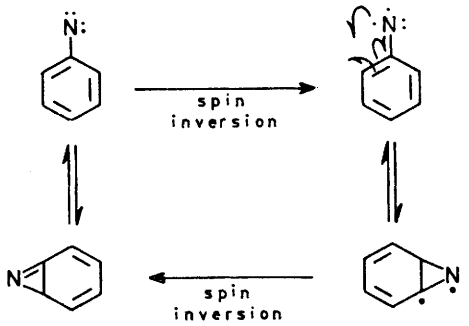
azide (15; X = N_3) gives different ratios of products from phosphite deoxygenation of (15; X = NO_2). This is attributed to preferential reaction of the nitrenoid [15; X = $\bar{N}$–O–$\overset{+}{P}(OEt)_3$] with the adjacent ring before its collapse to the nitrene, a result confirmed and extended recently by Holliman and his co-workers.[14] In the present instance no such adjacent ring is available for attack and the ultimate product depends only on the intermediacy of the azabicycloheptatriene and not on its mode of formation.

(iii) *Reactions with* p- *and* o-*nitroarenes*. *p*-Nitroarenes, with tervalent phosphorus reagents in an excess of diethylamine, gave 5-substituted 2-diethylamino-3*H*-azepines in good yields (Table 1: 36—76%). Reactions of the corresponding *ortho*-isomers gave tarry products but no azepines, except in the case of *o*-nitrotoluene, which gave 2-diethylamino-3-methyl-3*H*-azepine (36%) [Scheme 3, reaction (iv)], but no azepine corresponding to the alternative cyclisation. This is noteworthy because the corresponding reaction with triethyl phosphite as nucleophile as well as deoxygenating agent gave diethyl 2-methyl-3*H*-azepin-7-ylphosphonate (4). These results point to reaction as in Scheme 3 wherein the first formed nitrene, or its precursor, can form two

[14] P. K. Brooke, R. B. Herbert, and E. G. Holliman, *Tetrahedron Letters*, 1973, 761.

possible azabicyclic intermediates, (13) and (12), in equilibrium. Of these, the latter would be expected to predominate on steric grounds, and in the presence of a relatively small nucleophile, such as diethylamine, there would be no barrier to reaction to give the observed 2-diethylamino-3-methyl-3*H*-azepine (11). Reaction with the large nucleophile, triethyl phosphite, would be expected to be severely hindered, however, and in this instance reaction with the alternative intermediate (13) could become relatively favoured thus leading to the observed 7-substituted azepine (4).

(iv) *The question of the spin multiplicity of the nitrene.* (a) *In the deoxygenation of nitroarenes.* 3*H*-Azepines and anilines were the two major identified products from the reactions of both aryl azides and nitroarenes.



SCHEME 7

While anilines are generally accepted to be products of triplet arylnitrene there is no *a priori* reason to suppose that the 7-azabicyclo[4.1.0]heptatriene (2), which leads to the 3*H*-azepine, is not formed from both singlet and triplet nitrenes (Scheme 7). At first sight it might appear that the pattern of product produced in the diethyl methylphosphonite deoxygenation of various nitroarenes in diethylamine (Table 3) points to

TABLE 3

Products (%) from $(EtO)_2PMe$–$XC_6H_4{\cdot}NO_2$–Et_2NH

X =	*p*-Me	*p*-MeO	*m*-Cl	*p*-Cl	*p*-Br	*m*-Br
3*H*-Azepine	74	73	70	78	74	44·5
$XC_6H_4{\cdot}NH_2$	Trace	Trace	Trace	Trace	7	45

the predominant participation of a singlet nitrene in the formation of the 3*H*-azepine. Thus, *m*- and/or *p*-methyl, methoxy-, and chloro-substituents all lead to high yields of 3*H*-azepine, and to traces, only, of the corresponding aniline, the typical abstraction product of triplet nitrene. The presence of the 3-bromo-substituent however, leads to a marked suppression of the yield of 3*H*-azepine with a correspondingly large increase in the yield of the bromoanilines. This could be attributed to the well known heavy atom effect [15] of bromo-compounds in promoting intersystem crossing of singlet to triplet nitrenes, were it not for our observation that addition of 1,4-dibromobenzene, which would be expected to lead to a similar heavy atom effect, albeit intermolecular, did not affect the ratio of 3*H*-azepine to aniline produced in the case of *p*-chloronitrobenzene.

(b) *In the photolysis of phenyl azide.* Swenton [13] has shown that in photolysis of *o*-azidobiphenyl, addition of benzophenone increases the yield of triplet-derived products at the expense of singlet products, whereas added pyrene has the reverse effect, and acts as a singlet sensitiser, *in this system.* Following this, our experiments, described above, involving aryl azides in diethylamine, were also carried out in the presence of pyrene, with Pyrex filters, in the belief that this would maximise the yield of 3*H*-azepine, assuming that it was a singlet-derived product. Our control experiments (Table 4) show however that *in our system* pyrene does not clearly act as a singlet sensitiser.

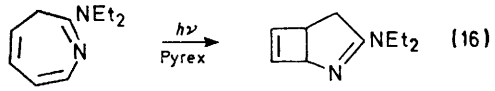
TABLE 4

Photolysis of PhN_3 in Et_2NH *

Sensitiser †	Reaction time (h)	Products (%) $PhNH_2$	3*H*-Azepine	Photo-isomer
None	5	6	32	11
None	18	7	23	25
Pyrene	18	17	49	5
Ph_2CO	18	25	30	7

* PhN_3 (0·56 g) in Et_2NH (150 ml) at room temperature in Pyrex. † 10 g.

First, however, we note that an additional product, identified as the bicyclic photoisomer (16) of 2-diethylamino-3*H*-azepine, was formed. This, isolated by g.l.c., had the expected n.m.r. and mass spectra. Its yield increased, at the expense of 3*H*-azepine, with increased irradiation time. Similar phototransformations of azepines are known [16] and Odum [17] has produced the dimethylamino-analogue of (16) by irradiation of the



parent 3*H*-azepine in hydrocarbons. This photoisomer, for the purpose of the present discussion, is therefore accountable as 3*H*-azepine.

If it is accepted that aniline is derived from triplet phenylnitrene, these results show that benzophenone is acting as a triplet sensitiser and is diverting singlet nitrene to triplet. This is in accord with the known energy levels of the relevant reactants.[18] It can also be said that the azepine is formed, at least partially, from singlet phenylnitrene, the extent of this process depending on the efficiency (unknown) of benzophenone in this system. That pyrene is acting as a singlet sensitiser is not supported, however. If anything it increases the yield of triplet-derived products, which is

[15] W. Lwowski and T. W. Mattingley, *Tetrahedron Letters*, 1962, 277; J. S. McConaghy and W. Lwowski, *J. Amer. Chem. Soc.*, 1967, **89**, 2357; A. G. Anastassiou, *ibid.*, 1966, **88**, 2322; 1967, **89**, 3184.

[16] O. L. Chapman and E. D. Hoganson, *J. Amer. Chem. Soc.*, 1964, **86**, 498; L. A. Paquette, *ibid.*, p. 500; L. A. Paquette and W. C. Farley, *J. Org. Chem.*, 1967, **32**, 2725; L. A. Paquette, *J. Amer. Chem. Soc.*, 1964, **86**, 4092; G. V. Smith and H. Kriloff, *ibid.*, 1963, **85**, 2016.

[17] R. A. Odum, *Chem. Comm.*, 1969, 1299.

[18] F. D. Lewis and W. H. Saunders, *J. Amer. Chem. Soc.*, 1968, **90**, 7033; F. D. Lewis and J. C. Dalton, *ibid.*, 1969, **91**, 5260.

in contrast to the influence of pyrene on the course of photolysis of 2-azidobiphenyl.[13] The only role of pyrene which we can identify is that of a filter, rather than a sensitiser, leading to suppression of the photoisomerisation of the 3*H*-azepine to (16). The results of our experiments do not exclude the possibility, therefore, of the participation of both singlet and triplet phenylnitrene in the formation of 2-diethylamino-3*H*-azepine, in this system.

(v) *Reaction of* m- *and* p-*chloronitrobenzenes with tris-(diethylamino)phosphine* (2 *mol. equiv.*) *in t-butyl alcohol* (40 *mol. equiv.*). These experiments, conceived in an attempt to effect ring expansion under the influence of t-butyl alcohol rather than diethylamine, led to unexpected results. Good yields of 5-chloro-2-diethylamino-3*H*-azepine (54% based on *p*-chloronitrobenzene) and a mixture (81% based on *m*-chloronitrobenzene) of 6- and 4-chloro-2-diethylamino-3*H*-azepines (in the ratio 66 : 34, respectively). These results show that t-butyl alcoholysis of tris(diethylamino)phosphine to give free diethylamine had occurred [$(Et_2N)_3P + Bu^tOH \longrightarrow (Et_2N)_2POBu^t + Et_2NH$ *etc.*], and that even this small amount of diethylamine was sufficient to trap preferentially the intermediate nitrene to give the observed 2-diethylamino-3*H*-azepines. These results parallel those of Sundberg,[10] who found that methanol–diethylamine mixtures in reactions of aryl azides gave exclusively 2-diethylamino- rather than 2-methoxy-3*H*-azepines. Methanol is more effective than diethylamine as an agent for the ring expansion of nitrenes only in the case of *o*-acylnitrenes produced by photolysis of anthranils [9] (Scheme 2) or *o*-azidobenzamides.[19]

EXPERIMENTAL

Reagents.—Trialkyl phosphites, diethyl methylphosphonite, and trisdiethylaminophosphine were purified as described previously.[7] Ethyl diphenylphosphinite, b.p. 110—122° at 0·7 mmHg, was prepared according to Rabonitz and Pellon.[20] Aryl azides were prepared by Smith's method.[21]

Reactions of Nitro-compounds with Tervalent Phosphorus Reagents in Diethylamine.—General procedure. The nitrocompound in diethylamine (*ca.* 70 mol. equiv.) was either boiled under reflux (56·5°) with the tervalent phosphorus reagent (2—5 mol. equiv.) under nitrogen or kept in a bomb at 56·5°, until g.l.c. showed that reaction was complete (*ca.* 4—7 days). Excess of diethylamine was evaporated off and the residue was chromatographed on alumina; the eluate was monitored by g.l.c. and n.m.r. spectroscopy. The fractions containing 2-diethylamino-3*H*-azepines were distilled where necessary and identified by microanalysis, g.l.c., and mass and n.m.r. spectra, all the results of which were within the prescribed limits. The azepines produced are listed in Tables 1 and 3 and their physical and spectral characteristics were entirely as expected.[3,7,11,12,22] The composition of isomeric mixtures was determined by n.m.r. (ratio of integrals) and confirmed by g.l.c. (instrument equipped with a gas density balance; method of Cadogan and Sadler [23]). The azepines, being light-sensitive, were protected during work-up and storage.

Also obtained in some cases were amines corresponding to the nitroarenes used.

Reactions in which t-butyl alcohol was used instead of diethylamine (see Discussion section) were carried out similarly.

Details of 3H-*Azepines.*—*2-Diethylamino-5-methyl-*3H-*azepine* had b.p. 120° at 0·1 mmHg (Found: C, 74·3; H, 9·9; N, 16·1. $C_{11}H_{18}N_2$ requires C, 74·2; H, 10·0; N, 15·8%); δ ($CDCl_3$) 1·15 (6H, t), 1·65 (3H, s), 2·56 (2H, d), 3·34 (4H, q), 4·86 (1H, t), 5·58 (1H, d), and 6·96 (1H, d).

*5-Bromo-2-diethylamino-*3H-*azepine* had b.p. 80° at 0·15 mmHg (Found: C, 49·6; H, 6·2; N, 11·8. $C_{10}H_{15}BrN_2$ requires C, 49·5; H, 6·1; N, 11·55%); δ ($CDCl_3$) 1·05 (6H, t), 2·57 (2H, d), 3·25 (4H, q), 5·15 (1H, t), 5·65 (1H, m), and 6·92 (1H, d).

*Ethyl 2-diethylamino-*3H-*azepine-5-carboxylate* (Found: C, 65·75; H, 8·5; N, 11·5. $C_{13}H_{20}N_2O_2$ requires C, 65·95; H, 8·5; N, 11·8%); δ ($CDCl_3$) 1·25 (9H, m), 2·73 (2H, m), 3·37 (4H, q), 4·24 (2H, q), 6·15 (2H, m), and 7·20 (1H, d).

*2-Diethylamino-3-methyl-*3H-*azepine* had b.p. 70—75° at 0·01 mmHg (Found: C, 74·1; H, 10·0; N, 15·95. $C_{11}H_{18}N_2$ requires C, 74·2; H, 10·1; N, 15·75%); δ ($CDCl_3$) 0·75 (3H, d), 1·12 (6H, t), 3·40 (4H, q), 4·15 (1H, q), 5·17 (1H, t), 5·59 (1H, t), 6·23 (1H, m), and 7·06 (1H, d).

The 4- and 6-substituted 2-diethylamino-3*H*-azepines were not obtained as pure isomers but the mixtures were identified by mass spectrometry and checked for impurities by analysis (see Table 5) and g.l.c. before determination of the isomer ratios by n.m.r. spectroscopy.

TABLE 5

Analytical data for mixtures of 4- and 6-X-2-diethylamino-3*H*-azepines

		Found (%)			Required (%)		
X		C	H	N	C	H	N
Me	$C_{11}H_{18}N_2$	74·3	9·85	15·8	74·2	10·0	15·8
MeO	$C_{11}H_{18}N_2O$	68·0	9·2	14·55	68·0	9·3	14·4
Cl	$C_{10}H_{15}ClN_2$	60·5	7·5	14·4	60·1	7·5	14·1
Br	$C_{10}H_{15}BrN_2$	49·7	6·25	11·65	49·5	6·1	11·55
EtO_2C	$C_{13}H_{20}N_2O_2$	65·1	8·6	12·0	65·0	8·5	11·8

Photolysis of Aryl Azides in Diethylamine in the Presence of Pyrene.—General procedure. The azide and pyrene (4 mol. equiv.) in diethylamine (70 mol. equiv.) were boiled under reflux (56·5°) while being irradiated through a Pyrex filter for 5 h. When the mixture was cool, pyrene was filtered off, excess of diethylamine was removed and the product (*ca.* 50%) was chromatographed on alumina to give the 3*H*-azepine as described above. The results are given in Table 2.

The results of experiments involving benzophenone as sensitiser, and no sensitiser are summarised in Table 4. The unsensitised decomposition gave, as an additional product, the photoisomer 3-diethylamino-2-azabicyclo-[3.2.0]hepta-2,6-diene; δ ($CDCl_3$) 1·10 (6H, t), 2·49 (2H, m), 3·28 (5H, q), 4·82 (1H, m), 6·19 (1H, t), and 6·41 (1H, d) (the structure was confirmed by standard decoupling procedures); *m/e* 164 (77%), 149 (27), 135 (83), 92 (83), 93 (100), 72 (73), and 73 (47).

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