

## The Photoaddition of Aliphatic Amines to Benzene

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Primary, secondary, and tertiary aliphatic amines undergo photoaddition to benzene *via* photoexcitation of benzene to the  $S_1$  state. Primary amines give products of 1,2-, 1,3-, and 1,4-addition of the N-H bond, although the 1,3-adducts are derived from secondary photoreactions of the 1,2-adducts by way of hexa-1,3,5-triene intermediates. Secondary amines react similarly, but give only 1,2- and 1,4-adducts. The photoadditions of tertiary amines involve an  $\alpha$ -C-H bond in the amine and occur 1,4- to the benzene ring, but little addition occurs in the absence of methanol or other proton donors. The mechanisms of these reactions have been investigated, and the findings are discussed: charge-transfer processes and both polar and radical intermediates appear to be involved.

IN 1967 we first reported the 1,4-photoaddition of aliphatic amines and pyrrole to benzene.<sup>1,2</sup> Since this time we have shown that the reaction yields both 1,2- and 1,4-adducts with primary and secondary aliphatic amines<sup>3</sup> and 1,4-adducts with tertiary aliphatic amines;<sup>4</sup> primary aliphatic amines were exceptional in also giving 1,3-adducts through secondary photoisomerisation of an initially formed 1,2-adduct.<sup>3</sup> The reactions could in some cases be accelerated in the presence of proton donor solvents,<sup>4</sup> and intramolecular analogous were reported to occur with certain arylamines of type  $\text{Ph}[\text{CH}_2]_n\text{NMe}_2$ .<sup>5</sup> Other workers have subsequently shown that naphthalene<sup>6</sup> and anthracene<sup>7</sup> undergo photoaddition of various amines. We have further

reported that pyridine and fluoropyridines differ from benzenes in their formation of substitution products with aliphatic amines,<sup>8</sup> and other workers have shown that irradiation of styrenes<sup>9</sup> and phenylacetylenes<sup>10</sup> in similar systems causes addition of the amine to the ethylenic and acetylenic bonds respectively rather than to the aromatic ring. Physical aspects of the interaction of aromatic hydrocarbons with amines have been extensively studied and discussed.<sup>11</sup>

The present paper brings together, describes, and extends the work on aliphatic amine-benzene photoadditions outlined in our previous communications, and

<sup>1</sup> (a) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, 1973, **95**, 5783; (b) S. Vaidyanathan and V. Ramakrishnan, *Indian J. Chem.*, 1975, **13**, 257 and references therein.

<sup>2</sup> D. Bryce-Smith, A. Gilbert, and S. Krestonosich, *Tetrahedron Letters*, 1977, 385.

<sup>3</sup> R. C. Cookson, S. M. de B. Costa, and J. Hudec, *Chem. Comm.*, 1969, 753.

<sup>4</sup> M. Kawamsi and K. Matsunaga, *J.C.S. Chem. Comm.*, 1972, 313.

<sup>5</sup> See for example: 'The Exciplex' ed. M. Gordon and W. R. Ware, Academic Press, New York, 1975; R. S. Davidson, 'Molecular Associations,' ed. R. Foster, Academic Press, New York, 1975, p. 215; M. Ottolenghi, *Accounts Chem. Research*, 1973, **6**, 153; A. Weller, *Pure and App. Chem.*, 1968 **16**, 115 and references therein.

<sup>1</sup> M. Bellas, D. Bryce-Smith, and A. Gilbert, *Chem. Comm.*, 1967, 862.

<sup>2</sup> M. Bellas, D. Bryce-Smith, and A. Gilbert, *Chem. Comm.*, 1967, 263.

<sup>3</sup> D. Bryce-Smith, A. Gilbert, and C. Manning, *Angew. Chem.*, 1974, **86**, 350.

<sup>4</sup> D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunkin, and C. Manning, *Chem. Comm.*, 1971, 916.

<sup>5</sup> D. Bryce-Smith, A. Gilbert, and G. Klunkin, *J.C.S. Chem. Comm.*, 1973, 330.

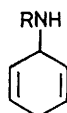
<sup>6</sup> (a) J. A. Barltrop and R. J. Owers, *Chem. Comm.*, 1970, 1462; (b) J. A. Barltrop, *Pure and App. Chem.*, 1973, **33**, No. 2-3, 179.

also includes a discussion of the mechanisms which operate. The photoadditions of pyrroles to benzene will form the subject of a separate paper. It may at this stage be convenient to note that although aliphatic amines themselves are well known to be photolabile, giving products derived from homolysis of C-N, C-H, and N-H bonds,<sup>12</sup> the present photoadditions have it in common that under de-gassed conditions they proceed *via*  $S_0 \rightarrow S_1$  photoexcitation of benzene rather than the amine component.

The photoadditions are of both synthetic and mechanistic interest, but as the experimental conditions found most convenient for synthetic runs have not in general been well suited for mechanistic studies, we shall first discuss the findings largely from a preparative viewpoint. Most of the mechanistic work to be described later has involved the triethylamine-benzene system.

## RESULTS

**Primary Amines.**—We have earlier reported that irradiation of cyclohexylamine and benzene yields a four-component mixture of 1:1 adducts, of which the major component was identified as the 1,4-adduct (*ca.* 60%) (1a).<sup>1</sup> The reaction has now been studied in detail



(1)

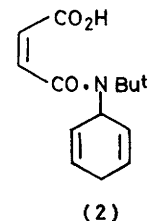
- a; R = cyclohexyl  
b; R = But

and all the products from several primary amines have been characterised. Following the initial experiments with cyclohexylamine, *t*-butylamine was chosen as the amine since this gave adducts having simpler n.m.r. spectra: the signal associated with the *t*-butyl group did not interfere with those from more structurally significant protons derived from the benzene.

Prolonged irradiation of rigorously de-oxygenated equivolume mixtures of *t*-butylamine and benzene (see Experimental section for conditions) gave a mixture of four 1:1 adducts, A, B, C, and D in order of increasing g.l.c. retention times, which finally reached the photo-stationary state composition of 1:1:2:5 respectively. Of these, only C and D were primary photochemical products: components A and B were subsequently shown to be derived by irradiation of C, whereas D was essentially light stable. Passage of dry hydrogen chloride into an ethereal solution of the four-component mixture gave a white precipitate of the hydrochlorides of C and D leaving those of A and B in solution.

Component D was obtained in 96% purity by fractional crystallisation of the hydrochloride mixture from 7:3

benzene-ethanol mixtures. On the basis of its chemical and spectroscopic properties adduct D, regenerated from its hydrochloride, was assigned structure (1b). Reaction



(2)

of ethereal solutions of (1b) with maleic anhydride gave a white solid (m.p. 115–117°), soluble in water, dilute acids, and bases, and common polar organic solvents. This was assigned structure (2) from its spectral and chemical properties, and is considered to arise simply by thermal nucleophilic attack of the amine on one of the anhydride carbonyl groups.

Adduct C was obtained as a colourless liquid of *ca.* 98% purity by preparative g.l.c. and like (1b) was readily dehydrogenated to *N*-*t*-butylaniline either by palladium on carbon, or non-catalytically at temperatures in excess of 250 °C. Spectral analysis of C clearly showed the presence of a conjugated diene moiety and the data were wholly consistent with the 1,2-adduct structure (3). Reaction with maleic anhydride yielded not the expected Diels-Alder product but a compound analogous to (2) from which C was regenerated by treatment with dilute sodium hydroxide solution. On the other hand, treatment of C with *N*-phenylmaleimide afforded a 1:1:1 benzene-amine-dienophile adduct, m.p. 195–198 °C, which from spectroscopic evidence is assigned structure (4), thereby confirming structure (3) for C.

After removal of components C and D from the adduct mixture as their hydrochlorides, adducts A and B were separated by preparative g.l.c. Adduct A, obtained as a colourless liquid of *ca.* 98% purity, was shown to be the bicyclo[3.1.0]hexene(s) (5) from consideration of its spectroscopic properties, particularly its n.m.r. spectrum which was in good agreement with that reported by Kaplan *et al.* for structurally related systems.<sup>13</sup> Compound (5) is formally a 1,3-adduct of *t*-butylamine and benzene although, as we have noted, and discuss further below, it is not a primary photoproduct.

Product B is assigned the hexatriene structure (6), although attempts to obtain a pure sample were frustrated by its marked tendency to isomerise to an approximately 5:2 mixture of (3) and (5) respectively under conditions of preparative g.l.c. (100 °C). By use of the lowest possible temperature (*ca.* 80°), sufficient of B was eventually obtained as a dilute solution in hexane for measurement of its u.v. spectrum. This showed  $\lambda_{\text{max}}$  338 nm: the extinction coefficient appeared high, but could not be determined owing to the rapid formation of brown tarry matter. No u.v. spectra for trienamines

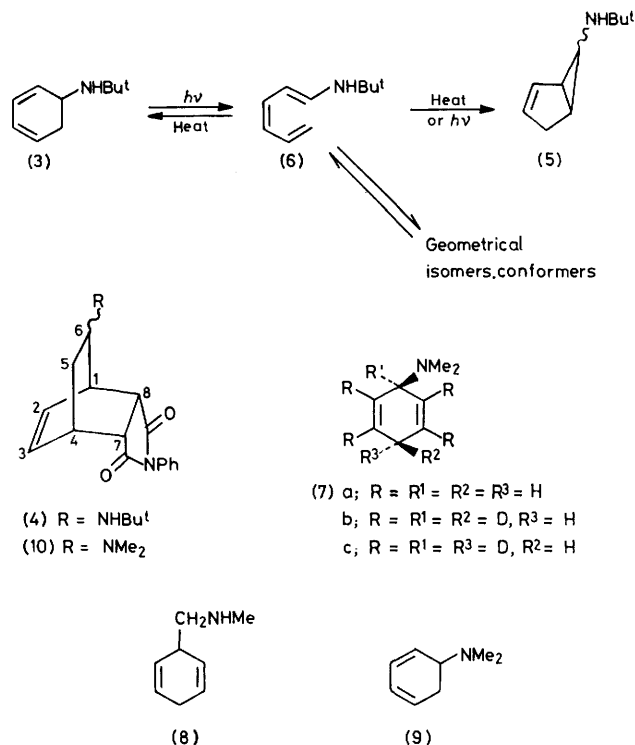
<sup>12</sup> L. T. Allan and G. A. Swan, *J. Chem. Soc.*, 1965, 4434 and 4822; K. G. Hancock and D. A. Dickinson, *J. Org. Chem.*, 1975, 40, 969; *ibid.*, 39, 331.

<sup>13</sup> L. Kaplan, J. S. Richter, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, 1966, 88, 2881.

appear to have been recorded, but introduction of a 1-diethylamino-substituent into buta-1,3-diene ( $\lambda_{\max}$ , 219 nm in hexane) causes a strong bathochromic shift to  $\lambda_{\max}$ , 281 nm.<sup>14</sup> A corresponding shift in hexa-1,3,5-triene would lead to a predicted  $\lambda_{\max}$ , 329 nm for the diethylamino-derivative, in good agreement with the value of 338 nm observed for compound (6). Photoisomerisation of (3) to (6) would be expected to occur in a conrotatory sense, and to lead only to the indicated *trans*-isomer: models indicate that the corresponding 'all-*cis*' isomer would be seriously overcrowded. Con-

that concerted thermal isomerisation of (6) to (5) would have to proceed *via* the novel ( $2\pi_a + 4\pi_a$ ) pathway, and models indicate the feasibility of this.

The major uncertainty still remaining is whether the hexatriene (6) undergoes photoisomerisation to the cyclohexadiene (3) under the conditions employed. The instability of the triene (6) has prevented direct observation of the photoisomerisation to (6) to (5), but this process may reasonably be inferred from the formation of (5) on irradiation of (3) at 20 °C, a temperature at which the thermal isomerisation of (6) to (5) is not observed.



certed processes of the type (6)  $\rightarrow$  (5) can, in principle, occur by three pathways, (a)  $2\pi_a + 4\pi_s$ , (b) ( $2\pi_s + 4\pi_a$ ), and (c) ( $2\pi_a + 4\pi_a$ ). The two *sa* processes are thermally forbidden and photochemically allowed:<sup>15</sup> (a) would give the *exo*-isomer of (5), and (b) the corresponding *endo*-isomer; (c) represents a thermal pathway. Studies with  $\alpha$ -phellandrene<sup>16</sup> suggest that the *exo*-isomer would tend to predominate. Experimental determination of the stereochemistry of (5) by n.m.r. spectroscopy has been hindered by overlapping resonances, and the complexity of the spectrum would suggest a mixture of *exo*- and *endo*-isomers.

Photoisomerisations of hexa-1,3,5-trienes to bicyclo-[3.1.0]hexenes are, of course, well known. On the other hand, we are not aware of any previously reported examples of the corresponding thermal process: the thermal isomerisation of hexa-1,3,5-trienes normally gives only the cyclohexa-1,3-dienes. It is interesting

<sup>14</sup> K. Bowden, E. A. Braude, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 45.

It may be noted that *direct* photoisomerisation of (3) to (5) is not structurally possible.

Cyclohexylamine and 1- and 2-aminobutanes behaved in broadly similar fashion to that described for *t*-butylamine: product ratios varied slightly although in all cases the major product was the 1,4-adduct analogous to (1).

Methanol did not promote the addition of primary amines to benzene. The photoadditions are, in general, favoured by solvents of low dielectric constant such as cyclohexane or diethyl ether. In the light of the behaviour of tertiary amines (see below), for which the presence of a proton-donor is virtually essential, it seems probable that the primary amines have also a role as proton-donors in these photoadditions.

Small amounts of neutral products were produced from the irradiation of primary amines and benzene, the

<sup>15</sup> R. B. Woodward and R. Hoffman, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970, p. 79.

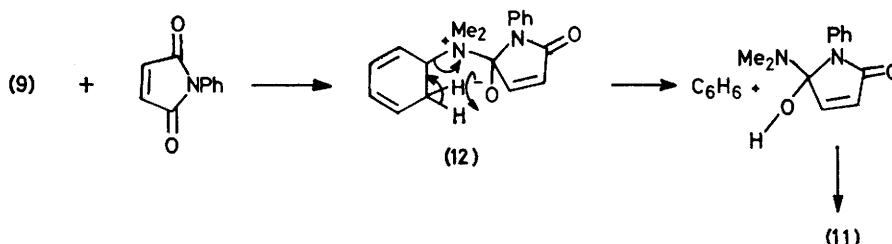
<sup>16</sup> J. Meinwald and P. H. Mazzocchi, *J. Amer. Chem. Soc.*, 1966, **88**, 2850.

composition of the mixture being independent of the nature of the amine. These neutral products are described in the section which covers reactions with tertiary amines. Although tertiary amines give rise to dehydro-dimers and other amine-derived by-products, only traces of these are formed from the primary and secondary amines.

**Secondary Amines.**—The secondary amines chosen for this study were dimethylamine, diethylamine, and piperidine. Irradiation of a 1:1 (v/v) solution of dimethylamine in benzene gave, after work-up, a pale yellow basic oil (b.p. 30–35 °C/10 mmHg), which contained several components. G.l.c. appeared to resolve one major component constituting 80% of the mixture and m.s./g.l.c. indicated a 1:1 adduct. N.m.r. studies (see below) established that this was in fact a two-component mixture. The remaining basic components were identical with those formed from irradiation of the amine alone and were not examined further. The neutral fraction was found to be identical with that obtained

filtrate gave (7a) free from (9) as evidenced by the absence of the resonance at 3.26 p.p.m. and the absorption at 1635  $\text{cm}^{-1}$ . The n.m.r. spectrum of (7a) is detailed in the Experimental section: important features are the long-range transannular coupling ( $J = 8$  Hz) between the ring methine and methylene protons and the coupling of 10.5 Hz between the  $H_\alpha$  and  $H_\beta$  ring vinyl protons.

Elemental analysis and molecular weight (mass spectrum) of the above white solid (m.p. 183–186 °C decomp.) showed that this was not the expected Diels–Alder adduct (10); but they were consistent with  $\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_2$ , *i.e.* a 1:1 adduct of *N*-phenylmaleimide and dimethylamine. From these data and the spectroscopic properties of the white solid it was deduced that the compound formed from the adduct mixture and *N*-phenylmaleimide had structure (11): subsequent examination of the ether filtrate showed that benzene had been formed in the reaction of (9) with the dienophile. Formation of (11) from (9) presents an interesting mechanistic



during the photolysis of tertiary amines and benzene (see below). The above adduct mixture was readily converted into *NN*-dimethylaniline by dehydrogenation with *p*-chloranil, 10% palladium on charcoal, tetracyanoethylene,<sup>17</sup> or thermally at temperatures in excess of 200 °C, and the major component (*ca.* 85%) was assigned structure (7a), *i.e.* the expected 1,4-adduct. I.r., n.m.r., and mass spectra were all basically consistent with this assignment, but the n.m.r. spectrum indicated the presence of *ca.* 15% of an isomer of (7a). Thus, apart from a multiplet at 3.58 p.p.m. due to the ring methine in (7a), a much smaller resonance at 3.26 p.p.m. was evident. Simultaneous irradiation at 5.86 and 5.62 (*i.e.* the vinyl protons) resolved both of the higher field multiplets into triplets with  $J = 8$  Hz for the more intense resonance and  $J = 9$  Hz for the weaker signal. Two structures (8) and (9) may be considered for this minor isomer. Structure (8) is ruled out both by the lack of spectroscopic evidence for N–H and the absence of *N*-methylbenzylamine in the dehydrogenated product. On the other hand, the 1,2-adduct (9) is consistent with all the foregoing data including a previously unassigned weak i.r. band at 1635  $\text{cm}^{-1}$  (C=C stretch in a conjugated diene). Addition of the adduct mixture to an ethereal solution of *N*-phenylmaleimide gave a white solid in amounts consistent with reaction of only *ca.* 10–15% of the adduct mixture. Removal of the ether from the

problem. Although secondary amines ( $\text{Et}_2\text{NH}$ , piperidine) react rapidly with *N*-phenylmaleimide at 20 °C to yield bis-amides, the corresponding reaction with primary amines (cyclohexylamine,  $\text{EtNH}_2$ ) is anomalous in being much slower, and simple tertiary amines ( $\text{Et}_3\text{N}$ ,  $\text{Bu}_3\text{N}$ ) do not react. The question also arises as to why the 1,4-adduct (7a) does not react in this way, especially since dehydrogenation of cyclohexa-1,4-diene to benzene is allowed as a concerted thermal process, whereas the corresponding dehydrogenation of cyclohexa-1,3-diene is not. One might suppose that the cyclohexa-1,3-diene (9) and *N*-phenylmaleimide undergo complexation which induces decomposition to give the free amine and benzene rather than proceeding to the normally-expected Diels–Alder adduct (10): the free dimethylamine then reacts normally with the *N*-phenylmaleimide to give the bis-amide (11). A better explanation is, however, that the adduct (9) reacts with *N*-phenylmaleimide to yield an intermediate such as (12) which undergoes a *syn*-elimination as shown in the Scheme: such a mechanism explains the failure of (7a), the 1,4-adduct, to react with this dienophile.\*

In contrast with these results, the cyclohexa-1,3-diene (3) reacted with *N*-phenylmaleimide in a conventional manner to yield the Diels–Alder adduct (4). This behaviour clearly indicates that the Diels–Alder addition of (3) is much faster than its reaction as a secondary

\* We are grateful to a referee for drawing our attention to this possibility.

<sup>17</sup> D. T. Longone and G. L. Smith, *Tetrahedron Letters*, 1962, 205.

amine, and renders it most unlikely that the 1,4-adduct (10) is an intermediate in formation of the bis-amide (11). Another surprising difference between the 1,2-adducts is that (3) and similar adducts from other primary amines are photolabile whereas (9) is comparatively photostable.

Irradiation of benzene solutions of diethylamine and piperidine gave 1,4- and 1,2-adducts in approximate ratios of 9:1 and 6:1 respectively. Again the 1,4-adduct could be purified from the 1,2-adduct by reaction of the mixture with *N*-phenylmaleimide although in the case of diethylamine no pure product was obtained from the 1,2-adduct.

The reaction of secondary amines and benzene to yield the 1,4-adducts appears to be a non-concerted process since the product from hexadeuteriobenzene and dimethylamine lost equal amounts of HD and D<sub>2</sub> on pyrolysis to form the *NN*-dimethylaniline, corresponding to a 1:1 mixture of (7b) and (7c). This observation is consistent with a kinetically distinct proton-transfer step as discussed further below. With all secondary amines, some (*ca.* 8%) photosubstitution into the benzene ring to give the *NN*-dialkylaniline was observed, but corresponding products from primary amines have not as yet been found. Photonucleophilic substitution into benzene seems rather less likely than a homolytic substitution mechanism involving R<sub>2</sub>N· radicals; but as yet we have no definite evidence on this point.

The effect of added solvents upon the photoreactions of benzene and secondary amines was found to be similar to that observed with primary amines. Likewise, added methanol was not essential, so it may be assumed that the secondary amine also appears to act as a proton source under the reaction conditions.

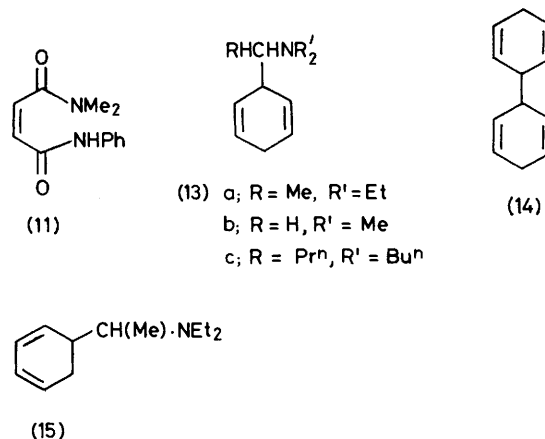
**Tertiary Amines.**—Irradiation under nitrogen (see Experimental section for conditions) of a de-aerated and anhydrous 1:1 (v/v) mixture of triethylamine and benzene for 24 h caused the initially colourless solution to become pale yellow.\* Vacuum distillation of the residue after removal of the starting materials gave a pale yellow oil containing dehydro-dimers and other products derived from the amine alone (*cf.* Allan and Swan<sup>12</sup>), together with two minor compounds in the ratio *ca.* 8:1 which were shown by m.s./g.l.c. to have parent ions of *m/e* 179 and 158 m.u. respectively. As shown below, these were identified as the 1,4-adduct (13a) and 1,1',4,4'-tetrahydrobiphenyl (14) respectively.

Mechanistic considerations (see below) suggested that the photoaddition reaction might proceed more readily in the presence of a proton donor; and so it transpired. Methanol, water, or triethylammonium trifluoroacetate could be used, but methanol was the most convenient. Thus incorporation of 5% methanol into the amine-benzene mixture prior to preparative irradiations gave a

\* Our earlier reported results<sup>4</sup> were obtained using unfiltered radiation from a medium-pressure mercury lamp and the amounts and relative proportions of products were somewhat sensitive to the reactant proportions. The present proportions, *etc.*, of products were more readily reproducible and refer to the use of 254-nm radiation from a low-pressure mercury source.

fourfold increase in the total yield of photoproducts, and compounds (13a) and (14) were now the major constituents, although their ratio to each other was unchanged at 8:1. The implications of the effects of methanol and other solvents are discussed later. It is interesting in the light of the results obtained with primary and secondary aliphatic amines that no trace of a 1,2-adduct (15) could be detected.

The adduct (13a) was obtained in *ca.* 98% purity by



preparative g.l.c. and its structure was established as follows. It did not react with common dienophiles and was thermally dehydrogenated at *ca.* 350 °C, and at lower temperatures by both *p*-chloranil and 10% palladium on charcoal (but surprisingly not by tetracyanoethylene<sup>17</sup>), to yield *NN*-diethyl- $\alpha$ -methylbenzylamine which was identical with authentic material synthesised from ethylbenzene. This behaviour was consistent with structure (13a), and the assignment was confirmed by the spectroscopic data. Thus its u.v. spectrum (cyclohexane) had  $\lambda_{\text{max}}$  at 205 nm, and the i.r. spectrum showed structurally significant absorption at 3 040 (=C-H stretch), 1 635 (C=C stretch), 1 406 (HC=CH in-plane deformation), 1 206 (C-N stretch in *tert.*-amine), and 680 cm<sup>-1</sup> (HC=CH out-of-plane deformation). The 100 MHz <sup>1</sup>H n.m.r. spectrum of the adduct in C<sub>6</sub>D<sub>6</sub> is tabulated in the Experimental section: but the most significant features were the presence of the two methyl resonances, one a doublet ( $J = 6.5$  Hz) and the other a triplet ( $J = 7.5$  Hz), and the characteristic<sup>18</sup> long-range 1,4-transannular coupling between the ring methine proton (2.14 p.p.m.) and the ring methylene protons to produce a triplet of  $J = 8$  Hz.

The tetrahydrobiphenyl (14) constituted *ca.* 80% of the neutral reaction products. (Incidentally, we have observed that this compound is not present among the products of Birch reduction of biphenyl<sup>19</sup>). Other minor neutral products included biphenyl and cyclohexa-1,4-diene. The formation of this latter provides the first known example of photoreduction of benzene.

The photoaddition process has been extended to other

<sup>18</sup> L. J. Durham, J. Studebaker, and M. J. Perkins, *Chem. Comm.*, 1965, 456.

<sup>19</sup> W. Huckel and R. Schwen, *Chem. Ber.*, 1956, **89**, 150.

tertiary amines. Thus trimethylamine and tri-*n*-butylamine gave the adducts (13b) and (13c) respectively.

It was of interest to compare the reactivity of an *N*-methyl group with that of an *N*-methylene group. Irradiations of *NN*-dimethylethylamine and *NN*-diethylmethylamine in benzene both gave two 1,4-adducts of type (13). These were separated by preparative g.l.c. and their structures established by spectroscopic methods. With *NN*-dimethylethylamine, reaction at the methyl group was the more favoured (*ca.* 6 : 1), and with *NN*-diethylmethylamine the corresponding ratio was *ca.* 2 : 1. Therefore, the reactivity of an *N*-methyl hydrogen was approximately twice that of an *N*-methylene hydrogen, consistent with loss as a proton but not a hydrogen atom.

The above addition reactions of tertiary amines were greatly promoted in the presence of methanol, but the ratio of adduct (13) to 1,1',4,4'-tetrahydrobiphenyl remained essentially constant. In the absence of a proton source, cyclohexane and ether had little effect on the slow rate of reaction observed with the neat addends, but acetonitrile completely quenched the photoaddition process. In order to clarify further the effects of methanol and other solvents on the photoaddition process, solutions of 5% of triethylamine and 5% benzene in cyclohexane containing 1, 5, and 10% (all v/v) of methanol were irradiated. It was found that product (13a) was formed under standard irradiation conditions approximately as fast in the 1% methanol solution as in that containing 5%, but the rate of reaction was definitely reduced in the solution containing 10% methanol. (Under such conditions only traces of dehydro-dimers of the amine were formed). It appeared from these observations, and the inhibiting effect of acetonitrile, that the presence of a proton-donor tends to promote the photoaddition, whereas increased solvent polarity tends to hinder it: 1—5% of methanol in cyclohexane appears to represent the best compromise. This conclusion was strongly supported by comparison of the results of irradiating solutions of triethylamine (5%), benzene (5%), and methanol (1%) in cyclohexane, ethyl acetate, and acetonitrile. The rate of formation of adduct (13a) decreased markedly in the order cyclohexane > ethyl acetate > acetonitrile, *i.e.* with increasing solvent polarity. The formation of tetrahydrobiphenyl was similarly affected, but the proportion of dehydro-dimers of the amine increased with increasing solvent polarity, and in acetonitrile these were the major reaction products. The active participation of methanol in the reaction was further demonstrated by the reaction of triethylamine and benzene in the presence of MeOD when (13a) was produced with incorporation of deuterium into both the *syn* and *anti* 4-positions in approximately equal amounts, and two atoms of deuterium were

present in the tetrahydrobiphenyl. The present 1,4-addition of tertiary amines to benzene in the presence or absence of methanol certainly appears to be a non-concerted intermolecular process. Thus the 1,4-adduct of trimethylamine and hexadeuteriobenzene formed in the absence of methanol undergoes thermal (*ca.* 300 °C) elimination of HD and D<sub>2</sub> in equal proportions to form the pentadeuterio- and tetradeuterio-*N*-benzylidimethylamines in a 1 : 1 ratio: the adduct from benzene in the presence of MeOD behaved similarly. Thermal eliminations of H<sub>2</sub> from cyclohexa-1,4-dienes are well known to have *cis*-stereospecificity. The observation that scrupulously dried benzene and triethylamine still form traces of the 1 : 1 adduct (13a) on irradiation indicates that triethylamine itself, or more probably its radical-cation, can act as a feeble proton donor: \* triethylamine has been reported to provide an  $\alpha$ -proton during the photoreduction of aryl ketones<sup>20</sup> and aromatic hydrocarbons.<sup>21</sup>

Oxygen-free mixtures of triethylamine and benzene show u.v. absorption which is substantially additive of the components. Brief exposure of such mixtures to air leads to the appearance of a marked new absorption band having a  $\lambda_{\text{max}}$  at *ca.* 290 nm; this disappears on de-gassing. Although we have considered the possibility that this new band might correspond to an oxygen-promoted S<sub>0</sub>→T<sub>1</sub> transition in benzene, we are now inclined to believe that it results from charge-transfer absorption in an amine-oxygen complex,<sup>22</sup> since closely similar absorption can be observed in the absence of benzene. Irradiation behind a Pyrex filter of degassed benzene-triethylamine mixtures produced no products; but a similar experiment in the presence of oxygen gave small amounts of the 1 : 1 adduct (13a) together with much tarry material which acted as an internal filter. This appears to provide a unique example of oxygen acting as a photosensitiser.

We have not observed any reactions between benzene and *N*-alkyl- or *NN*-dialkylanilines, but this apparent unreactivity may simply reflect the difficulty of exciting benzene in the presence of these much more extensively absorbing aromatic amines. It has been shown that excitation of anthracene in the presence of either aniline<sup>7b</sup> or *N*-methylaniline<sup>7a</sup> leads to adducts and reduction products of the arene.

*Mechanistic Discussion.*—Although there is some evidence from heats of mixing that arenes and amines form loose ground state complexes,<sup>23</sup> there are no indications from our n.m.r. studies of mixtures of benzene with *t*-butylamine, diethylamine, or triethylamine to suggest any preferred orientation (see, however, ref. 24 for orientated complexes between benzene and pyrroles), and the u.v. spectra are additive of those of the com-

<sup>21</sup> Ref. 6 and R. S. Davidson, P. F. Lambeth, F. A. Younis, and R. Wilson, *J. Chem. Soc. (C)*, 1969, 2203.

<sup>22</sup> H. Tsubomura and R. S. Mulliken, *J. Amer. Chem. Soc.*, 1960, **82**, 5966.

<sup>23</sup> H. Kehiaian, 'Abstracts of Chemical Society Anniversary Meeting,' Exeter, 3—6 April, 1967, C 12.

<sup>24</sup> G. L. D. Ritchie and P. J. Stiles, *J. Chem. Soc. (B)*, 1968, 148.

\* We believe this statement to be true, but as we remarked in a previous paper,<sup>4</sup> the notorious ubiquity of water discourages us from placing undue emphasis on the point.

<sup>20</sup> S. G. Cohen and J. I. Cohen, *J. Amer. Chem. Soc.*, 1967, **89**, 164.

ponents. Thus, ground-state complexes showing charge-transfer absorption are not formed.

It is, however, known that amines (and tertiary amines have been the most studied) strongly quench the fluorescence of arenes other than benzene: such quenching can lead to the formation of exciplexes which in some cases are themselves fluorescent.<sup>11</sup> We have observed that primary, secondary, and tertiary aliphatic amines quench the fluorescence of benzene in cyclohexane at a diffusion-controlled rate, but in no case was this quenching accompanied by exciplex emission even in experiments conducted at  $-50^\circ\text{C}$ .

Some authors have attempted to distinguish between exciplexes and 'encounter complexes' in photoreactions between polycyclic arenes and amines;<sup>6b</sup> but in the absence of emission attributable to intermediate complexes in our benzene-amine systems, we feel that any extended discussion of the character of the complexes would be excessively speculative. The above-mentioned behaviour of polycyclic arenes does, however, lead us to suspect that the absence of observable emission from any comparable complexes involving benzene is more likely to be due to their rapid non-radiative decay than to their non-formation.

In an attempt to determine the multiplicity of the reaction intermediates, we have examined the relative rate of formation of (13a) from benzene and triethylamine in cyclohexane solution containing 1% of methanol under argon and xenon atmospheres. It is known that xenon can strongly promote singlet-triplet intersystem crossing in aromatic molecules by a heavy-atom effect.<sup>25</sup> In repeated experiments, xenon reduced the rate of formation of (13a) to *ca.* 70% of that measured under argon. Thus the enhancement of intersystem crossing at any step in the reaction (excited benzene and/or complex) is evidently disadvantageous. We conclude that the photoaddition process involves intermediates of singlet type.

It is clear from our experiments with methanol and other proton-donors that proton transfer is a vital step in the reaction sequence, and that markedly polar intermediates are involved. Methanol is effective as a proton donor in the photoaddition of tertiary amines but is not necessary (and can even be disadvantageous for polarity reasons—see below) for the addition of primary or secondary amines: doubtless these serve in the dual capacity of addends and proton donors. On the other hand, the photoaddition is increasingly inhibited as the polarity of the solvent is increased: at first sight, this effect might be thought to be inconsistent with any suggestion that the transition state is more polar than the reactants. We reconcile the observations as follows.

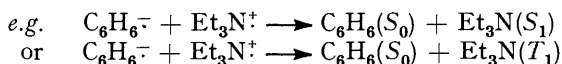
Firstly, we propose that the initially-formed  $S_1$  benzene acts as an electron acceptor from free or loosely complexed  $S_0$  amine to form a benzene-amine complex having marked polar character. In non-polar solvents, this complex is envisaged to have polarity character-

<sup>25</sup> R. B. Cundall and A. J. R. Voss, *Chem. Comm.*, 1968, 902; H. Morrison, T. Nylund, and F. Palensky, *J.C.S. Chem. Comm.*, 1976, 4.

istics which might range from those of an encounter complex through an exciplex to an intimate radical-ion pair, and indeed a succession of such complexes could well be involved, as in other systems. For reasons previously indicated, we are unable to distinguish between these possibilities in the present cases; but the complexes are evidently sufficiently polar to undergo proton-transfer from methanol, primary or secondary amine, or other proton-donor, giving a radical pair in a solvent cage. Primary combination of this radical pair gives the benzene-amine adduct, whereas diffusion of the radicals from the solvent cage leads to the formation of reduction products and dehydro-dimers of the amine.

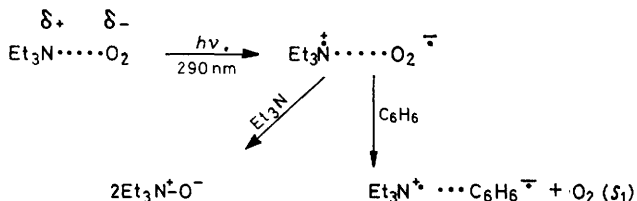
On the other hand, increased solvent polarity would be expected to promote the formation of solvent-separated and more strongly solvated radical-anions and -cations. Experimentally, we observe that increased solvent polarity leads not only to reduced yields of the chemical adducts, but also to increased formation of amine-derived products of the types produced by irradiation of the amine alone (*i.e. via*  $S_1$  amine): yet these amine-derived products are not accompanied by more than traces of benzene-derived compounds such as tetrahydrobiphenyl (14) and cyclohexa-1,4-diene unless large proportions of methanol are also present in the polar solvent.

It therefore appears necessary to postulate that the *solvent-separated* radical-ions undergo retro-electron transfer much more readily than chemical combination, and that this electron transfer leads to the formation of  $S_1$ , or more probably  $T_1$ , amine plus  $S_0$  benzene:



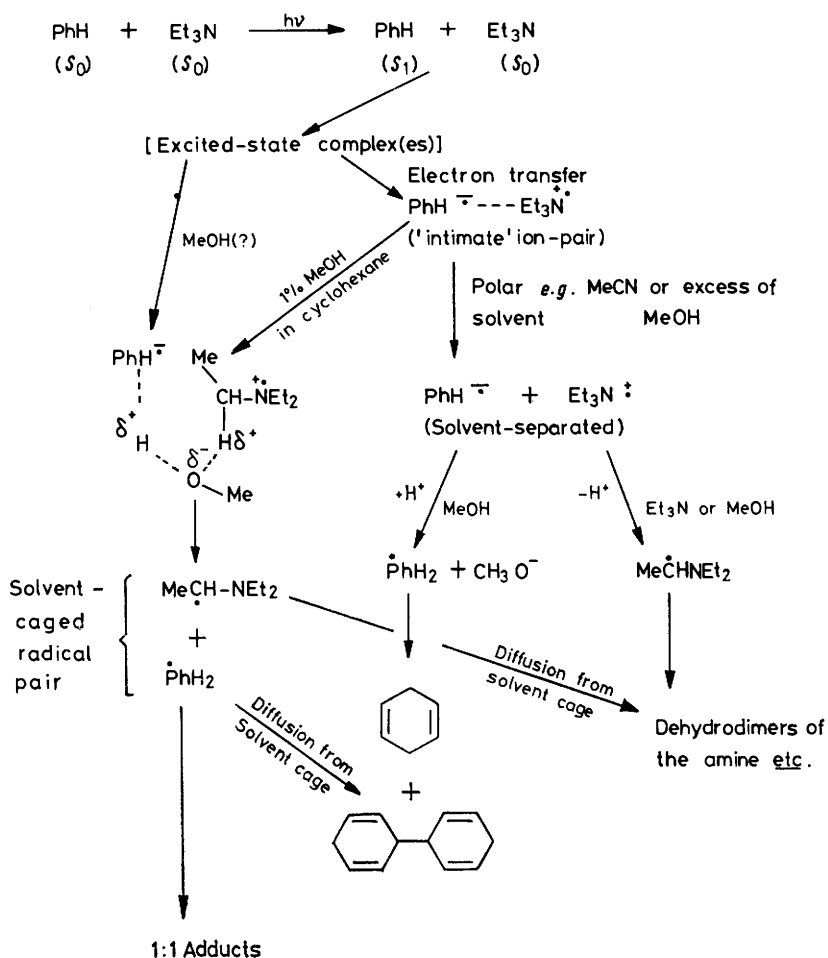
This somewhat unconventional process has the merit of explaining why polar solvents not only inhibit the formation of chemical adducts, but also why they promote the formation of by-products derived from the amine but not from the benzene.

We refer in conclusion to the observation that in the presence of oxygen, irradiation of a mixture of triethylamine and benzene beyond the benzene solvent front in the region corresponding to charge-transfer absorption by the amine-oxygen complex leads to the adduct (13a) together with triethylamine *N*-oxide, and the usual mixture of dehydro-dimers and other products derived exclusively from the amine. Under these conditions, the  $S_1$  benzene which is normally required for adduct formation obviously cannot be formed by direct absorption. We suggest that the benzene-amine radical-anion radical-cation pair (or equivalent polar complex) may arise indirectly as follows:



These conclusions are summarised in the following Scheme.

and D in the same ratio as in the original mixture. The solid hydrochloride mixture was dissolved in the minimum



SCHEME Mechanism for the photoaddition of benzene to aliphatic amines

#### EXPERIMENTAL

All irradiations were performed in quartz tubes of varying capacity using light from Hanovia 15-W low-pressure mercury-arc lamps. The solutions were flushed with nitrogen for 30 min prior to the reaction and the tubes were then sealed.

*Irradiation of t-Butylamine and Benzene.*—The benzene (100 ml) and t-butylamine (100 ml) mixture was irradiated for 24 h. The low boiling materials were removed by rotary evaporation at water pump pressure and the residue was separated into basic and neutral fractions. Vacuum distillation of the basic fraction gave 5 ml of a pale yellow oil (b.p. 34–38 °C; 0.03 mmHg) containing the four adducts A, B, C, and D (mass spectral parent ions at  $m/e = 151$  m.u.) as described in the text. Analytical g.l.c. was carried out using a column packed with 7% Apiezon L + 2% KOH on Universal B support. Passage of hydrogen chloride through a 10% solution of the adduct mixture for 1 min produced a white precipitate. A portion of the white precipitate was dissolved in water and the solution basified with 2M-sodium hydroxide solution when the mixture became turbid. The mixture was extracted with diethyl ether and the ethereal layer yielded the adducts C

amount of a boiling mixture of benzene (70%) and ethanol (30%) and the solution was allowed to cool. The amine from the crystallised hydrochloride was found to be the adduct D in *ca.* 96% purity. Adduct C was obtained as a colourless liquid of *ca.* 98% purity by preparative g.l.c. (Apiezon L + KOH column) from the mixture of adducts C and D obtained by hydrolysis of the solid hydrochloride mixture. Adduct A was also isolated by preparative g.l.c. after removal from the adduct mixture of the adducts C and D as their hydrochlorides. Attempts to isolate adduct B by similar techniques were only partially successful (see text). The longest wavelength absorption maxima of the 1:1 adducts A, B, C, and D were at 225, 338, 254, and 222 nm respectively, and salient features of the i.r. spectra (liquid smear) of A, C, and D were: adduct A 3 650br (NH stretch), 3 040m (*cis*-CH=CH, CH stretch), 2 970s and 1 042m (CH<sub>2</sub> in cyclopropane), and 655w cm<sup>-1</sup> (HC=CH, CH deformation); adduct C 3 650br (NH stretch), 3 040m (HC=CH, CH stretch), 1 640w (conj. C=C stretch), 1 395m and 1 370m (CH<sub>3</sub> in Bu<sup>t</sup>), and 690s cm<sup>-1</sup> (HC=CH, CH deformation); and adduct D 3 600br (NH stretch), 3 010m (CH=CH, CH stretch), 1 680w (C=C stretch), 1 390m and 1 360w (CH<sub>3</sub> in Bu<sup>t</sup>), and 705s (HC=CH, CH deformation).



*N.m.r. Spectra of the 1:1 Adducts.*—Adduct A:  $\delta(\text{CCl}_4)$  0.91br (10 H, s, t-butyl and NH), 1.70 (1 H, m, H gem to t-butyl amino), 1.80 (2 H, m, allylic methylene), 2.00 (2 H, m, bridgehead H's), 5.55 (1 H, m, vinyl H), and 5.80 (1 H, m, vinyl H). Adduct C:  $\delta(\text{CCl}_4)$  0.73br (1 H, s, NH), 1.02 (9 H, s, t-butyl), 2.25 (2 H, m, methylene), 3.23 (1 H, m, methine), and 5.72 (4 H, s, vinyl). Adduct D:  $\delta(\text{CCl}_4)$  1.07 (10 H, s, t-butyl and NH), 2.49 (2 H, dbt,  $J = 8$  Hz, methylene), 3.52 (1 H, t,  $J = 8$  Hz, methine), and 5.61br (4 H, s, vinyl).

*Reaction of Adducts C and D with Maleic Anhydride.*—The addition of maleic anhydride to ethereal solutions of either adduct D or C led to the immediate formation of white precipitates. Elemental analysis and the mass spectra of these compounds were consistent with their formulation as 1:1 adducts of C and D with maleic anhydride. The adduct from D had the following n.m.r. spectrum:  $\delta(\text{CDCl}_3)$  1.51 (9 H, s, t-butyl), 2.74 (2 H, m, methylene), 4.50 (1 H, m, methine), 6.10 (4 H, m, ring vinyl), 6.60 (2 H, s, vinyl), and 8.80br (1 H, s, NH), and is assigned structure (2). The corresponding spectrum of the adduct of maleic anhydride and C had resonances at  $\delta(\text{D}_2\text{O})$  1.35 (9 H, s, t-butyl), 2.6 (2 H, m, methylene), 4.10 (1 H, m, methine), and 6.00–6.40 (6 H, m and s, ring vinyl and vinyl). The maleic anhydride adducts of both C and D were decomposed back to C and D by refluxing their solutions (0.5 g, in 5 ml.) in 2M-sodium hydroxide solution for 3 h.

*Dehydrogenation of Adducts C and D.*—The 1:1 adducts C and D (0.1 g) when refluxed in toluene (10 ml) with 10% palladium on charcoal (0.2 g) for 8 h yielded *N*-(t-butyl)aniline (ca. 0.07 g) in each case.

*Reaction of Adduct C with N-Phenylmaleimide.*—The adduct C (0.15 g) and *N*-phenylmaleimide (0.2 g) were dissolved in diethyl ether (5 ml). After 15 h at room temperature, the ether was removed and light petroleum (b.p. 60–80 °C; 5 ml) was added. The mixture was cooled to 0 °C and the colourless crystalline solid (m.p. 195–198 °C) 1:1:1 adduct was filtered off. The n.m.r. spectrum of this adduct was as follows:  $\delta(\text{CDCl}_3)$  1.08 (10 H, s, t-butyl and NH), 2.16 (2 H, m, 5-H), 3.1–2.9 (3 H, m, 6-, 7-, and 8-H), 3.15 (2 H, m, 1- and 4-H), 6.30 (2 H, m, 2- and 3-H), and 7.4–7.1 (5 H, m, Ar). The i.r. spectrum (Nujol mull) of (4) had significant absorptions at 3400br (NH stretch), 1710s (C=O in 5-membered imide ring), 1395m and 1375m ( $\text{CH}_3$  in  $\text{Bu}^t$ ), and 695w  $\text{cm}^{-1}$  (*cis*-olefin).

*Photolysis of Adduct C.*—Adduct C (0.01 g) was dissolved in benzene (1 ml) and irradiated in a quartz tube with a low-pressure mercury-arc lamp. The progress of the reaction was followed by g.l.c. The first-formed product was adduct B and continued irradiation produced adduct A. The photostationary state concentration of the three adducts produced by photolysis of C appeared to be ca. 50% adduct A, 30% adduct B, and 20% adduct C: prolonged irradiation led to decomposition of the adducts, a coloured solution, and polymer deposits.

*Irradiation of Benzene with Other Primary Aliphatic Amines.*—The irradiation of benzene with the primary aliphatic amines, cyclohexylamine, and 1- and 2-aminobutanes were performed in a manner similar to that described for benzene and t-butylamine. Work-up and analytical procedures were also of a similar nature.

*Solvent Effects.*—These were studied using 25% (v/v) solutions of each of benzene and t-butylamine in cyclo-

hexane, diethyl ether, ethyl acetate, acetonitrile, and methanol (total volume 1.0 ml). The reactions were followed by g.l.c. This procedure was also adopted for the study of solvent effects on other benzene-amine systems unless otherwise stated in the text.

*Irradiation of Benzene with Secondary Amines.*—Benzene (100 ml) and dimethylamine (diethylamine or piperidine) (100 ml) were irradiated in the usual manner for 12 h. The starting materials were distilled from the golden-yellow coloured solution and the resulting oil was separated into neutral and basic fractions. The basic fraction was distilled at reduced pressure (b.p. 30–35 °C 10 mmHg) to give ca. 2 ml of a pale yellow liquid. Analytical g.l.c. was performed on a 7% Apiezon L + 2% KOH on Universal B support column.

Correspondingly similar results were obtained using diethylamine or piperidine (100 ml) in place of dimethylamine.

*Dehydrogenation of the 1:1 Adduct Mixture from Benzene and Dimethylamine.*—(a) *With p-chloranil.* A sample of the adduct (0.1 g) was dissolved in toluene (10 ml) and *p*-chloranil (0.25 g) was added. The mixture was refluxed for 3 h after which time it was extracted with 2M-hydrochloric acid. The acid layer was treated with excess of 2M-sodium hydroxide solution and then extracted with diethyl ether. Removal of the ether gave a compound which had spectroscopic and chromatographic properties identical with those of an authentic sample of *NN*-dimethylaniline.

(b) *With 10% palladium on charcoal or with tetracyanoethylene.* When a sample of the adduct (0.1 g) was refluxed overnight in toluene (10 ml) in the presence of either 10% Pd/C or tetracyanoethylene (0.25 g), an essentially quantitative yield of *NN*-dimethylaniline was produced.

(c) *Thermal dehydrogenation.* Injection of samples of the adduct into a g.l.c. injection block at a temperature in excess of ca. 300 °C caused complete thermolysis and the presence of *NN*-dimethylaniline was observed in the subsequent chromatogram. Reversion to starting materials was also observed.

The above procedures were also used for the dehydrogenation of other amine-benzene adducts including those from tertiary amines.

*Reaction of the Adduct of Dimethylamine and Benzene with N-Phenylmaleimide.*—The adduct (0.1 g) was added to a solution of *N*-phenylmaleimide (0.1 g) in diethyl ether (10 ml). The solution was stored at 0 °C for 15 h by which time a white solid (ca. 15 mg) had deposited. The solid was filtered off and the ethereal layer provided a sample of the 1:1 adduct (7a) free from the adduct (9). The n.m.r. spectrum of (7a) was as follows:  $\delta(\text{CCl}_4)$  2.16 (6 H, s, Me), 2.6 (2 H, m,  $J = 8$  Hz, methylene), 3.58 (1 H, m,  $J = 8$  Hz, methine), and 5.75 (4 H, m,  $J = 10.5$  Hz, vinyl), and the i.r. spectrum (liquid smear) had salient absorptions at 3030s ( $\text{HC}=\text{CH}$ , CH stretch), 2780s ( $\text{NCH}_3$ , CH stretch), 1678w (C=C stretch), and 680 ( $\text{HC}=\text{CH}$ , CH deformation). The solid produced from the 1:1 adduct with *N*-phenylmaleimide had m.p. 183–186 °C (decomp.), its mass spectrum had  $M^+ = 218$  m.u. (Found: C, 66.65; H, 6.4; N, 12.7.  $\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_2$  requires C, 66.10; H, 6.43; N, 12.85%). The n.m.r. spectrum of the white solid was as follows:  $\delta(\text{CDCl}_3)$  2.07 (6 H, d,  $J = 3.5$  Hz, Me<sup>2a</sup>), 6.25 (1 H, d,  $J = 10.5$  Hz, vinyl), 6.50 (1 H, d,  $J = 10.5$  Hz, vinyl), and 7.8–7.0 (6 H, m, NH, and Ar).

<sup>2a</sup> W. D. Phillips, *J. Chem. Phys.*, 1955, **23**, 1363.

*Irradiation of Triethylamine and Benzene.*—A mixture of benzene (100 ml) and triethylamine (100 ml) was irradiated for 24 h in the manner previously described. The starting materials were removed from the pale yellow solution and the resulting brown oil was distilled (b.p. 30–35 °C/0.02 mmHg) to give *ca.* 0.75 ml of a colourless oil. Two components of interest in this oil had  $M^+$  values of 179 and 158 m.u. Incorporation of 5% methanol or trifluoroacetic acid into the benzene–triethylamine solution before irradiation produced a 4-fold increase in the yield of these products. A similar effect was achieved by saturating the solution with water prior to irradiation. The products were separated into basic and neutral fractions by shaking ethereal solutions of them with an equal volume of 2M-hydrochloric acid. The 1:1 adduct (13a) was obtained in *ca.* 98% purity by preparative g.l.c. on Apiezon L-KOH supported on Chromosorb W columns. Dehydrogenation procedures were carried out as above. The n.m.r. spectrum of (13a) was as follows:  $\delta(\text{C}_6\text{D}_6)$  0.94 (3 H, d,  $J = 6.5$  Hz, Me), 0.97 (6 H, t,  $J = 7.5$  Hz, Me), 2.14 (1 H, t,  $J = 8$  Hz, ring methine), 2.38 (4 H, q,  $J = 7.5$  Hz, N-CH<sub>2</sub>), 2.55 (2 H, m, ring methylene), 2.7 (1 H, m, N-Me), and 5.65 (4 H, m, vinyl). The mass spectrum of (13a) had  $M^+$  and  $(M - 2)^+$  ions at  $m/e = 179$  and 177 m.u. of equal intensity but the fragmentation was typified by abundant ions at 100 m.u. (Me  $\dot{\text{C}}\text{H NEt}_2$ ) (base peak) and 78 m.u. (C<sub>6</sub>H<sub>6</sub>)<sup>+</sup>.

Other tertiary amines which were examined in this photoreaction with benzene were trimethylamine, tri-*n*-butylamine, dimethylethylamine, and diethylmethylamine. The products from the reactions were separated into neutral and basic components and then subjected to preparative g.l.c. The structures were proved by spectroscopic methods and dehydrogenation to the aromatic compounds.

*Neutral Products from Benzene–Aliphatic Amine Photo-reactions.*—Neutral products were formed from all benzene–amine irradiations and were separated from the basic components by extraction of the latter with hydrochloric acid. The neutral products from several benzene–amine irradiations were bulked and distilled (b.p. 48–56 °C/0.05 mmHg) to give a colourless oil. G.l.c. analysis of this oil using columns packed with 8% Carbowax 20M on Universal B support revealed the presence of several compounds of which one ( $M^+ = 158$  m.u.) constituted 80% of the mixture.

Chromatographic procedures identified biphenyl as one of the minor components of the oil, but the other trace components were not identified. The major neutral product was isolated by preparative g.l.c. and shown not to react with common dienophiles. Its spectroscopic properties were consistent with 1,1',4,4'-tetrahydrobiphenyl. The u.v. spectrum of the compound in *n*-hexane had  $\lambda_{\text{max}}$  at 267 nm and significant i.r. absorptions at 3 025s, 1 640w, 1 425m, 1 408w, and 790s cm<sup>-1</sup>. The n.m.r. spectrum of the tetrahydrobiphenyl in CCl<sub>4</sub> solution had resonances at  $\delta 2.6$  (2 H, m, methylene), 2.7 (1 H, m, methine), and 5.6 (4 H, m, vinyl). The fraction of the reaction mixture which was volatile at 50 °C and water-pump pressure was subjected to acid extraction with 2M-hydrochloric acid to remove the unchanged amine. The neutral fraction was then examined by g.l.c. using a column packed with 10% dinonyl phthalate on Universal B support. By such a procedure the presence of cyclohexa-1,4-diene but not the corresponding 1,3-isomer was positively identified; this result was further confirmed using a  $\beta\beta'$ -oxydipropionitrile column.

*Quantum Yield Measurements.*—Quantum yields for the formation of the aliphatic amine–benzene adducts were determined using equivolume solutions of the amine and benzene and in the case of triethylamine 5% (v/v) of methanol was also incorporated. The deoxygenated solutions (400  $\mu\text{l}$ ) were sealed in quartz cells of 1-mm path-length and irradiated with light ( $1.07 \times 10^{-7}$  Einsteins/min) from a low-pressure mercury-arc lamp. Chemical actinometry (potassium ferrioxalate<sup>27</sup>) was used to monitor the lamp emission and light absorption of the irradiated solutions. The values thus determined for (1b), (3), [(7a) + (9)], and (13a) were respectively 0.004, 0.003, 0.012, and 0.005.

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<sup>27</sup> C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, **A235**, 518.