1055. *The Chemical Effects of γ-Radiation on Organic Systems. Part XII.*[1] *The Addition of Tertiary Amines to Alkenes*

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Under the influence of γ-radiation triethylamine undergoes addition to oct-1-ene to yield 2-diethylaminodecane (I) and other products.

The addition of amines to olefins, induced by t-butyl peroxide [2] is considered to be a chain reaction in which the t-butoxy radical attacks a hydrogen atom attached to an α-carbon atom of the amine, and the resulting radical derived from the amine may then attack the olefinic double bond. The formation of 1 : 1 addition products in relatively high yield, even without the amine in excess has been explained as due to chain termination by disproportionation of the radicals derived from the amine. Primary amines reacted satisfactorily but, of the secondary amines investigated, only piperidine and pyrrolidine gave satisfactory yields. It was suggested that this might be due to the difficult accessibility of the α-hydrogen atom, although statistical considerations are also relevant. The yields of the addition products of triethylamine and diethylamine with oct-1-ene were too small to isolate.

γ-Irradiation of triethylamine yields *meso*- and racemic 2,3-bisdiethylaminobutane, which together account for 89% of the distillable products, less volatile than triethylamine.[1] This suggests that the predominant radical formed is $Et_2N{\cdot}CHMe{\cdot}$. We therefore studied the effect of γ-radiation on mixtures of triethylamine and oct-1-ene in the molar ratios 18 : 1 and 4 : 3. After irradiation, the mixture was distilled and the material of b. p. 110—150° (bath temp.)/5 mm. was subjected to gas–liquid chromatography (g.l.c.) on Carbowax 1000. A high-boiling residue remained after the distillation. The weights of distillate and of residue were both greater in the case of the 18 : 1 mixture than of the 4 : 3, but the ratio of the weight of the residue to distillate was much higher in the latter case. The distillate contained *meso*- and racemic 2,3-bisdiethylaminobutane and the expected addition compound, 2-diethylaminodecane (I).

$$Et_2N{\cdot}CHMe{\cdot} + CH_2{=}CH{\cdot}[CH_2]_5{\cdot}Me \longrightarrow Et_2N{\cdot}CHMe{\cdot}[CH_2]_7{\cdot}Me \quad (I)$$

The latter was also obtained by methylation of 2-aminodecane,[3] prepared from methyl octyl ketone by a Leuckart reaction. The *G* values for these compounds are shown in Table 1.

The three compounds mentioned account for only 67% of the distillate in the case of the 18 : 1 mixture and 24% in the case of the 4 : 3 mixture. The gas chromatograms contain many other peaks. By treatment with acid, the material was separated into basic and non-basic fractions; but it was found that only one, minor, peak was due to a non-basic compound. The unknown peaks of greatest area were all eluted after 2-diethylaminodecane. It seemed that telomers were produced in preference to the monomeric

[1] Part XI, L. T. Allan and G. A. Swan, 1965, 4434.
[2] W. H. Urry and O. O. Juveland, *J. Amer. Chem. Soc.*, 1958, **80**, 3322.
[3] F. S. Crossley and M. L. Moore, *J. Org. Chem.*, 1944, **9**, 529.

TABLE 1

G Values of products formed by irradiation of triethylamine–oct-1-ene mixtures

Compound	Molar ratio (NEt_3 : C_8H_{16}) 18 : 1	4 : 3
meso-2,3-Bisdiethylaminobutane	0·32	0·05
Racemic ,,	0·37	0·04
2-Diethylaminodecane	0·12	0·11

addition product. The low yield, moreover, could not be due to difficult accessibility of the α-hydrogen atom, as suggested in the case of peroxide-initiated reactions.[2]

We also irradiated mixtures of 1-methylpiperidine and oct-1-ene in molar ratios 21 : 1, 16 : 1, and 4 : 3. Unfortunately, however, we were unable to separate the 1 : 1 adduct (1-methyl-2-octylpiperidine) from the mixture of 1,1′-dimethyl-2,2′-bipiperidyl and 1-methyl-(2-piperidinomethyl)piperidine.[4] On Carbowax 1000, all these compounds were eluted together, so that only their combined yield (A) could be measured. From the analysis of the radiolysis products of pure 1-methylpiperidine [1] the ratio of yields of 1,1′-dimethyl-2,2′-bipiperidyl plus 1-methyl-(2-piperidinomethyl)piperidine to 1,2-dipiperidinoethane (B) was known. On the assumption that this ratio would be the same when a mixture of 1-methylpiperidine and oct-1-ene was irradiated, a yield of 1-methyl-2-octylpiperidine was estimated; the results are shown in Table 2. The chromatogram also

TABLE 2

Estimated *G* values of 1-methyl-2-octylpiperidine formed by irradiation of mixtures of 1-methylpiperidine and oct-1-ene

Amine : octene (molar ratio)	Composition of product A (%)	B (%)	1-Methyl-2-octylpiperidine Estimated (%)	Estimated *G*
(*a*) 21 : 1	60·7	13·8	15·5	0·14
(*b*) 16 : 1	56·2	11·4	19·1	0·18
(*c*) 4 : 3	31·0	6·1	11·1	0·10

indicated that the irradiated 1-methylpiperidine–octene mixture contained three other compounds which were absent in irradiated 1-methylpiperidine. One of these was 1-nonylpiperidine, the *G* values for which were 0·06 (16 : 1) and 0·14 (4 : 3). These three compounds, together with 1-methyl-2-octylpiperidine, also accounted for 89% of the product, b. p. 140—180° (bath temp.)/5 mm., obtained by heating a mixture of 1-methylpiperidine and oct-1-ene with t-butyl peroxide.

One interesting feature of the above results is the fact that when the radicals are produced by γ-irradiation, dimers are formed, even in the presence of octene, whereas when the radicals are produced in a mixture of amine and octene in the same proportions through the agency of t-butyl peroxide, no dimers were detected. A factor which might favour dimerisation would be if the radiolytically produced radicals were formed in clusters. On the other hand, addition to the octene might be favoured by the higher temperature of the chemically-induced reaction, which might also be more specific in producing radicals at the $>N\cdot CH_2-$ group, rather than at the $>N\cdot Me$ group.

We also irradiated 1-allylpiperidine [5] and *N*-(but-3-en-1-yl)piperidine to discover whether the radical formed by loss of hydrogen atom from the 2-position of the piperidine ring might add on to the double bond to yield the indolizidine or quinolizidine system. However, we were unable to detect such products, although 1-allylpiperidine and indolizidine could be well separated by g.l.c. Apart from unchanged material, only small amounts of high-boiling products were obtained from these irradiations.

[4] G. Smith and G. A. Swan, *J.*, 1962, 886.
[5] N. H. Cromwell and A. Hassner, *J. Amer. Chem. Soc.*, 1955, **77**, 1568.

Experimental

General Directions.—These were as in Part XI.[1]

Irradiation of a Mixture of Triethylamine and Oct-1-ene.—(*a*) *Molar ratio*, 18 : 1. A mixture of triethylamine (230 ml.) and oct-1-ene (14·5 ml.) was irradiated for 479 hr. (total dose $3{\cdot}69 \times 10^{23}$ ev), then fractionally distilled. The distillate, b. p. 110—150° (bath temp.)/5 mm. (1·51 g.) was chromatographed on Carbowax 1000 at 72° (flow rate 30 ml./min.) and thus found to contain *meso*- (26·1%) and racemic (30·4%) 2,3-bisdiethylaminobutane and 2-diethylaminodecane (10·5%). The retention times of these were 19·5, 23·5, and 71·5 min., respectively. These compounds could also be separated on Apiezon L at 117°, with retention times of 19·0, 22·25, and 66·25 min., respectively. The residue from the distillation weighed 0·83 g.

(*b*) *Molar ratio*, 4 : 3. A mixture of triethylamine (11 ml.) and oct-1-ene (9 ml.) was irradiated for 474 hr. (total dose $2{\cdot}99 \times 10^{22}$ ev). The distillate (0·09 g.) contained the above three products to the extent of 6·2, 5·0, and 13·0%, respectively, and the residue weighed 0·30 g.

2-*Aminodecane.*—Methyl octyl ketone (5·4 g.) was allowed to react with a mixture of ammonium hydroxide (10 ml.) and 90% formic acid (10 ml.) as described in analogous cases by Crossley and Moore.[3] 2-*Formylaminodecane* crystallised from chloroform–ether and had m. p. 74—75° (Found: N, 7·5. $C_{11}H_{23}NO$ requires N, 7·55%). This was refluxed with concentrated hydrochloric acid for 48 hr. and the mixture evaporated to dryness. Crystallisation of the residue from light petroleum (b. p. 60—80°) afforded 2-aminodecane hydrochloride, m. p. 66—68°.

2-*Diethylaminodecane* (I).—The above hydrochloride (1·57 g.), ethyl iodide (5·41 g.), sodium carbonate (6·5 g.), and water (60 ml.) were refluxed for 46 hr. The mixture was basified with 40% sodium hydroxide solution (5 ml.) and extracted with ether (3 × 100 ml.). The extract was dried (Na_2SO_4), the ether removed, and the residue heated at 60° for 2 hr. with acetic anhydride (6 ml.) in benzene (20 ml.). The solution was shaken with 10% sodium carbonate solution to decompose unchanged acetic anhydride, dried (Na_2SO_4), and benzene removed. The residue (1·06 g.) yielded the *hydrochloride*, which after crystallisation from ethanol–light petroleum had m. p. 71° (Found: C, 68·1; H, 12·8; N, 5·5. $C_{14}H_{32}ClN$ requires C, 67·35; H, 12·9; N, 5·6%).

Irradiation of a Mixture of 1-*Methylpiperidine and Oct-1-ene.*—1-Methylpiperidine was purified as described earlier.[4] (*a*) A mixture of this (233 ml.) and oct-1-ene (14·5 ml.) (*i.e.*, in molar ratio 21 : 1) was irradiated for 568 hr. (total dose $4{\cdot}44 \times 10^{23}$ ev). (*b*) A mixture of 1-methylpiperidine (220 ml.) and oct-1-ene (18 ml.) (16 : 1) was irradiated for 376 hr. (total dose $2{\cdot}82 \times 10^{23}$ ev). (*c*) A mixture of 1-methylpiperidine (100 ml.) and oct-1-ene (100 ml.) (4 : 3) was irradiated for 376 hr. (total dose $2{\cdot}32 \times 10^{23}$ ev). In each case, the material was fractionally distilled, the fraction of b. p. 130—160° (bath temp.)/5 mm. being collected. The weights of distillate were (*a*) 1·40 g., (*b*) 0·91 g., (*c*) 0·75 g., and the weights of residue were 1·0, 1·35, and 2·81 g., respectively. The distillate was chromatographed on Carbowax 1000 at 117° (flow rate 30 ml./min.). The retention times of 1,1′-dimethyl-2,2′-bipiperidyl, 1-methyl-(2-piperidinomethyl)piperidine, and 1-methyl-2-octylpiperidine (A) was 36·75 min. and of 1,2-dipiperidinoethane (B) 46·25 min.; that of 1-nonylpiperidine was 30·25 min.

The latter was prepared by reduction of *N*-pelargonylpiperidine with lithium aluminium hydride in ether.

Irradiation of 1-*Allylpiperidine.*—1-Allypiperidine (5 ml.),[5] shown by g.l.c. to be free from piperidine, was irradiated for 330 hr. (total dose $7{\cdot}36 \times 10^{21}$ ev) and then distilled, only a very small amount of residue remaining. Gas chromatography failed to detect the presence of anything except 1-allylpiperidine in the distillate.

Indolizidine.—1-Trichloromethyl-2-2′-pyridylethanol, prepared by Einhorn's method [6] was hydrolysed to β-2-pyridylacrylic acid.[7] A solution of the latter (0·75 g.) in acetic acid (100 ml.), in the presence of Adams catalyst (0·2 g.) took up the required amount of hydrogen in 5 hr. The solution was filtered, mixed with concentrated hydrochloric acid (5 ml.), and evaporated to dryness. β-2-Piperidylpropionic acid was obtained from the hydrochloride, as described by Galinovsky, Vogl, and Weiser,[8] and when crystallised from water had m. p. 142—143° (Found: N, 8·55. Calc. for $C_8H_{15}NO_2$: N, 8·9%). This was converted into indolizidine as described by the latter authors.

[6] A. Einhorn, *Annalen*, 1891, **265**, 208.
[7] J. A. King, V. Hofmann, and F. H. McMillan, *J. Org. Chem.*, 1951, **16**, 1100.
[8] F. Galinovsky, O. Vogl, and R. Weiser, *Monatsh.*, 1952, **83**, 114.

When 1-allylpiperidine and this were chromatographed on Carbowax 1000 on alkali-washed Celite 545 at 48°, with a flow rate of 30 ml./min., the retention times were 19·5 and 27·25 min., respectively. On Fluoropak 80, the corresponding times were 45·5 and 79·0 min.

N-(*But*-3-*en*-1-*yl*)*piperidine*.—But-3-en-1-yl bromide [9] (0·02 mole) and piperidine (0·02 mole) were refluxed in benzene (5 ml.) in the presence of potassium carbonate for 10 hr. Sodium hydroxide solution was added and the organic layer separated, dried ($MgSO_4$), and distilled to give the base, b. p. 152°. The *picrate*, from ethanol, had m. p. 117—118° (Found: C, 49·2; H, 5·5; N, 15·45. $C_9H_{17}N,C_6H_3N_3O_7$ requires C, 48·9; H, 5·45; N, 15·2%). The *picrolonate*, from ethanol, had m. p. 160—163° (Found: C, 56·5; H, 6·4; N, 17·35. $C_9H_{17}N,C_{10}H_8N_4O_5$ requires C, 56·55; H, 6·25; N, 17·35%). The homogeneity of the base was checked by g.l.c.

Irradiation of N-(*But*-3-*en*-1-*yl*)*piperidine*.—The base (4 ml.) was irradiated for 835 hr. (total dose $1·49 \times 10^{22}$ ev). Gas chromatography failed to detect any new product in the material.

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[9] R. P. Linstead and H. N. Rydon, *J.*, 1934, 1995.