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EXCITED STATE REACTIONS OF ARENE-ETHENE-AMINE TRICHROMOPHORIC SYSTEMS

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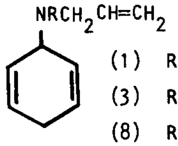
Summary. The efficiency and type of photochemical reaction of allylamines and benzene varies with N-alkyl substitution and from the secondary but not primary amines novel cyclic adducts involving both chromophores of the addend are formed

A wide variety of ethylenes undergo 1,2- and/or 1,3-photocycloaddition to benzenoid compounds[1] and 1,2- and 1,4-acyclic 1 1 addition products result from 254 nm irradiation of aliphatic amines and arenes [2] In contrast N,N-dialkylallyl amines display neither type of addition process and yield only minor amounts of amine-derived products from irradiation of their benzene solutions [3] The lack of photoreaction or reduction in efficiency of the addition of such bichromophoric addends to arenes is not uncommon and may result from energy dissipation within the exciplexes, proposed as intermediates for the two addition processes,[1,2] by through bond interaction between the chromophores of the potential addend [4] We now report some studies into this type of energy dissipation in inter- and intra-molecular trichromophoric systems and describe novel photoadducts between benzene and allylamines.

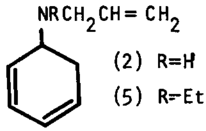
The efficiency of energy dissipation by the bichromophoric addend and hence its probability of photoreaction with benzene may be influenced by variations in the relative electron donor-acceptor characteristics of the chromophores Such possibilities have been investigated by a study of the photoreactions of benzene with N,N-diethylallylamine, N-ethylallylamine and allylamine Mixtures of benzene and the allylamine (1 0 6 molar ratio respectively) were irradiated (254 nm) under nitrogen in sealed quartz tubes and the progress of the reaction monitored by g.l c (7% Apiezon, 2% KOH) Allylamine and N-ethylallylamine both produced two 1 1 adducts (m s /g l c $\underline{M}^+$ = 135 and 163 m u respectively for each adduct) in ratios of 0 45 1 00 for the primary amine and 1 00 0 65 for the secondary amine (relative g l c retention times) the efficiencies for formation of these adducts were comparable with those from other primary and secondary amines and benzene under similar conditions.[2] In contrast but consistent with previous studies,[3] N,N-diethylallylamine produced only small amounts of solely amine derived material.

The 1:1 adducts from each system were isolated by preparative g.l.c. (column temp. <90°C) with purities in excess of 95%: the impurity being the other isomer but thermal interconversions were discounted and further purification proved impractical. The major and minor 1:1 adduct isomers from irradiation of benzene with allylamine were assigned structures (1) and (2) on the basis of analytical data, spectroscopic properties and comparison of the latter with those of compounds of closely similar structures. The major 1:1 adduct isomer from irradiation of N-ethylallylamine and benzene was also assigned the 1,4-acyclic addition structure but the minor isomer was deduced to have the novel structure (4) on the basis of analytical data and spectroscopic properties. In particular the ^1H n.m.r. spectrum (250 MHz $CDCl_3$) had resonances at δ values of 6.40 (1H, triplet J=7Hz, minor coupling of _ca_.1Hz), 6.06 (1H, triplet J=7Hz, minor coupling of _ca_. 1Hz), 3.01-2.88 (2H, six line unsymmetrical multiplet), 2.83-2.73 (1H. broadened quartet, J=5Hz), 2.63 (2H, quartet J=7Hz, minor coupling of _ca_. 1Hz), 2.51-2.40 (2H, doublet J=10Hz superimposed on very broad singlet), 2.05-1.95 (1H, 5 line symmetrical multiplet), 1.65-1.45 (2H, very complex multiplet of at least 12 lines), 1.35-1.26 (1H, broadened doublet), 1.24-1.11 (1H, very complex resonance), and 1.08 p.p.m. (3H, triplet J=7Hz). The infrared spectrum (liquid smear) had significant absorptions centered at 3050, 2970, 2980, 2900, 2860, 2800, 1620, 1450, 1380 and 1350 cm^{-1}. The formation of (4) is novel and intriguing as it has formally involved both chromophores of the addend. Formation of (4) by initial ethene 1,4-photocycloaddition to benzenes followed by attack of the amine moiety onto an ethene in the cyclohexa-1,4-diene residue is considered unlikely in view of the known low yield of such arene-ethene adducts compared to the _ortho_ and _meta_ modes of reaction[5] and as this pathway to (4) may be expected to be a two photon process its involvement is discounted by the linear formation of the isomer extrapolated to zero time. It also appears unlikely that (4) is formed from the unobserved 1,2-acyclic addition product (5) during work-up _via_ a thermal intramolecular Diels-Alder reaction since (2) the 1,2-acyclic addition isomer from allylamine and benzene was stable and isolated under identical conditions to (4) and in particular its cyclised isomer (6) was not detected.

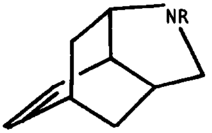
The proportion of the novel type of addition product in the mixture of isomers was increased significantly in the irradiations of benzene with diallylamine: the isomers (7) and (8) were formed in approximately equal amounts. The structures of (7) and (8) were again assigned on the basis of analytical and spectroscopic data. The ^1H n.m.r. spectrum (250 MHz, $CDCl_3$) of (7) had δ values of 6.38(1H, triplet J=7.5 Hz, minor coupling of _ca_. 1,5 Hz), 6.05 (1H, triplet J=7.5 Hz, minor coupling of _ca_. 1.5Hz), 5.96-5.80(1H, complex multiplet), 5.20-5.00(2H,complex multiplet, this and the previous resonance had multiplicity typical of $-CH=CH_2$ in allyl grouping), 3.33-3 13(2H, complex multiplet comprising two triplets centered at *ca*. 3.21 and 3.27, and a quartet at *ca*. 3.24, J values *ca*. 1.5Hz), 2.94-2.80 (2H, complex multiplet of at least six lines), 2.78-2.69(1H, broadened quartet J=5Hz), 2.55(1H, doublet J=9.5Hz), 2 48-2.38(1H, very broad singlet), 2 05-1.93 (1H, five line multiplet), 1.63-1.48(2H, very distorted triplet of triplets), 1.40-1 30(1H, doublet with minor splitting) and 1.30-1.15 p.p.m. (1H,complex multiplet of at least eleven lines) The infrared spectrum of (7) (liquid smear) had significant absorption at 3080, 3050, 3020, 2940,2860, 2800, 1645, 1620, 1420, 1375, 1350, 920 and 700 cm^{-1}. The structure of (8) was assigned in similar manner to (1) and (3) At present, there is no obvious reason why (4) and (7) are formed from irradiation of benzene with N-ethylallylamine and diallylamine respectively whereas products of this type involving both chromophores are not observed in the system incorporating allylamines but it is most noteworthy that no adducts involving solely ethene photoaddition to the arene were detected in any system



(1) R=H
(3) R=Et
(8) R=allyl

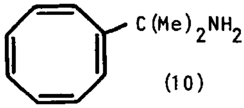


(2) R=H
(5) R=Et



(4) R=Et
(6) R=H
(7) R=allyl

Ph$(CH_2)_n$NMe-$CH_2CH=CH_2$
(9) a,n=2, b, n=3, c, n=1, d, n=0.



(10)

The allylamines quenched the fluorescence of benzene with increasing Stern-Volmer constants with increase in N-alkylation but from no system was emission attributable to that from an excited state complex observed. However, comparison of the fluorescene emission properties of the phenyl-amino-ethenyl trichromophoric systems (9) with those of mono *n*-alkyl benzenes, and phenyl-amino and phenyl-ethenyl non-conjugated bichromophoric systems showed that the allyl group may have a marked effect on the emission characteristics of such systems and does indeed effectively quench the arene-amine exciplex. For example the relative emission intensities (λ_{max} nm. 0.004M, cyclohexane)[6] of Ph-$(CH_2)_2$-N(Me)-*n*Pr (312), (9a)(310), Ph-$(CH_2)_3$-N(Me)-*n*Pr (332), and (9b)(315) were 24 1 35 3 respectively Further, consistent with the intermolecular systems involving N,N-dialkylallylamines and benzene, 254 nm irradiation of the trichromophoric systems (9a-d) gave no intramolecular adducts (contrast phenyl-amino[7] and phenyl-ethenyl bichromophoric systems[8]) but instead yielded mainly the fragmentation products N-methyl-2-phenethylamine, N-methyl-3-phenpropylamine, bibenzyl, and N-methyl aniline respectively.

Thus we suggest that for the inter- and intra-molecular tertiary amine-arene-ethene systems interaction of the three chromophores in the electronically excited state can, within geometrical restrictions, be very efficient and may result from either quenching of the exciplex precursors of the arene-ethene arene-amino addition processes by the second chromophore of the addend, or by quenching of the excited arene itself by the bichromophoric system, but whether either or both mechanisms lead to terplex formation has yet to be established.

Interestingly the amine-arene reaction appears to be little affected by the yne grouping since propargyl amines, even N,N-dialkyl derivatives, yield cyclohexa-1,4-diene derivatives (cf. (1)) from irradiation in benzene but isolation of the cyclo-octatetraene (10) from the photoreaction of 1,1-dimethylpropargyl amine and benzene provided the only example from the present study of a photoaddition reaction of the unsaturated chromophore of the addend to the arene.

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References and Notes

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