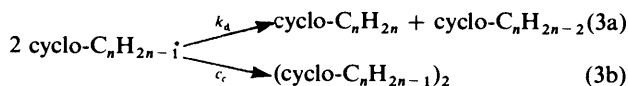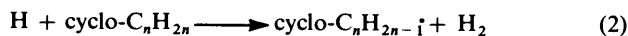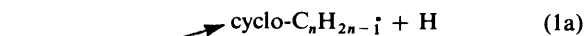# Termination Reactions of C_5—C_{12} Cycloalkyl Radicals and Carbenes

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Reactions of C_5—C_{12} cycloalkyl radicals and carbenes produced during radiolysis, vacuum-u.v. photo-lysis, and decomposition of cycloalkanone p-tosylhydrazones were investigated. The disproportionation to combination ratios of radicals are *ca.* 1 and agree with the ratios of linear secondary radicals. The disproportionation of smaller cycloalkyl radicals yields *cis*-cycloalkenes and cycloalkanes; from C_9 and C_{10} *cis*- and *trans*-cycloalkenes and cycloalkanes and from C_{11} and C_{12} *trans*-cycloalkenes and cycloalkanes are produced. Both atoms of H_2 given off in the elimination reaction from excited cycloalkane molecules originate from the same carbon atom and in this process carbenes are formed. Rearrangement of small (C_5, C_6) and large (C_{11}, C_{12}) cycloalkylcarbenes in the solvent of the given cycloalkane occurs by 1,2-hydrogen migration. C_7—C_{10} carbenes rearrange both by hydrogen atom migration and transannular insertion.

It is well known[1] that during radiolysis and vacuum-u.v. photolysis of liquid cyclopentane and cyclohexane the main reaction, *viz.* hydrogen formation, takes place by two mechanisms with atomic and with molecular elimination of hydrogen [reactions (1)—(3) where cyclo-C_nH_{2n}* stands for

$$\text{cyclo-}C_nH_{2n}\text{*} \begin{cases} \longrightarrow \text{cyclo-}C_nH_{2n-1} + H & (1a) \\ \longrightarrow \text{cyclo-}C_nH_{2n-2} + H_2 & (1b) \end{cases}$$

$$H + \text{cyclo-}C_nH_{2n} \longrightarrow \text{cyclo-}C_nH_{2n-1} + H_2 \qquad (2)$$

$$2\text{ cyclo-}C_nH_{2n-1} \begin{cases} \xrightarrow{k_d} \text{cyclo-}C_nH_{2n} + \text{cyclo-}C_nH_{2n-2} & (3a) \\ \xrightarrow{c_c} (\text{cyclo-}C_nH_{2n-1})_2 & (3b) \end{cases}$$

an electronically excited molecule].

During atomic hydrogen formation in reactions (1a) and (2) cycloalkyl radicals are produced giving cycloalkane, cyclo-alkene, and dicycloalkyl as final products in the self-disproportionation and combination reactions (3a,b). Radical acceptors such as I_2, NO, SO_2, or O_2 greatly suppress dicycloalkyl formation; however, in radiolysis the yield never decreases to zero. The production of a dimer unscavengeable by radical acceptors is a special feature of radiolytic reactions.[1] Some of the radicals form in close proximity to each other (in the so-called spur) and there is a high probability of their reacting with each other before diffusing into the bulk of liquid. The non-scavengeable dimer yield is more or less independent of the nature of the scavenger and also of its concentration (at least up to 10^{-2} mol dm^{-3}) provided that the scavenger is not completely used up before the end of irradiation.

The cycloalkene yield also decreases in the presence of radical scavengers. However, the ratio cycloalkene:dicycloalkyl is much higher in the presence of radical acceptors than in their absence. This is because cycloalkene forms in two reactions: one of them (3a) is influenced by the scavenger and the other one (1b) is not.

The measurement of the yields of alkene (X, Y) and dicycloalkyl (U, Z) in the absence and presence of radical scavengers gives the rate constant ratio k_{3a}/k_{3b}, *i.e.* the disproportionation to combination ratio of the relevant radicals (k_d/k_c).[2-7]

$$\frac{X - Y}{U - Z} = \frac{k_{3a}}{k_{3b}} = \frac{k_d}{k_c} \qquad (4)$$

The elimination of H_2 from smaller alkane molecules occurs predominantly from a single carbon atom.[8] A carbene intermediate is assumed to be left behind which is then rapidly transformed to alkene.

The larger cyclic carbenes, produced in thermal decomposition of tosylhydrazone sodium salts of ketones, in addition to transformations to alkenes, can rearrange to bridged bicyclic alkanes in transannular insertion.[9-11] In a paper published recently[12] it was found that the distribution of products formed in H_2 elimination from cyclo-octane (cyclo-octene, bicyclo-[3.3.0]octane, and bicyclo[5.1.0]octane) agrees with the distribution of products obtained in the stabilization of cyclo-octylcarbene in the same solvent. It was concluded that H_2 elimination from cyclo-octane occurs exclusively from a single carbon atom.

In the present paper we investigate and compare the stabilizing reactions of 5—12-membered cyclic carbenes and also the self-termination reactions of cycloalkyl radicals.

Experimental

The cycloalkanes investigated were Fluka products with the exception of cyclononane and cycloundecane, though these compounds were prepared starting with Fluka cycloalkanones. All compounds were purified by preparative g.l.c. and percolation through activated silica gel. Cycloalkanone p-tosylhydrazones were synthesized in the usual way.[13]

Radiolytic experiments were carried out by ^{60}Co γ-irradiation.[4,7] The yields measured in pure alkanes were extrapolated to zero irradiation dose whereas in cycloalkane–scavenger systems the data used for our discussion were obtained at relatively low doses, *ca.* 20 kGy. As scavengers we used I_2 or O_2 in concentrations of several times 10^{-3} mol dm^{-3}. Typical results related to cyclodecane radiolysis are collected in Table 1. The yields are given in G units which means the number of molecules produced upon absorption of 100 eV radiation energy.

For the photolytic experiments on alkanes, an irradiation system involving a 7.6 eV bromine lamp was utilized.[12] Photolysis of p-tosylhydrazone sodium salts of cycloalkanones was carried out in the given cycloalkane solvent by means of a high-pressure mercury lamp with a Pyrex filter. The sodium salt was prepared *in situ* by adding excess of sodium ethoxide or sodium hydride to the solution of tosylhydrazone in cycloalkane. Because of the low solubilities low tosylhydrazone concentrations had to be applied (1—5 × 10^{-3} mol cm^{-3}). The solutions

Table 1. Dehydrogenation product formation from cyclodecane during radiolysis in the absence and presence of I_2 radical scavenger

| | G | | | | |
Products	Without scavenger	With 2×10^{3} mol dm^3 I_2	$k_d/k_c{}^a$	G Unimolecular^b	G Radical^c
cis-Cyclodecene	1.14	0.79	0.30	0.57^d (28%)	0.57^e
trans-Cyclodecene	2.55	1.58	0.84	0.95^d (47%)	1.60
cis-Bicyclo[5.3.0]decane	0.38	0.36		0.38 (19%)	
cis-Bicyclo[4.4.0]decane	0.12	0.12		0.12 (6%)	
Dicyclodecyl	1.90	0.75			1.90

^{a} Calculated by equation (4). ^{b} Product formation in unimolecular H_2 elimination [reaction (1b)]. ^{c} Product formation in radical reactions (3a and b). ^{d} Calculated by equation (5). ^{e} Calculated by $G = X - G(\text{cycloalkene})_{\text{unimol.}}$
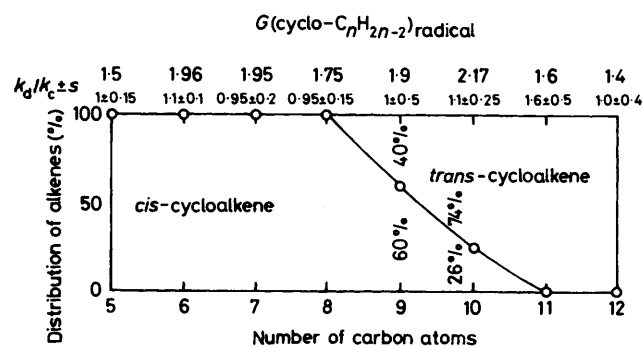
Figure 1. G value and percentage distribution of alkenes formed in radical reactions during radiolysis and the k_d/k_c ratios of radicals

were mixed for 1 h under argon before photolysis and were kept under argon during photolysis. Without photolysis no tosylhydrazone decomposition was observed.

The experiments were carried out at 25 °C. Since cyclododecane melts at 59 °C, measurements with this compound were carried out at 70 °C.

The products were analysed by g.l.c.

Results and Discussion

Of the decomposition products formed during the radiolysis of cyclodecane, cis-bicyclo[5.3.0]decane and cis-bicyclo[4.4.0]-decane originate from H_2 elimination reaction (1b), and dicyclodecyl comes from the dimerization reaction (3b) and therefore its formation is connected with the atomic hydrogen detachment (1a). cis- and trans-cyclodecenes originate from both reactions. Supposing that k_d/k_c in the spur does not differ appreciably from that in the bulk medium,[1] the yield of cycloalkene produced in a unimolecular reaction can be calculated by subtracting from the total cycloalkene yield the fraction which is formed in radical reactions [equation (5)].

$$G(\text{cycloalkene})_{\text{unimol.}} = X - (k_d/k_c)\,U \qquad (5)$$

The radiolytic results obtained from radical reactions and from unimolecular H_2 elimination in the C_5—C_{12} cycloalkanes are demonstrated in Figures 1 and 2, respectively. Errors in k_d/k_c were calculated by equation (6) which takes into account the Gaussian propagation of errors. s_X, s_Y, s_U, and s_Z stand for

$$s = \frac{1}{Z - U}\sqrt{s_X{}^2 + s_Y{}^2 + (k_d/k_c)^2(s_U{}^2 + s_Z{}^2)} \qquad (6)$$

the error in X, Y, U, and Z. The ratio of H and H_2 detachments is approximately 2.5:1 in radiolysis and 1:5 in photolysis.

Radical Reactions.—The data in Figure 1 indicate that k_d/k_c is
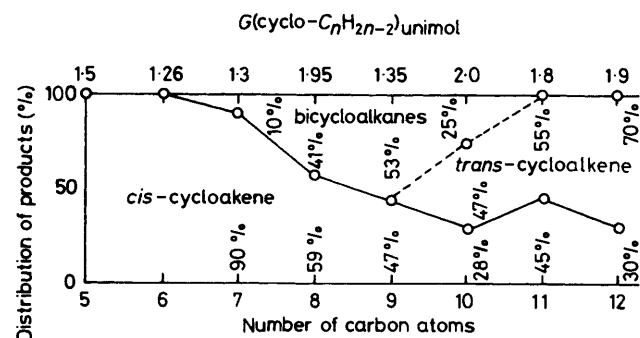
Figure 2. G value and percentage distribution of products formed in unimolecular H_2 elimination from cycloalkanes in radiolysis. Bicycloalkanes observed and their percentage yields are as follows: C_7 cis-bicyclo[4.1.0]heptane 10%; C_8 cis-bicyclo[3.3.0]octane 38%, cis-bicyclo[5.1.0]octane 3%; C_9 cis-bicyclo[4.3.0]nonane 42%, cis-bicyclo[6.1.0]nonane 11%; C_{10} cis-bicyclo[5.3.0]decane 19%, cis-bicyclo[4.4.0]decane 6%

independent of the size of the cycloalkyl radicals (k_d/k_c ca. 1); only the ratio for cycloundecyl radicals slightly exceeds this value. Ratios of ca. 1 were also found for linear secondary alkyl radicals.[14]

During the encounter of two radicals the steric arrangement is favourable for disproportionation when the axis of the p orbital of the unpaired electron (perpendicular to the plane of the paper) is close to the plane determined by C(2), C(3), and H(1). [The last, H(1), is being abstracted in the reaction.] Such an arrangement in linear alkyl radicals can easily develop by internal rotation. In cyclic radicals, however, the development of the favourable orientation may be hindered. On the basis of the relatively high value of k_d/k_c of the cycloalkyl radicals being independent of the ring size and equal to the ratio of linear secondary radicals, it is reasonable to suppose that the system here can also easily overcome the steric constraints and a favourable arrangement can develop with small deformation. (It is worth mentioning that in pulsed experiments the rate of disappearance of cyclopentyl and cyclohexyl radicals was found to be equal to the diffusion-controlled limit.[15] That means every encounter of singlet radical pairs leads to a termination reaction, to disproportionation, or to combination.)

In the disproportionation of smaller cycloalkyl radicals only cis-cycloalkenes are produced; from cyclononane and cyclo-

Table 2. Distribution of products formed during H_2 elimination from cyclodecane and during decomposition of cyclodecanone tosylhydrazone sodium salt

Solvent	Product Method	cis-Cyclodecene (%)	trans-Cyclodecene (%)	cis-Bicyclo[5.3.0]decane (%)	cis-Bicyclo[4.4.0]decane (%)
Cyclodecane	Photolysis of tosylate	30	45	19	6
	Radiolysis	28	47	19	6
	7.6 eV photolysis	28	47	20	5
Diethylene glycol	Thermal decomposition	14 [a]	6	62	18
diethyl ether	of tosylate	15.5 [b]	3.5	63	18
Diglyme		40 [c]	7	23	30

[a] Ref. 9. [b] Ref. 10. [c] Ref. 11.

decane both *cis*- and *trans*-isomers are formed; from cyclo-undecane and cyclododecane only the *trans*-forms are produced.

The formation of *cis*- and *trans*-isomers depends on the steric arrangement of the radical site just before hydrogen abstraction. If the C(4) atom is in the '*anti*'-like position with respect to C(1) before abstraction the formation of *trans*-alkene is favoured whereas the '*gauche*'-like position leads mainly to production of the *cis*-isomer. Naturally, in the case of smaller rings only the '*gauche*'-like position is accessible in the radical therefore we obtain the *cis*-isomer.

In the cyclononyl and cyclodecyl radical C(4) is probably in a position from which there is a possibility of moving into the '*anti*'-like or into the '*gauche*'-like position with respect to C(1). Alternatively the formation of *cis*- and *trans*-alkene occurs from two different conformers of the radicals. In the C_{11} and C_{12} radicals, C(1) and C(4) should be in the '*anti*'-like position. The saturated parts connecting C(1) and C(4) are very long here because they consist of 7 and 8 carbon atoms, respectively. When C(1) and C(4) are in the '*anti*'-like position the saturated seven- or eight-membered chain can take up a more favourable antiperiplanar conformation than in the case of a synclinal position of C(1) and C(4).

H_2 Elimination. Unimolecular Stabilization of Carbenes.—
Hydrogen elimination from 7—10-membered cycloalkanes results also in bicycloalkanes (Figure 2). The alkenes formed from rings larger than C_9 contain both the *cis*- and *trans*-isomers. The distribution of products shows qualitatively a close similarity to the product distribution formed in the thermal decomposition of sodium salts of cycloalkanone *p*-tosyl-hydrazones under aprotic conditions.[9–11] In order to obtain comparable quantitative results we repeated the experiments with cycloalkanone tosylhydrazones, photolysing them in a solution of the given alkane. As an example, results obtained from the C_{10} ring are shown in Table 2. The distribution of products formed in the decomposition of tosylhydrazone agrees quite satisfactorily with that found during H_2 elimination in photolysis and radiolysis. We arrived at the same conclusion from the experiments with C_7—C_9 and C_{11}, C_{12} rings as well. The agreement among the product distributions indicates that, as was already noted for cyclo-octane,[12] H_2 is eliminated from a single carbon atom; this process results in the formation of a carbene intermediate. As the product ratio is independent of the method of carbene generation it is probable that this

intermediate thermally equilibrates before its further reactions.

Only one product, cyclopentene or cyclohexene, is formed in the stabilization of cyclopentyl- or cyclohexyl-carbene: these are the products of H_2 elimination as well. The present study does not contradict the idea that elimination also occurs mainly from a single carbon atom as has already been suggested for cyclohexane on the basis of deuterium-labelling experiments.[16–18]

It is noteworthy that the distribution of C_7—C_{12} carbene stabilization products very much depends on the solvent. This solvent dependence is highest in the case of cyclodecylcarbene: *viz.* cyclodecyl carbene rearranges first of all by 1,2-hydrogen migration in cyclodecane solvent, whereas transannular insertion is the main reaction in diethylene glycol diethyl ether. The rates of the two reactions are nearly equal in diglyme (Table 2). A possible explanation of the solvent effect could be the influence of the surroundings on the distribution of the ring conformers thereby also inducing a solvent effect in the carbene stabilization.

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