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RADIOLYTIC SYNTHESIS OF HIGH-MOLECULAR-WEIGHT ALKANES FOR CHROMATOGRAPHIC CHARACTERIZATION AND IDENTIFICATION PURPOSES

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SUMMARY

A radiolytic variant of the Wurtz and Wurtz–Grignard coupling reactions is described, requiring only very small amounts of haloalkane reactants and enabling synthesis of high-molecular-weight alkanes for chromatographic characterization and identification purposes. The method consists in the γ-irradiation at room temperature of dilute solutions of chloro- or bromoalkanes in *cis*- or *trans*-decalin. Chromatograms obtained after irradiation consisted of an easily recognizable pattern, that is characteristic for irradiated *cis*- or *trans*-decalin, containing either chloro- or bromoalkanes. Superimposed on this pattern was a very limited number of peaks that are dependent on the exact identity of the chloro- or bromoalkane. These extra peaks can easily be unambiguously assigned and may thus be used for chromatographic characterization and identification purposes. Under the conditions of the experiments, no radical isomerization was observed.

INTRODUCTION

Chromatographic identification may be accomplished by direct comparison of retention times in analyses performed under identical conditions or by comparison with retention indices taken from the literature. Also, more sophisticated equipment may be used, such as gas chromatographs coupled to mass or other spectrometers, allowing comparison of mass spectra or other types of spectra. Unfortunately, the number of compounds that is commercially available is restricted and the same applies to appropriate information available in the literature. Especially for high-molecular-weight compounds, neither the compounds themselves nor the appropriate literature information is often available. For a definite assignment of chromatographic peaks to specific compounds, these compounds must therefore be synthesized. This is not only time consuming; the high cost of the reactants involved and the relatively large amounts of products required (> 1 ml) may also make it prohibitively expensive in a number of cases.

In this work, a radiolytic variant of the Wurtz and Wurtz–Grignard coupling reactions is described that is easy to apply and that requires only very small amounts of

the haloalkane reactants. Only minute amounts of the high-molecular-weight alkanes are obtained by this method, but these are sufficient for chromatographic characterization and identification purposes.

PRINCIPLE OF THE METHOD

The method consists in the γ-irradiation at room temperature of the chloro- and bromoalkane reactants in low concentration in *cis*- or *trans*-decalin (decahydronaphthalene) solutions. Primarily, this irradiation mainly leads to excitation and ionization of decalin, since absorption of ionizing radiation by matter is non-selective:

$$\text{Decalin} \ \text{\Large\leadsto} \ \text{Decalin}^* \tag{1}$$

$$\text{\Large\leadsto} \ \text{Decalin}^+ \ + \ e^- \tag{2}$$

Due to the low ionization energy of decalin with respect to that of most chloro- and bromoalkanes[1,2], no hole transfer to these compounds occurs. Chloro- and bromoalkanes are however quite efficient electron scavengers and react with electrons by dissociative electron attachment[3], yielding neutral alkyl radicals:

$$RX + e^- \longrightarrow R^{\cdot} + X^- \tag{3}$$

(Excitation energy transfer, if occurring, also yields this radical.) The so-formed neutral radicals may react with radicals originating from the radiolysis of decalin, *e.g.*, formed by dissociation of excited decalin molecules or they may react mutually by disproportionation and combination. Combination leads to the formation of an alkane compound, containing twice as many carbon atoms as the chloro- or bromoalkane reactant:

$$R^{\cdot} + R^{\cdot} \longrightarrow R\text{--}R \tag{4}$$

By use of decalin solutions, containing two different chloro- or bromoalkanes, cross-combination products may also be obtained:

$$R_1X + e^- \longrightarrow R_1^{\cdot} + X^- \tag{5}$$

$$R_2X + e^- \longrightarrow R_2^{\cdot} + X^- \tag{6}$$

$$R_1^{\cdot} + R_2^{\cdot} \longrightarrow R_1\text{--}R_2 \tag{7}$$

In view of the above, it is expected that different chloro- or bromoalkanes affect the radiolysis of decalin in a similar way. The only appreciable difference anticipated is the nature of the alkyl radical formed by dissociative electron attachment and the products that originate from it by subsequent reactions. Chromatograms of irradiated

solutions may therefore be expected to consist of (i) a characteristic pattern that is identical for different solutions of either chloro- or bromoalkanes and (ii) a few peaks that are different and that are due to compounds originating from reactions of the alkyl radicals formed by dissociative electron attachment to the haloalkane reactant. In the high-molecular-weight region of the chromatogram, these may be anticipated to be products formed by mutual combination (and cross-combination if the solution contains two different haloalkanes) and by combination with neutral radicals originating from the radiolysis of decalin. As far as these are concerned and in view of the bicyclic nature of decalin, only $C_{10}H_{17}^{\cdot}$ radicals resulting from carbon–hydrogen bond scission are expected to be present in appreciable amounts; carbon–carbon bond scission leads to the formation of a biradical that disappears by mutual reaction of the two radical sites. The anticipated predominance of $C_{10}H_{17}^{\cdot}$ radicals is confirmed by the experimental observation that in the gamma radiolysis of liquid decalin the yield of C_1–C_5 hydrocarbons is very low[4]. The number of products that are specific for a particular chloro- or bromoalkane may therefore be expected to be quite small. Also, differentiation of the mutual combination product of the alkyl radicals formed by dissociative electron attachment to the haloalkane reactant, from combination products with $C_{10}H_{17}^{\cdot}$ radicals, should generally be easy to accomplish.

If all this corresponds to reality and if no radical isomerization occurs, then the combination product may be utilized for chromatographic characterization and identification purposes. The results presented in this paper show that this is indeed the case.

EXPERIMENTAL

Reagents used in this study were *cis*- and *trans*-decalin from Merck-Schuchardt, 1-chlorooctane, 1-bromoheptane and 1- and 2-bromooctane from Fluka and 3-bromooctane from K&K. The decalins were purified by passing through a column containing silica gel, which had been activated immediately prior to use by heating at 250°C for over 24 h. The other products, which were used as additives, were used as received.

Solutions, prepared by conventional techniques, were contained in cylindrical tubes made of quartz. Oxygen was removed by bubbling with argon for 30 min. After deoxygenation, samples were carefully sealed. Irradiations with ^{60}Co γ-rays were carried out at room temperature at the Institute for Radioelements at Fleurus. The absorbed dose was $6.7 \cdot 10^{20}$ eV g^{-1}.

Chromatographic analyses were performed on a Sigma 3 gas chromatograph (Perkin-Elmer) equipped with an inlet-splitting capillary injector and a flame ionization detector. A SCOT column (52 m × 0.5 mm I.D.) made of glass and coated with OV-101 was employed and helium was used as the carrier gas throughout the study.

RESULTS

Chromatograms obtained at a column temperature of 140°C after irradiation of *cis*-decalin containing respectively 1 mole-% 1-bromoheptane, 1-bromooctane and 2-bromooctane are shown in Fig. 1. They consist of an easily recognizable pattern, that
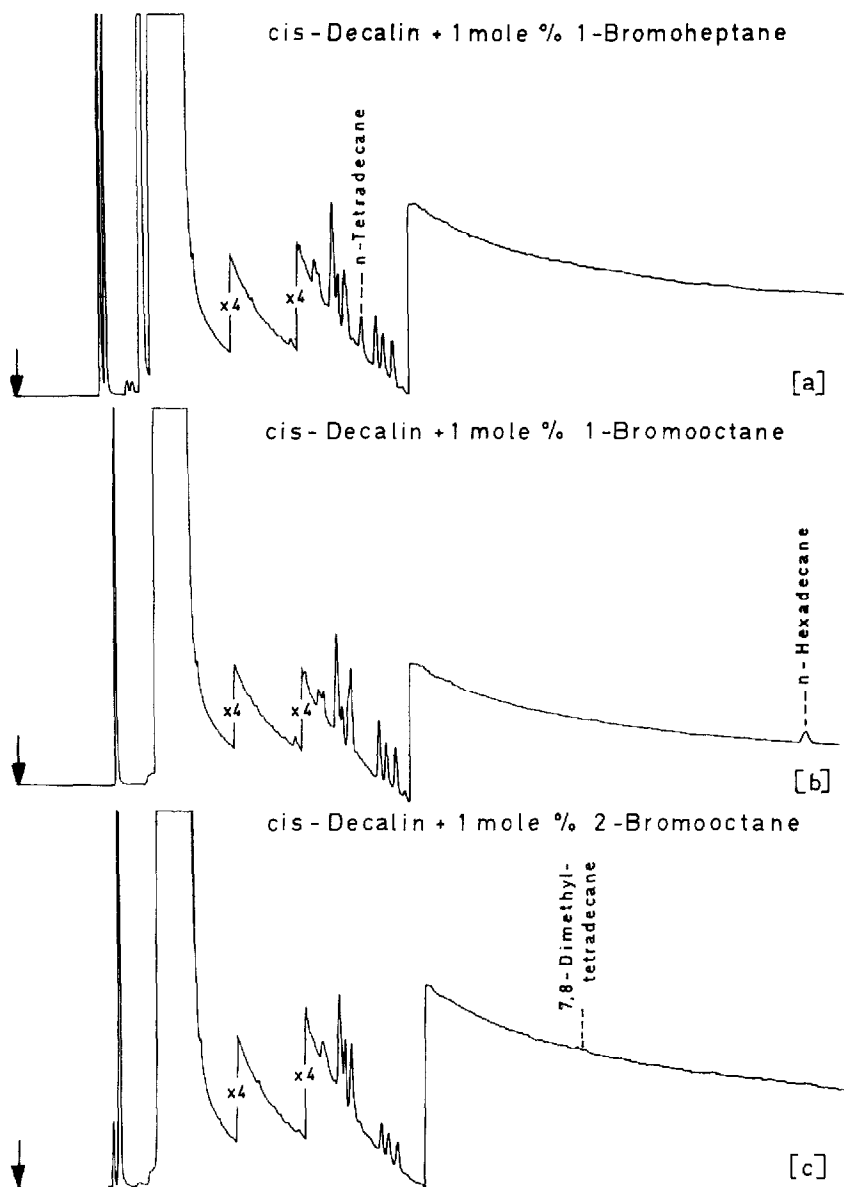
Fig. 1. Chromatograms obtained at a column temperature of 140°C after irradiation of *cis*-decalin, containing respectively 1 mole-% 1-bromoheptane (a), 1-bromooctane (b) and 2-bromooctane (c).

is quite analogous in all three cases. In addition to this characteristic pattern, one extra peak (marked respectively *n*-tetradecane and *n*-hexadecane) is observed after the elution of decalin in solutions containing 1-bromoheptane and 1-bromooctane. In the case of *cis*-decalin solutions, containing 2-bromooctane, the extra peak (marked 7,8-dimethyltetradecane) is both double and very weak.
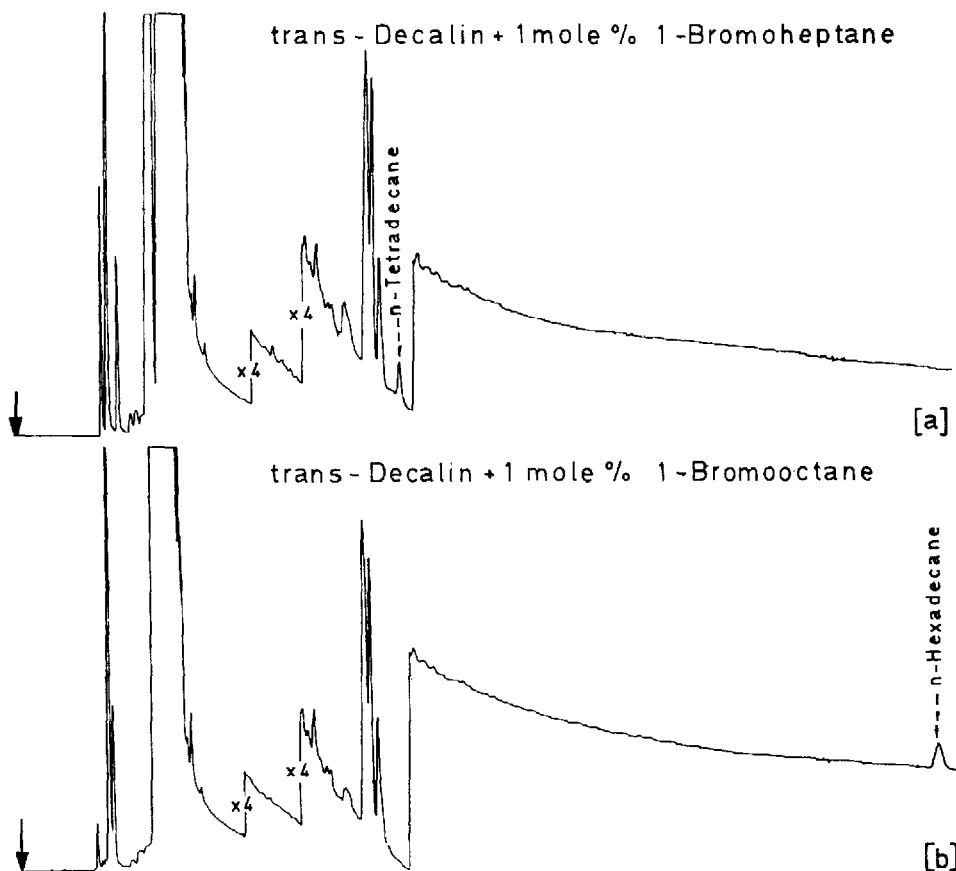
Fig. 2. Chromatograms obtained at a column temperature of 140°C after irradiation of *trans*-decalin, containing respectively 1 mole-% 1-bromoheptane (a) and 1-bromooctane (b).

Chromatograms obtained at a column temperature of 140°C after irradiation of *trans*-decalin containing respectively 1 mole-% 1-bromoheptane and 1-bromooctane are shown in Fig. 2. They again exhibit an easily recognizable pattern common to each case and one extra peak (after the elution of decalin) depending on the bromoalkane present.

Chromatograms obtained at a column temperature of 200°C after irradiation of *cis*-decalin containing respectively 1 mole-% 1- and 2-bromooctane are shown in Fig. 3. Two very prominent groups of peaks are observed in these chromatograms, the first one being dependent on the bromoalkane present and the second one being the same in each case. In addition, an early peak is present (after the elution of decalin) in the case of 1-bromooctane solutions, which is not observed for 2-bromooctane solutions.

Chromatograms obtained at a column temperature of 200°C after irradiation of *trans*-decalin containing respectively 1 mole-% 1-bromoheptane and 2-bromooctane are shown in Fig. 4. Again, two very prominent groups of peaks are observed in each case, the first one being dependent on the bromoalkane present and the second one being the same in each case.
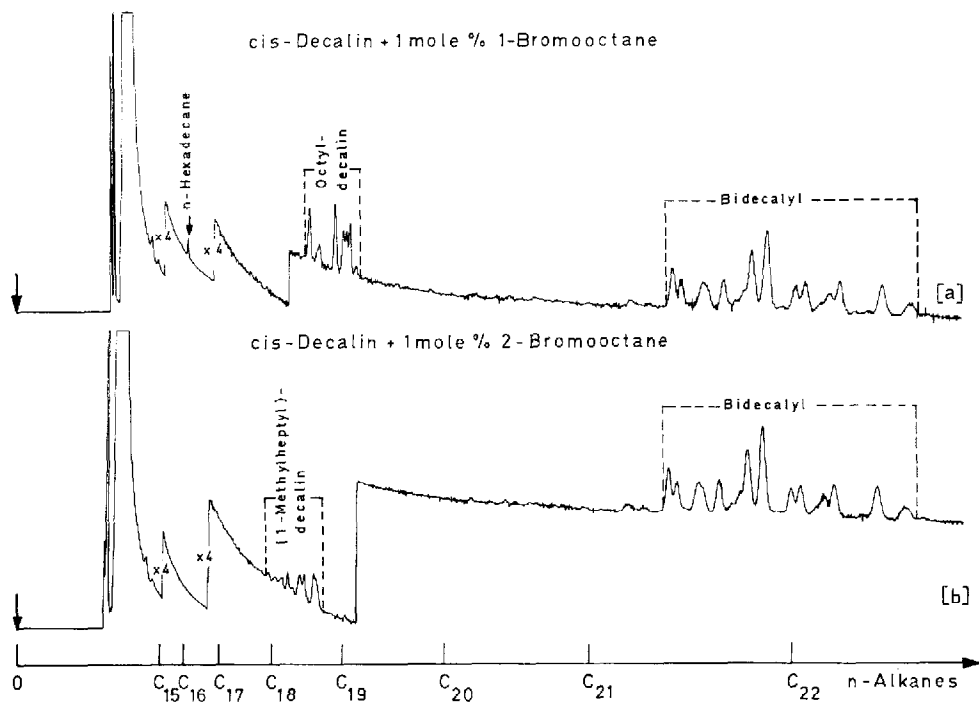
Fig. 3. Chromatograms obtained at a column temperature of 200°C after irradiation of *cis*-decalin, containing respectively 1 mole-% 1-bromooctane (a) and 2-bromooctane (b); the scale indicates the retention characteristics of *n*-alkanes.
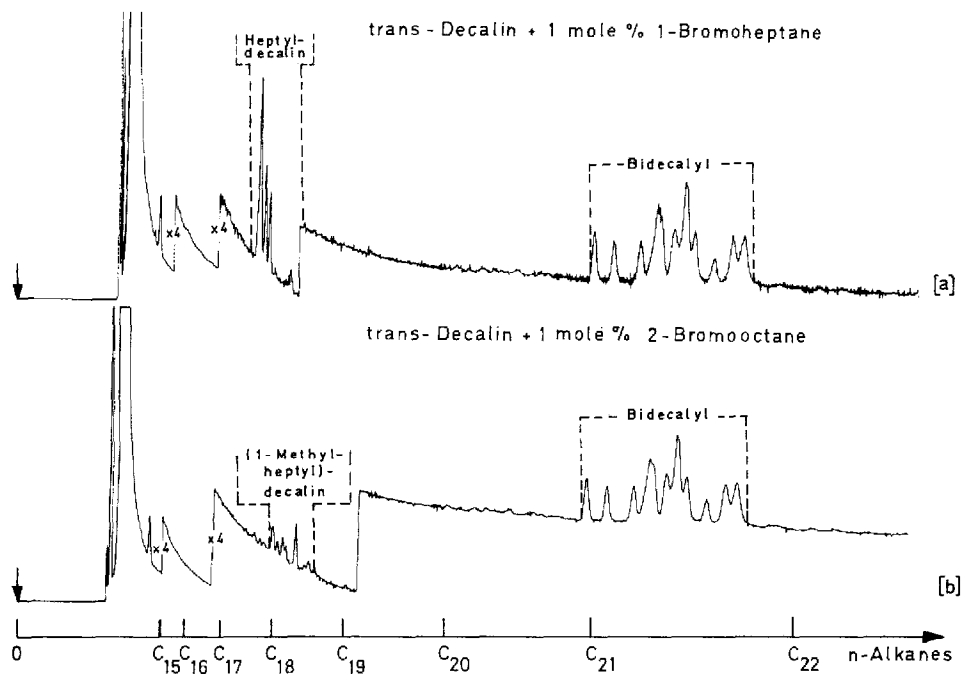

Fig. 4. Chromatograms obtained at a column temperature of 200°C after irradiation of *trans*-decalin, containing respectively 1 mole-% 1-bromoheptane (a) and 2-bromooctane (b); the scale indicates the retention characteristics of *n*-alkanes.

Chromatograms obtained after irradiation of *cis*-decalin containing 1 mole-% 1-chlorooctane at column temperatures of 140 and 200°C are shown in Fig. 5. The chromatogram at 140°C differs considerably from the one obtained after irradiation of *cis*-decalin containing 1 mole-% 1-bromooctane, but the extra peak associated with the presence of the latter compound is also present in this case. The chromatogram obtained at 200°C, on the other hand, corresponds very well with the one obtained after irradiation of *cis*-decalin containing 1 mole-% 1-bromooctane, though the relative importance of some of the peaks is somewhat different and the resolution is less good.

The chromatogram obtained at a column temperature of 140°C after irradiation of *cis*-decalin, containing 0.5 mole-% of both 1-bromoheptane and 1-bromooctane, is shown in Fig. 6. In addition to the characteristic pattern of irradiated *cis*-decalin, containing a bromoalkane, three extra peaks are observed. Chromatograms obtained at a column temperature of 140°C after irradiation of *cis*-decalin, containing 0.5 mole-% of both 1- and 2-bromooctane and 0.5 mole-% of both 1- and 3-bromooctane, are shown in Fig. 7. In addition to the characteristic pattern of irradiated *cis*-decalin, containing a bromoalkane, two extra peaks can easily be discerned in each case.

The concentrations of the high-molecular-weight compounds formed by irradiation may evidently be increased by removal of part (about 80%) of the decalin
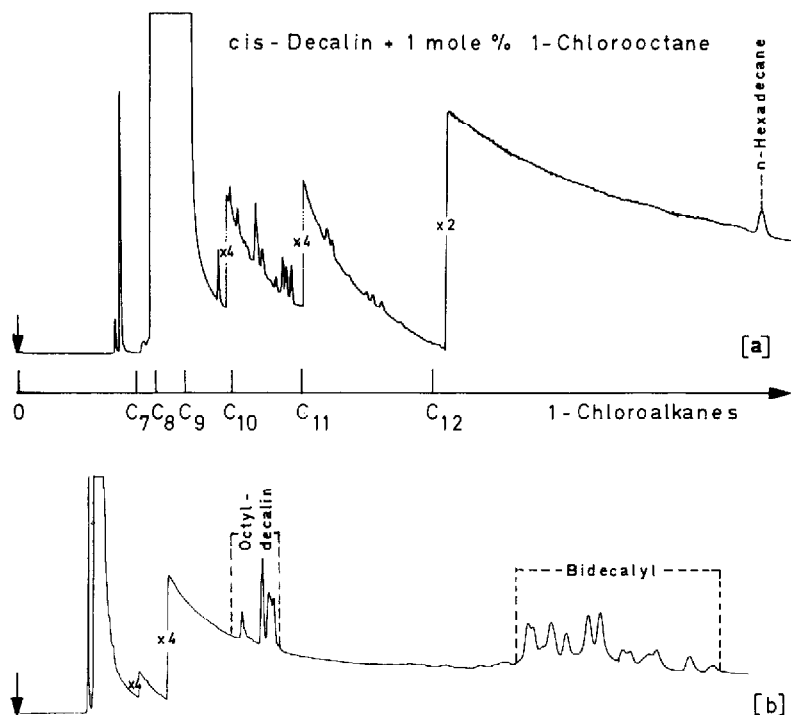

Fig. 5. Chromatograms obtained at a column temperature of respectively 140 (a) and 200°C (b) after irradiation of *cis*-decalin containing 1 mole-% 1-chlorooctane; the scale indicates the retention characteristics of 1-chloroalkanes at 140°C.
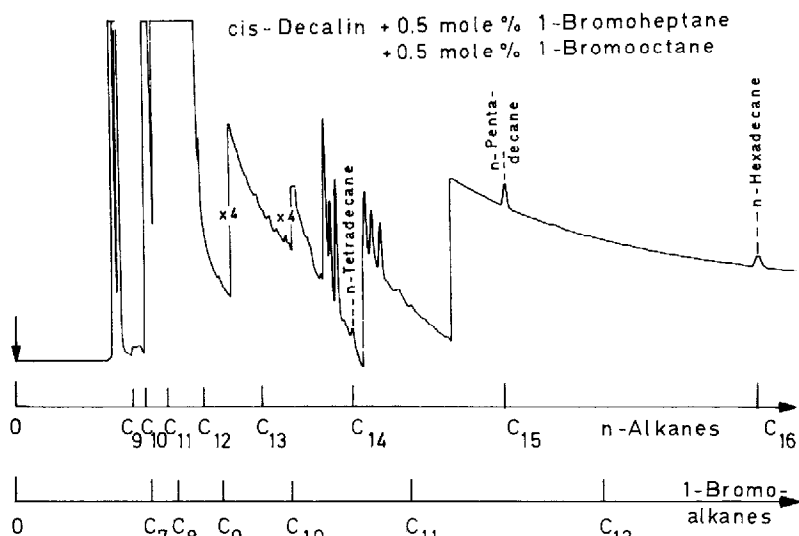
Fig. 6. Chromatogram obtained at a column temperature of 140°C after irradiation of *cis*-decalin, containing 0.5 mole-% of both 1-bromoheptane and 1-bromooctane; the scales indicate the retention characteristics of *n*-alkanes and 1-bromoalkanes.
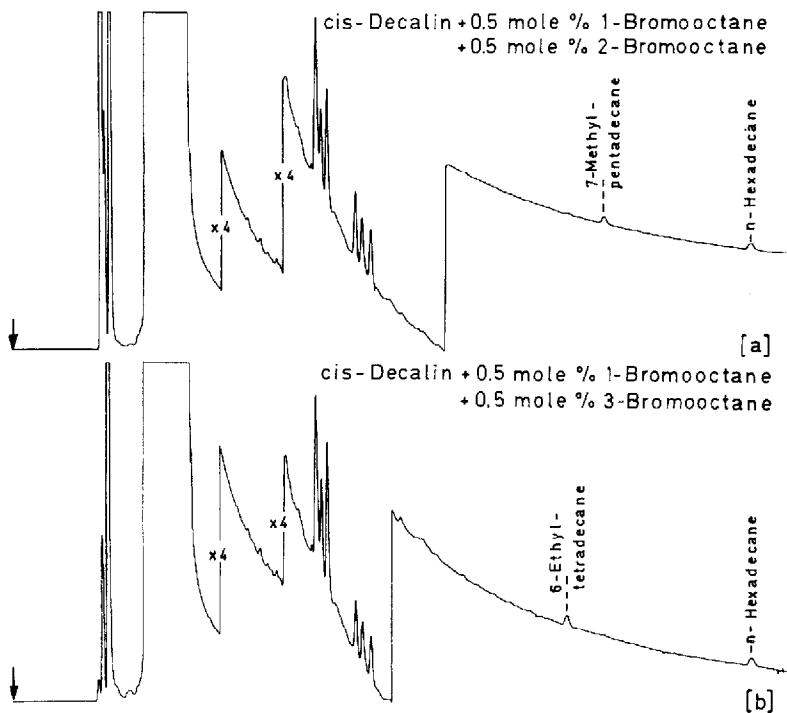
Fig. 7. Chromatograms obtained at a column temperature of 140°C after irradiation of *cis*-decalin, containing respectively 0.5 mole-% of both 1- and 2-bromooctane (a) and of both 1- and 3-bromooctane (b).
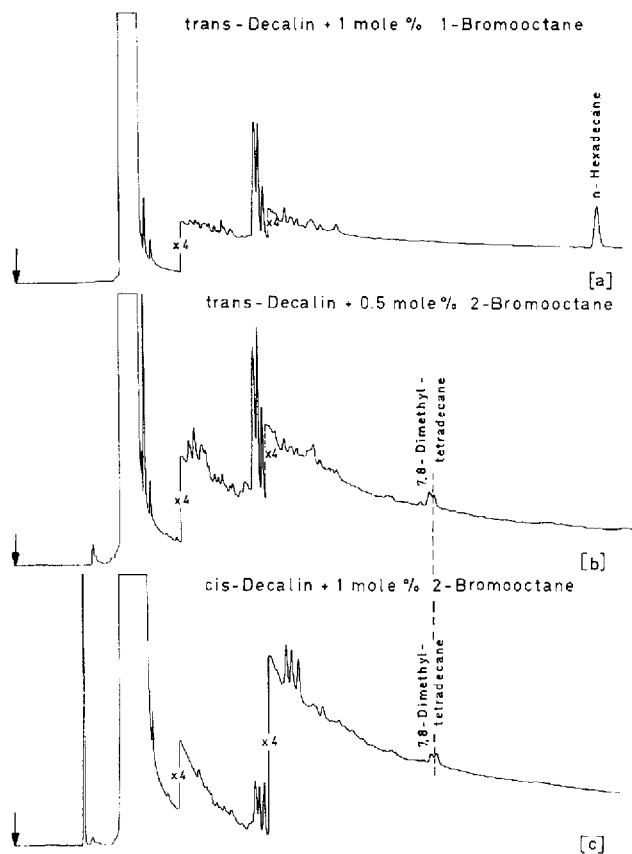
Fig. 8. Chromatograms obtained at a column temperature of 140°C after irradiation and subsequent evaporation by vacuum distillation of *trans*-decalin, containing respectively 1 mole-% 1-bromooctane (a) and 0.5 mole-% 2-bromooctane (b) and of *cis*-decalin containing 1 mole-% 2-bromooctane (c).

solvent by vacuum distillation. Chromatograms obtained at a column temperature of 140°C, after irradiation and subsequent evaporation by vacuum distillation of *trans*-decalin containing either 1 mole-% 1-bromooctane or 0.5 mole-% 2-bromo-octane, and of *cis*-decalin containing 1 mole-% 2-bromooctane, are shown in Fig. 8. The two upper chromatograms correspond reasonably well, exhibiting a pattern that is characteristic for irradiated and evaporated *trans*-decalin containing a bromoalkane. In addition to this characteristic pattern, one extra peak is observed in the first chromatogram and a double peak is observed in the second one. The chromatogram obtained after irradiation and subsequent evaporation by vacuum distillation of *cis*-decalin containing 1 mole-% 2-bromooctane largely corresponds with the characteristic pattern obtained after simple irradiation of *cis*-decalin containing a bromoalkane. In addition, the double peak that is superimposed on the characteristic pattern in the chromatogram obtained after irradiation and evaporation of *trans*-decalin containing 0.5 mole-% 2-bromooctane also is observed in this case.

The validity of the method for synthesis of higher-molecular-weight alkanes was

TABLE I

RADIOLYTIC SYNTHESIS AND RETENTION INDICES OF DIFFERENT METHYLEICOSANES

Column temperature: 200°C.

Synthesis product	Reactants	Retention index
3-Methyleicosane	1-Bromoheptadecane + 2-bromobutane	a
4-Methyleicosane	1-Bromohexadecane + 2-bromopentane	2058.8
5-Methyleicosane	1-Bromopentadecane + 2-bromohexane	2054.4
6-Methyleicosane	1-Bromotetradecane + 2-bromoheptane	2048.4
7-Methyleicosane	1-Bromotridecane + 2-bromooctane	2044.8

a Synthesis product coincides with 1-bromoheptadecane.

tested by a study of different methyleicosanes. Data obtained are given in Table I. The results clearly show that the method can be extended without problems to higher-molecular-weight alkanes.

DISCUSSION

Assignment of the peaks observed

The chromatograms obtained after irradiation of *cis*- and *trans*-decalin, containing chloro- or bromoalkanes, exhibit two series of peaks. One series is characteristic for irradiated *cis*- or *trans*-decalin, containing either chloro- or bromoalkanes, and is independent of the specific identity of the chloro- or bromoalkane. The compounds responsible for these peaks are of no real relevance to this work and their identification is therefore only briefly discussed. The second series of peaks, on the other hand, is dependent on the specific identity of the chloro- or bromoalkane and constitutes the subject of this study. The compounds responsible for these peaks may be utilized for chromatographic characterization and identification purposes.

Insight into the identity of some of the compounds responsible for the first series of peaks may be obtained by comparison of chromatograms of irradiated *cis*-decalin containing either 1-chlorooctane or 1-bromooctane. Towards the end of the chromatograms obtained at a column temperature of 200°C a very characteristic pattern is observed consisting of at least twelve peaks, which is analogous for 1-chlorooctane and 1-bromooctane. This group of peaks undoubtedly is due to bidecalyls, formed by combination of decalyl radicals. Their retention is in the range of C_{22} aliphatic alkanes, which may at first sight seem high for C_{20} products. These retention characteristics are however not at all abnormal, if one considers the boiling point and vapour pressure characteristics of decalins. The boiling point of *cis*-decalin (195°C), for instance, corresponds with that of undecane (195°C) rather than with that of decane (174°C). On the column employed, the retention time of *cis*-decalin also nearly

corresponds with that of undecane. It is not surprising therefore that the retention characteristics of bidecalyls, which of course contain two decalyl groups, correspond with those of C_{22} rather than with those of C_{20} aliphatic alkanes. The formation of bidecalyls by irradiation results in the appearance of a number of peaks (at least twelve), which is due to both structural and stereoisomerism.

The characteristic pattern in the chromatograms obtained at a column temperature of 140°C cannot be assigned as easily to specific compounds. Comparison of chromatograms, obtained after irradiation of *cis*-decalin containing either 1-chlorooctane or 1-bromooctane, reveals that in the former case some peaks are eluted at considerably shorter times which indicates that they are due to chlorinated decalins and that the corresponding peaks in the latter chromatogram are due to brominated decalins. Some of the minor common peaks, on the other hand, are in all likelihood due to alkyl derivatives of decalin, since processes involving scission of two carbon–carbon bonds in the same molecule apparently occur to some extent in the gamma radiolysis of liquid decalin[4]. A definite assignment can however difficultly be made on the basis of the information available. Knowledge of the exact identity of the compounds responsible for this characteristic pattern is not essential for the applicability of the method, however. The method is based on the extra peaks that are dependent on the chloro- or bromoalkanes present in small concentration and these can be identified unambiguously.

In the high-molecular-weight region of the chromatograms, extra peaks that are dependent on the chloro- or bromoalkanes present in small concentration are due to two different types of products. The first type results from mutual combination of alkyl radicals, formed by dissociative electron attachment to the chloro- or bromoalkanes. In the present work, they are always found in the chromatograms obtained at a column temperature of 140°C. The presence of 1-bromoheptane, for instance, results in the formation of *n*-tetradecane, the presence of 1-bromooctane in the formation of *n*-hexadecane and the presence of both 1-bromoheptane and 1-bromooctane in the same sample in the formation of *n*-tetradecane, *n*-pentadecane and *n*-hexadecane. The second type of extra peaks, that are dependent on the chloro- or bromoalkanes present in small concentration, also is dependent on the nature of the decalin (*cis* or *trans*). These peaks may be assigned to products resulting from combination of alkyl radicals, formed by dissociative electron attachment to the chloro- or bromoalkanes, with decalyl radicals formed by radiolysis of decalin. In the present work, they are always found in the chromatograms obtained at a column temperature of 200°C. Due to the presence of both structural and stereoisomers, a number of peaks are observed for this type of products.

The situation for the first type of extra peaks, which are characteristic for secondary chloro- or bromoalkanes present in small concentration, appears at first sight less simple and rational than in the case of primary chloro- or bromoalkanes. After irradiation of *cis*-decalin containing 1 mol % 2-bromooctane, no clear extra peak is observed at a column temperature of 140°C (see Fig. 1). Also, after irradiation of *cis*-decalin containing both either 1- and 2-bromooctane or 1- and 3-bromooctane, only two extra peaks in each case are observed in the chromatogram obtained at a column temperature of 140°C (see Fig. 7). By removing part (about 80%) of the decalin after irradiation by vacuum distillation, the missing peaks may be made to appear, however. This is clearly seen in Fig. 8, for 2-bromooctane in both *cis*- and

trans-decalin. A clear peak for 7,8-dimethyltetradecane is now observed, which is actually a double peak as a result of optical isomerism; two asymmetric carbon atoms are present in this compound, resulting in the occurrence of diastereomers that are partly separated in the analysis. It thus appears that alkanes formed by mutual combination of secondary alkyl radicals are formed less efficiently than alkanes resulting from the combination of secondary with primary alkyl radicals and from the mutual combination of primary alkyl radicals. This undoubtedly is due to differences in the rate constant ratios for disproportionation to combination. Such ratios are indeed considerably larger for secondary than for primary alkyl radicals[5]. The effect may not be due to inefficient formation of secondary alkyl radicals by dissociative electron attachment, since the yields of cross-combination products of primary and secondary alkyl radicals are comparable to those of compounds formed by mutual combination of primary alkyl radicals. The effect is, on the other hand, not restricted to secondary alkyl radicals. In view of trends in the rate constant ratios for disproportionation to combination, similar but even stronger effects are expected for tertiary alkyl radicals. It thus appears that the radiolytic synthesis method is most easily applied to combination and cross-combination products, whereby at least one of the alkyl radicals is primary. This already covers a wide range of combinations. Other combinations may also be studied if a subsequent vacuum distillation is carried out. The assignment of the radiolytic synthesis product may however be more difficult in this case.

Absence of radical isomerization
        The results obtained clearly indicate that radical isomerization is not important under the conditions of the experiments, which is of fundamental importance to the applicability of the radiolytic synthesis method. Kossiakoff and Rice[6] originally postulated that long-chain alkyl radicals can undergo unimolecular isomerization by hydrogen atom transfer reactions involving cyclic transition states. Important results have been reported on isomerizations of vibrationally excited alkyl radicals, resulting from the addition of hydrogen atoms to olefins[7]. Only processes involving transition states with ring sizes of five and larger were observed. The isomerizations are characterized by activation energies[8,9] that are of the same order of magnitude as for those for hydrogen transfer reactions from alkanes to alkyl radicals. In the case of isomerizations involving five-membered ring activated complexes, the activation energy is higher as a result of ring strain energy[7-9]. Radicals formed by addition of hydrogen atoms to olefins contain considerable amounts of excess internal energy from the exothermicity and activation energy of the addition reaction. In contrast, radicals formed by dissociative electron attachment of thermal or near-thermal electrons to chloro- or bromoalkanes have little excess internal energy. Indeed, the electron affinity of chlorine atoms[10] is about equal to the strength of carbon–chlorine bonds in chloroalkanes[11]. Similarly, the electron affinity of bromine atoms[10] is not much larger than the strength of carbon–bromine bonds in bromoalkanes[11]. Electron swarm studies indicate[12], on the other hand, that while the attachment rates of some lower bromoalkanes peak at considerable electron energies (about 0.75 eV), those of higher bromoalkanes peak at quite low electron energies, *i.e.*, 0.2 eV for 1-bromo-octane and thermal energies for 1-bromodecane, so that higher alkyl radicals are formed with little excess energy. Isomerization is on the other hand quite unlikely for lower alkyl radicals because of ring restrictions (see above).

In the radiolytic synthesis method, combination products of radicals directly formed by dissociative electron attachment are observed but not of radicals subsequently formed by isomerization. This indicates that in this method radicals generally have no time to isomerize before they react with another radical or disappear by other means. This may be due to: (i) the low excess internal energy the radicals possess upon their formation as indicated above and the ease with which they can dissipate this energy because experiments are performed in the condensed state; (ii) the relatively low temperature at which the irradiations are performed (room temperature) and/or (iii) a relatively high (local) concentration of radicals making radical recombination occur quicker than in the pyrolytic and photolytic studies mentioned above. It may be interesting in this regard to remark that, in contrast to pyrolytic and photolytic experiments, energy deposition by absorption of high-energy ionizing radiation is inhomogeneous. Electrons ejected as a consequence of the ionization produced by radiation may themselves be sufficiently energetic to produce further ionization and excitation. If the energy of these secondary electrons is relatively small, less than about 100 eV, their range in liquid or solid materials will be short and any secondary ionizations and excitations they produce will be situated close to the original ionization, giving a small cluster or spur of excited and ionized species. Thus, local radical concentrations at some points are likely to be higher than the average radical concentration.

All these considerations make the experimental observation, that no radical isomerization is observed in the radiolytic synthesis method, quite understandable.

Comparison with other synthesis methods

The main advantage of the method described in this work, with respect to different synthesis methods described in the literature[13], consists in the fact that in the radiolytic synthesis method only very small amounts of the haloalkane reactants are required. Many of the high-molecular-weight haloalkane reactants required are commercially available but their cost is often so high as to make it prohibitively expensive to use them in the classical synthesis methods. Due to the fact that, by irradiating decalin containing two different haloalkanes, cross-combination products may be obtained by the radiolytic synthesis method and to the fact that only very small amounts of haloalkane reactants are required, information on a great number of high-molecular-weight alkanes may by this method be obtained from one particular high-molecular-weight haloalkane; for the second haloalkane reactant a number of inexpensive low-molecular-weight haloalkanes may be utilized. The amount of high-molecular-weight alkane obtained is of course very small as well, but is sufficient for chromatographic characterization and identification purposes. The irradiation facilities required for the radiolytic synthesis method evidently are not available in every laboratory, but in many countries nowadays irradiations are commercially performed for a reasonable fee, making the method accessible to many scientists.

CONCLUSIONS

Chromatograms obtained after γ-irradiation at room temperature of dilute solutions of chloro- or bromoalkanes in *cis*- or *trans*-decalin consist of an easily recognizable pattern, that is characteristic for irradiated *cis*- or *trans*-decalin,

containing either chloro- or bromoalkanes. Superimposed on this pattern is a very limited number of peaks that are dependent on the exact identity of the chloro- or bromoalkane. These extra peaks can easily be unambiguously assigned and may thus be used for chromatographic characterization and identification purposes. In the high-molecular-weight region they are due to (i) an alkane compound resulting from mutual combination of alkyl radicals that are formed by dissociative electron attachment to the chloro- or bromoalkanes and (ii) alkyl decalins resulting from combination of these alkyl radicals with decalyl radicals formed by radiolysis of decalin. A cross-combination product is also formed when two different chloro- or bromoalkanes are present during irradiation. The method is most easily applied to combination and cross-combination products, whereby at least one of the alkyl radicals is primary. Under the conditions of the experiments, no radical isomerization is observed.

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