Identification and Structure Elucidation of the Components of Commercial Linear Alkylbenzenes

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ABSTRACT

A gas chromatography and gas chromatography mass spectrometry study was performed on four commercial linear alkylbenzenes (LAB). A preliminary detailed analysis was done on some model compounds: four tetralin mixtures obtained by alkylation of benzene with linear dichloro n-paraffins (C_{10}, C_{11}, C_{12}, and C_{13}), 1-methyl-4-heptyltetralin and 1-methyl-3-octylindane. We concentrated on the minor components (5-10%) present in the linear alkylbenzenes. Three different types of compounds were identified: A) branched alkylbenzenes, B) 1,4-dialkyltetralins with linear alkyl groups, and C) 1,4-dialkyltetralins with branched alkyl groups. Quantitative evaluation of these minor components was also done. No evidence of 1,3-dialkylindane structures, at least those with linear alkyl groups, was found in the commercial linear alkylbenzenes studied.

INTRODUCTION

Commercial alkylbenzenes can be divided into two main groups: A) those obtained by alkylation of benzene with tetrapropylene (DB), and B) those formed by alkylation with straight chain chloroparaffins or straight chain olefins (LAB). The first alkylates to be used commercially were the DBs, which are primarily branched dodecylbenzene isomers with varying amounts of other alkylbenzenes having chain lengths ranging from C_{10}-C_{15}. The DBs are complex mixtures for which a complete characterization cannot be accomplished. Gas chromatography (GC) can be used as analytical technique. However, only a general chromatographic pattern of qualitative use, indicating the molecular weight, can be obtained for these compounds. The LABs, on the contrary, are primarily straight side chain isomers with 10-14 carbon atoms. The number of possible isomers for the LABs is relatively small. In such a case, a complete characterization, again using GC, becomes reasonable. It is evident that any detailed information about the composition of the alkylbenzenes is of considerable importance both commercially and in research work because the properties that affect the application, that is surface activity, solubility, etc., and other important characteristics (1), such as biodegradability, fish toxicity, of alkylbenzene suphonates can be correlated with the structures of the components.

The GC analysis of the LABs is currently based on studies of well defined model compounds (2-6). It was found that at least three liquid coatings: Apiezon L (low pressure hydrocarbon grease), SE-30 (methylsilicone rubber), and DC-550 (polar methylphenyl silicone oil) on capillary columns (50 or 100 m long) separate almost all components of an LAB. Apiezon L gives a good separation, particularly for the internal isomers (7-, 6-, and 5-phenyl isomers). The high term 2-phenyl isomers are not sufficiently separated from the 7- and 6-phenyl isomers of the next higher homolog. By using SE-30, all 2-phenyl isomers are well separated at the expense of a loss of resolution for the internal phenyl isomers. DC-550 is a compromise between Apiezon L and SE-30. The characterization of an LAB is normally accomplished by GC using a capillary column. In this way, the distribution of the various linear phenyl alkanes and the total amount of the other minor components can be reasonably achieved. The characterization can be completed by an infrared analysis giving quantitative determination of disubstituted phenyl alkanes. The problem is still open for the characterization of the other minor components of an LAB, which amount to 5-10%. These components are believed to consist mainly of branched alkylbenzenes and disubstituted benzene derivatives, tetralins and/or indanes, the latter coming presumably from dichloro-paraffins or diolefins.

We have recently focused on these minor components of LABs to identify them and to explain their structures, when possible. We used mainly the combined gas chromatography-mass spectrometry (GC-MS) technique. Two combined GC-MS studies of commercial LABs have already been reported (7,8). In the first paper (7), attention was mainly devoted to the major components. The results given for the minor component fraction were not sufficiently explained and appear to be rather ambiguous.

In the second paper (8), the GC-MS analysis was carried out using a packed column, which has too low of a separating power to identify the various components of the LABs.

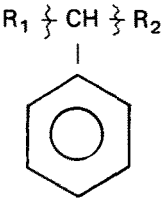
The present investigation was extended to four commercial products to get accurate and comparative data about the nature and concentration of minor components.

MASS SPECTRA ANALYSIS

Here we intend to summarize briefly the well known mass spectral behavior of the common classes supposed to be present in a commercial LAB, namely: A) linear alkylbenzenes, B) branched alkylbenzenes, and C) tetralin and indane type derivatives (9,10).

Linear Alkylbenzenes

Molecular ion peaks are quite high for these compounds. A characteristic homologous ion series is that at masses corresponding to $|C_6H_5(CH_2)_n|^+$ (m/e 77, 91, 105, 119 etc.); the abundances of the individual ions depend on the structure of the molecule. There is a strong tendency for ion stabilization by the aromatic nucleus. Consequently, the presence of a large peak, such as m/e 91, is very frequent but is not very significant, because it can be formed through a variety of fragmentation pathways. The most characteristic ions derive from the rupture of the benzylic bond. Assuming a general formula such as:



The peaks at masses $|M - R_1|^+$ and $|M - R_2|^+$ are always evident. Of these two peaks, the major one is normally that having the lowest mass. For the 2-phenyl isomers, $R_1 = CH_3$, the m/e 105 fragment $|M - R_2|^+$ is also the base peak of the spectrum, whereas the $|M - 15|^+$ fragment is almost absent. From these characteristic ions, one can easily define

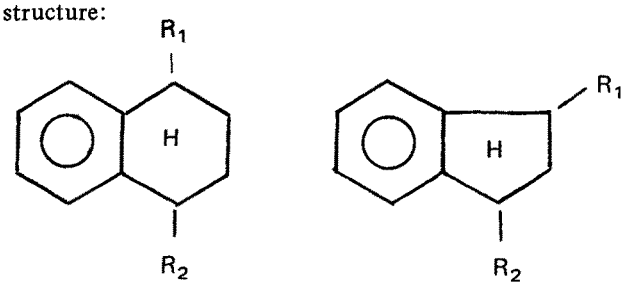
the various phenyl alkyl isomers of a commercial LAB. Figure 1 shows the typical mass spectrum of one phenyl alkyl isomer.

Branched Alkylbenzenes

The mass spectrum of these compounds is definitely more complex than that of one LAB. Molecular ion peaks are evident. Ion series at m/e 91, 105, 119, 123, etc., is a clear demonstration that the compound is an alkylbenzene. Other peaks, however, are present with unpredictable intensity. Consequently, it is difficult on the basis of the mass spectrum alone to state the exact structure of a branched alkylbenzene. One can, however, easily differentiate a branched alkylbenzene from the corresponding linear alkylbenzene.

Tetralin and Indane Type Derivatives

The tetralin and indane type derivatives which can be present in the commercial LABs have the following general structure:



tetralin indane

They originate in the alkylation step, coming, for example, from the dichloroparaffins. Their mass spectra are quite easy to interpret when they contain linear side chains. In such a case, besides a high molecular ion peak, benzylic bond rupture predominates and favors the appearance of $|M - R_1|^+$ and $|M - R_2|^+$ fragments. The tetralin skeleton structure gives a fragment at m/e 131, whereas that of an indane appears at m/e 117. These skeleton fragments do not allow differentiation of a tetralin derivative from an indane one; both peaks, in fact, can be present either in the tetralin or in the indane mass spectrum. However, the assignment to a tetralin or to an indane derivative can be made confidently on the basis of the parent peak and the $|M - R_1|^+$ and $|M - R_2|^+$ fragments. Figure 2 shows the typical mass spectrum of one tetralin coming from linear C_{12}. Figure 3 gives the mass spectra of two $C_{18}H_{28}$ isomers, 1-methyl-4-heptyltetralin and 1-methyl-4-octylindane. The $|M - 15|^+$ fragment, in such a case, coming from the rupture of one of the benzylic bonds, is absent.

The mass spectra of tetralin and indane derivatives containing branched side chains are more complicated. Molecular ion peaks are evident. Fragments at m/e 131 and 117, evidence of the tetralin or indane skeleton, are also quite intense. $|M - R_1|^+$ and $|M - R_2|^+$ fragments, on the contrary, are no longer distinguishable. Other peaks are present: the $|M - CH_3|^+$ peak is prominent, as well as the ion series $|M - 29|^+$, $|M - 43|^+$, etc., due to loss of methylene groups. These features, even if they still characterize a tetralin or indane derivative, are not sufficient to differentiate one compound from the other. This general behavior is illustrated in the spectrum shown in Figure 4.

EXPERIMENTAL PROCEDURES

Samples

Four model samples A, B, C, and D were prepared, using standard procedures, by the aluminum chloride catalyzed alkylation of benzene with dichloro n-paraffins C_{10}, C_{11}, C_{12}, and C_{13}. The dichloro n-paraffins were obtained by chlorination of the corresponding n-paraffins and purified by distillation.

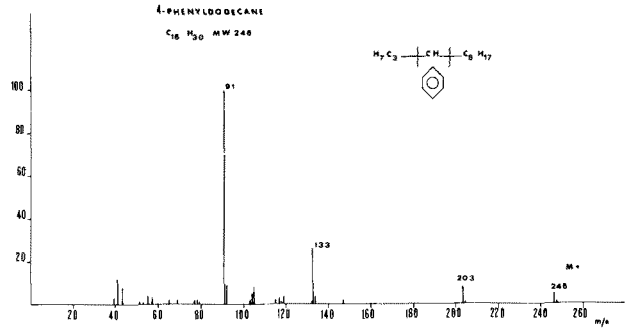


FIG. 1. Mass spectrum of one linear alkylbenzene, 4-dodecylbenzene.

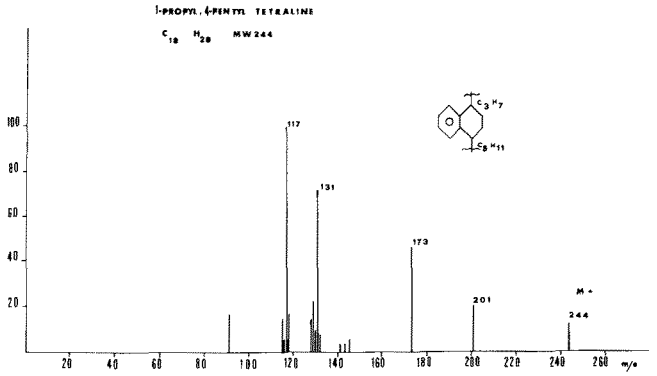


FIG. 2. Mass spectrum of one tetralin, 1-propyl-4-pentyltetralin.

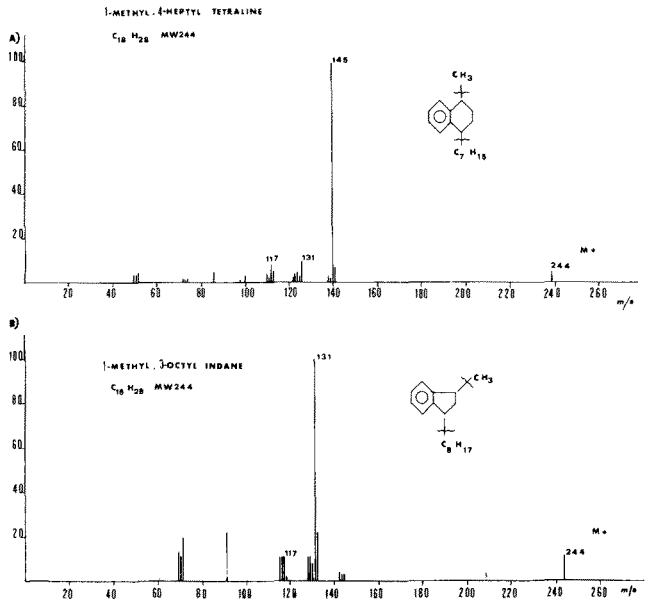
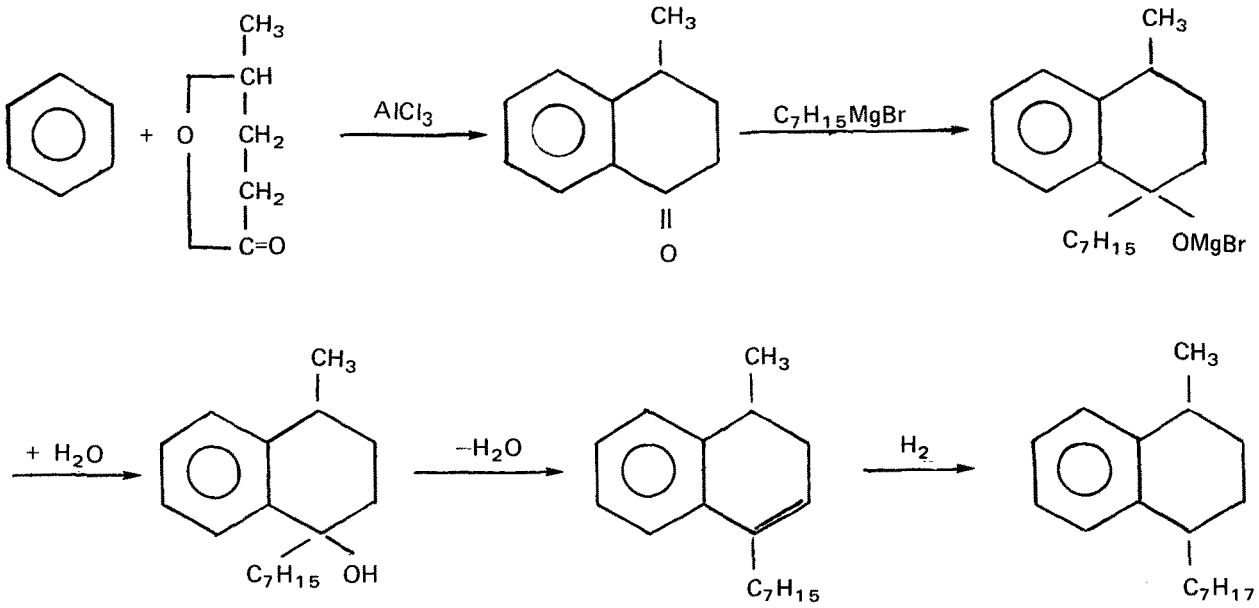


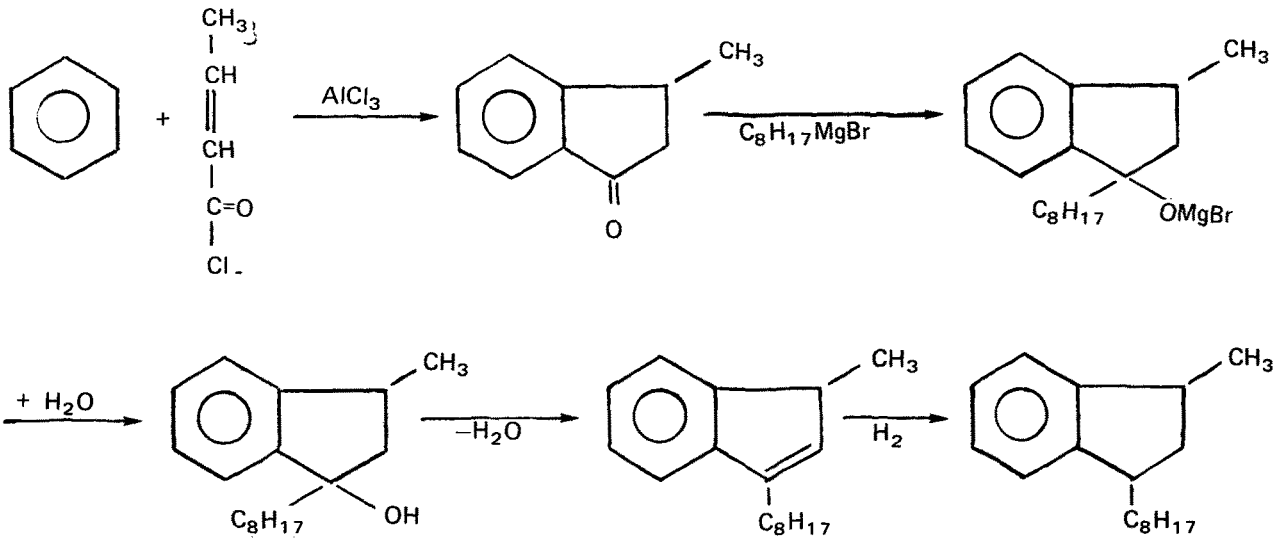
FIG. 3. Mass spectra of E and F model compounds: A) 1-methyl-4-heptyltetralin; B) 1-methyl-4-octylindane.

The reaction mixtures were distilled and the fraction boiling at 10 mm Hg in the following temperature ranges was used for the GC-MS analysis: A, 148-160 C; B, 160-175 C; C, 172-185 C, and D, 184-198 C. Quantitative GC measurements were done on fractions boiling at 5 mm Hg in a larger temperature range (50-190 C), in order not to lose any low- and high-boiling components.

Two single pure model compounds were also prepared: E, 1-methyl-4-heptyltetralin, and F, 1-methyl-4-octylindane. Model compound E was prepared by alkylating ben-



Model Compound E



Model Compound F

zene with γ-valerolactone in the presence of $AlCl_3$. The resulting 1-methyl-4-tetralone, treated with n-heptylmagnesium bromide, gave, after hydrolysis, 1-methyl-4-heptyl-4-hydroxytetralin, which, after dehydration over H_2SO_4, was converted to 1-methyl-4-heptyltetralin, model compound E, by hydrogenation over Pd on charcoal.

For model E, boiling point: 163 C at 5 mm Hg; elemental analysis: found, C: 88.91, H: 11.94; calculated C: 88.52, H: 11.47.

Model compound F was prepared by alkylating benzene with crotonyl chloride in the presence of $AlCl_3$. The resulting ketone after reaction with n-octylmagnesium bromide was treated to give 1-methyl-4-octylindane, model compound F, following the same reaction steps used for the synthesis of model compound E.

For model compound F, boiling point: 163-164 C at 5 mm Hg; elemental analysis: found, C: 88.58, H: 11.94; calculated, C: 88.52, H: 11.47.

Four commercial LABs were taken in consideration: G ($AlCl_3$ catalyzed alkylation of benzene with n-chloroparaffins), H, K, and I (three different commercial LABs, all obtained by HF catalyzed alkylation of benzene with n-olefins).

Apparatus

The various model samples and the LABs were analyzed with a gas chromatograph, Carlo Erba model 2300. The analysis conditions were: glass capillary column (50 m long and 0.25 mm internal diameter) coated with a liquid phase of Apiezon L and OV 101 (1:1 w/w); carrier gas: H_2; inlet pressure: 10 psi; column temperature: isothermal at 130 C for 18 min, programed from 130 C to ca. 210 C at 0.7 C/min; inlet port temperature: 250 C.

For the combined GC-MS system a Varian spectrometer, model CH-7, was used in conjunction with a Varian chromatograph, model 2860. For the analysis of the LABs, the conditions of the GC-MS system were: open tubular column (100 m long and 0.25 mm internal diameter) with Apiezon L as liquid phase; carrier gas: He; inlet pressure: 44 psi; flow rate: 1 ml/min, splitter 1:200; column temperature: isothermal at 130 C for 20 min, programed from 130-210 C with 1 C/min and then isothermal at 210 C; inlet

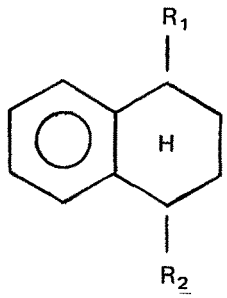
port temperature: 250 C; ionizing voltage: 70 eV; current at the filament: 300 μA; ion source temperature: 200 C; inlet tube temperature: 250 C.

A helium separator (Watson-Biemann type), single stage, provided by Varian, was used to minimize the possible loss of chromatographic resolution arising from interfacing the gas chromatograph with the mass spectrometer.

The 60 MHz proton spectra were obtained by using a Jeol JNM-C-60 HL nuclear magnetic resonance (NMR) spectrometer operating in the field-frequency mode; all spectra were calibrated with a Hewlett-Packard 5300 frequency counter. For the model compounds E, 1-methyl-4-heptyltetralin, and F, 1-methyl-3-octylindane, 100 MHz proton spectra were obtained with a Varian XL spectrometer, whereas ^{13}C NMR spectra were recorded with a Varian CFT-20 and a Bruker WH-90 spectrometer.

RESULTS AND DISCUSSION

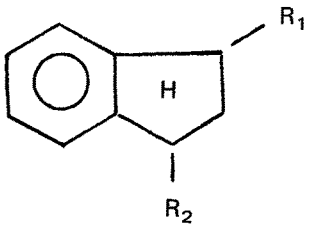
The four model samples, A, B, C, and D, were investigated by GC, GC-MS, and NMR. According to the preparation, as already described, one expects that every sample is a mixture of tetralin and indane derivatives. The number of isomers is restricted according to the chain length of the original paraffins. For example, the possible tetralin isomers coming from the C_{10} dichloroparaffin are six, namely:



R_1	R_2
CH_3	C_5H_{11}
C_2H_5	C_4H_9
C_3H_7	C_3H_7

where R_1 and R_2 can be *cis* or *trans*.

For the corresponding indane mixture, the isomers are still six, but the side chains R_1 and R_2 are different:



R_1	R_2
CH_3	C_6H_{13}
C_2H_5	C_5H_{11}
C_3H_7	C_4H_9

again with R_1 and R_2 in either *cis* or *trans* position. In theory, one more possible isomer exists for each tetralin and indane, having R_1 = H and $R_2 = C_6H_{13}$ or C_7H_{15}. These isomers, however, are very unlikely. In fact the reaction of alkylation involves the formation of carbonium-ion intermediates, which tend easily to rearrange to form stable carbonium ions. Secondary carbonium ions are definitely more stable than primary ones. The absence of the 1-phenyl isomers in the alkylbenzenes is due to the same reason. The same argument, applied to the other model samples, can predict the experimentally expected number of possible tetralin and indane isomers (Table I).

The GC-MS analysis of our four model samples revealed that only tetralin derivatives are present. In the mixture derived from the C_{13} dichloroparaffin, model sample D, however, trace amounts of indane derivatives were also identified. The formation of tetralins with the reaction conditions as already described is strongly favored with respect to that of indanes. The assignment of the various chromatographic peaks to tetralins by GC-MS technique is almost straightforward and follows the procedure already described. The *cis*- and *trans*- assignment follows from the results obtained for the model compounds E and F and is discussed below. In Tables II-V are the results of the analyses on these four mixtures with the assignments and the corresponding amounts of the various components.

A careful investigation was also performed on the model

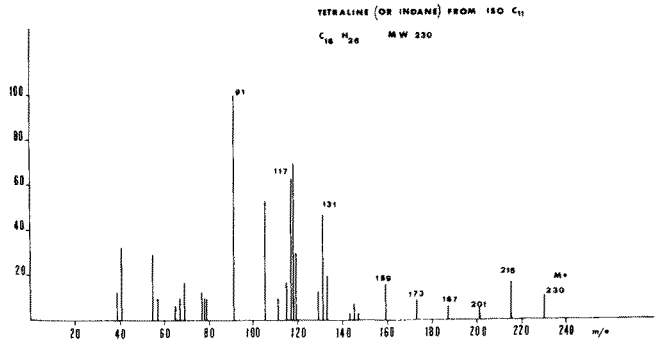


FIG. 4. Mass spectrum of a tetralin (or indane) coming from iso-C_{11}, $C_{16}H_{26}$.

TABLE I

Experimentally Expected Number of Possible Tetralin and Indane Isomers

Dichloroparaffin	Tetralin isomers	Indane isomers
C_{10}	6	6
C_{11}	6	8
C_{12}	8	8
C_{13}	8	10

TABLE II

Gas Chromatography-Mass Spectrometry Analytical Results on Sample A[a] Obtained by Alkylation of Benzene with Dichloro n-C_{10}

	Tetralin[b]	Amount (%)
1	*cis*-1-propyl-4-propyl	12.3
2	*cis*-1-ethyl-4-butyl + *trans*-1-propyl-4-propyl	30.0
3	*trans*-1-ethyl-4-butyl	11.5
4	*cis*-1-methyl-4-pentyl	23.8
5	*trans*-1-methyl-4-pentyl	22.4

[a]Nuclear magnetic resonance analysis: ratio between aromatic and alkyl protons equal to R = 1:4.8 (1:5.0 theory).

[b]The list corresponds to the order of chromatographic retention times.

TABLE III

Gas Chromatography-Mass Spectrometry Analytical Results on Sample B[a] Obtained by Alkylation of Benzene with Dichloro n-C_{11}

	Tetralin[b]	Amount (%)
1	*cis*-1-butyl-4-propyl	14.3
2	*trans*-1-butyl-4-propyl + *cis*-1-pentyl-4-ethyl	28.4
3	*trans*-1-pentyl-4-ethyl	11.5
4	*cis*-1-hexyl-4-methyl	24.3
5	*trans*-1-hexyl-4-methyl	21.5

[a]Nuclear magnetic resonance analysis: ratio between aromatic and alkyl protons equal to R = 1:5.13 (1:5.5 theory).

[b]See Table II.

TABLE IV

Gas Chromatography-Mass Spectrometry Analytical Results on Sample C[a] Obtained by Alkylation of Benzene with Dichloro n-C_{12}

	Tetralin[b]	Amount (%)
1	*cis*-1,4-dibutyl	6.9
2	*cis*-1-propyl-4-pentyl	11.7
3	*trans*-1,4-dibutyl	5.3
4	*trans*-1-propyl-4-pentyl	10.2
5	*cis*-1-ethyl-4-hexyl	14.0
6	*trans*-1-ethyl-4-hexyl	11.0
7	*cis*-1-methyl-4-heptyl	23.2
8	*trans*-1-methyl-4-heptyl	17.7

[a]Nuclear magnetic resonance analysis: ratio between aromatic and alkyl protons equal to R = 1:6.12 (1:6.0 theory).

[b]See Table II.

TABLE V

Gas Chromatography-Mass Spectrometry Analytical Results on Sample D[a] Obtained by Alkylation of Benzene with Dichloro n-C_{13}

	Tetralin[b]	Amount (%)
1	1-hexyl-3-butylindane	trace
2	1-heptyl-3-propylindane	trace
3	*cis*-1-pentyl-4-butyl	13.3
4	1-hexyl-3-butylindane 1-heptyl-3-propylindane	trace
5	*cis*-1-hexyl-4-propyl	10.9
6	*trans*-1-pentyl-4-butyl	9.3
7	*trans*-1-hexyl-4-propyl	8.5
8	*cis*-1-heptyl-4-ethyl	12.4
9	*trans*-1-heptyl-4-ethyl	9.4
10	*cis*-1-octyl-4-methyl	18.7
11	*trans*-1-octyl-4-methyl	17.5

[a]Nuclear magnetic resonance analysis: ratio between aromatic and alkyl protons equal to R = 1:6.30 (1:6.5 theory).

[b]See Table II.

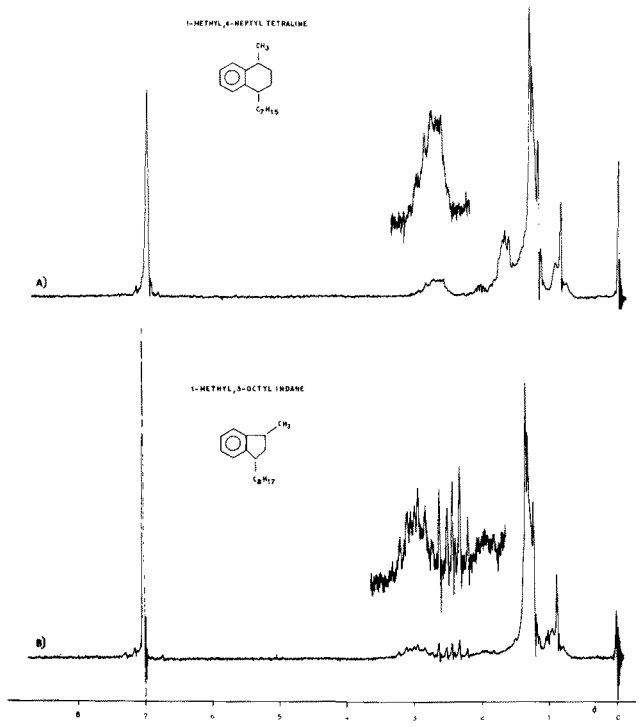


FIG. 5. 60 MHz nuclear magnetic resonance spectra in $CDCl_3$ of E and F model compounds: A) 1-methyl-4-heptyltetralin; B) 1-methyl-4-octylindane.

compounds, E, F, (1-methyl-4-heptyltetralin) and F (1-methyl-3-octylindane). The mass spectra of these two compounds are shown in Figure 3. Tetralin and indane skeleton

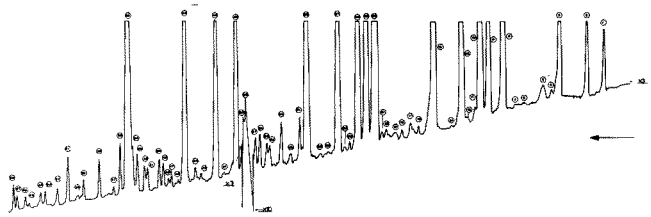


FIG. 6. Gas chromatogram of G linear alkylbenzene (LAB) using total ion monitor. See Table VI for key to peaks.

structures are identified by the masses at m/e 131 and 117. The relative structure of the compounds is defined considering, as already said, the peak set due to molecular ion and to the fragments which indicate the side paraffinic chain length. The tetralin and indane structure of model compounds E and F is also confirmed by the ^1H and ^{13}C NMR spectra. Figure 5 shows the proton NMR spectrum of model compounds E and F. The tetralin derivative displays two proton bands at ca. $\delta = 2.8$ due to the $>\underline{CH}$-group near the aromatic ring. The indane derivative, besides the similar two $>\underline{CH}$- resonances at ca. $\delta = 3.0$, shows a six peak absorption centered at $\delta = 2.47$ due to one proton. This resonance can be assigned to one of the C-2 methylene protons, namely that proton, which, according to the envelope conformation of the cyclopentene ring, is in the plane of the aromatic ring and consequently in its negative anisotropic cone.

Whereas model compound F indane is a chromatographic pure compound, the model compound E tetralin displays two distinct chromatographic peaks. This is not due to the existence of an impurity but comes from the two possible isomers, *cis*- and *trans*-1,4-alkyltetralin. A ^{13}C NMR study of model compound E allowed assignment of the *cis*- structure to the more abundant isomer. The complete ^{13}C NMR investigation of these model compounds, E and F, will be the subject of a forthcoming paper. The more abundant isomer of model compound E has a shorter retention time. This finding can be confidently extended to all other tetralins and was used to make the *cis*- and *trans*-assignment as reported in Tables II-V.

The results obtained from the analysis of all the model samples were used as a basis for interpretation of the GC-MS data of the minor component fraction of the four commercial LABs. Despite use of the combined GC-MS system, which inevitably gives a loss of GC resolution, good peak separation was achieved. As an example of GC resolution and of MS analysis, the chromatogram of G LAB, using the total ion monitor, is shown in Figure 6. At least one mass spectrum was recorded for each peak. Table VI presents the GC-MS analytical results of G LAB. The peak numbers on Figure 6 correspond to the compound numbers in Table VI. As shown, besides the identification of all the main peaks, which correspond to the various phenyl isomers, several minor peaks were identified. Among these minor components, three different main types of compounds can be recognized: A) branched alkyl benzenes, B) tetralins with linear side chains, and C) tetralins with branched side chains. For the branched alkylbenzene components, it is not possible to define the structure; only the total carbon number of the alkyl group can be given. The structure of the tetralins with linear side chain components, on the other hand, can be confidently assigned in a precise manner on the basis of data and results gained by the study of the model compounds. The tetralins with branched side components give a mass spectrum which reveals its tetralin and/or indane nature (presence of 91, 117, 131 m/e fragments and of a molecular ion diminished by 2 in respect to that of the corresponding alkylbenzene). The fragmentation, however, which clearly shows loss of CH_3 and $(CH_2)_n$

TABLE VI

Gas Chromatography-Mass Spectrometry Analytical Results on G LAB[a]

	Compound
1	5-phenyl C_{10}
2	4-phenyl C_{10}
3	3-phenyl C_{10}
4	phenyl iso-C_{11}
5	phenyl iso-C_{11}
6	phenyl iso-C_{11}
7	phenyl iso-C_{11}
8	2-phenyl C_{10}
9	6-phenyl C_{11}
10	5-phenyl C_{11}
11	phenyl iso-C_{11}
12	phenyl iso-C_{11}
13	4-phenyl C_{11}
14	phenyl iso-C_{11} + $C_{16}H_{24}$[b]
15	3-phenyl C_{11}
16	phenyl iso-C_{11}, + $C_{16}H_{24}$[b]
17	1-propyl-4-propyltetralin + phenyl iso-C_{11} + phenyl iso-C_{12}
18	1-ethyl-4-butyltetralin
19	1-propyl-4-propyltetralin phenyl iso-C_{12}
20	1-methyl-4-pentyltetralin
21	1-methyl-4-pentyltetralin + phenyl iso-C_{12}
22	2-phenyl C_{11}
23	6-phenyl C_{12}
24	5-phenyl C_{12}
25	phenyl iso-C_{12} + phenyl iso-C_{13}
26	phenyl iso-C_{12}
27	4-phenyl C_{12}
28	phenyl iso-C_{12} + phenyl iso-C_{13}
29	phenyl iso-C_{12}
30	3-phenyl C_{12}
31	1-propyl-4-butyltetralin + phenyl iso-C_{12} + phenyl iso-C_{13}
32	phenyl iso-C_{12} + phenyl iso-C_{13}
33	1-propyl-4-butyltetralin + 1-ethyl-4-pentyltetralin + phenyl iso-C_{13}
34	unknown
35	1-ethyl-4-pentyltetralin
36	1-methyl-4-hexyltetralin
37	1-methyl-4-hexyltetralin
38	2-phenyl C_{12}
39	6-phenyl C_{13}
40	5-phenyl C_{13}
41	phenyl iso-C_{13}
42	4-phenyl C_{13}
43	$C_{17}H_{26}$[b]
44	1,4-dibutyltetralin
45	3-phenyl C_{13}
46	phenyl iso-C_{13}
47	1,4-dibutyltetralin + phenyl iso-C_{13}
48	phenyl iso-C_{13} + $C_{18}H_{28}$[b]
49	1-propyl-4-pentyltetralin
50	1-ethyl-4-hexyltetralin
51	phenyl iso-C_{12}
52	1-ethyl-4-hexyltetralin
53	1-methyl-4-heptyltetralin
54	1-methyl-4-heptyltetralin
55	7-phenyl C_{14} + 6-phenyl C_{14} + + 2-phenyl C_{13}
56	5-phenyl C_{14}
57	phenyl iso-C_{14}
58	4-phenyl C_{14}
59	1-butyl-4-pentyltetralin
60	$C_{29}H_{30}$[b]
61	3-phenyl C_{14} + + 1-propyl-4-hexyltetralin
62	1-butyl-4-pentyltetralin
63	1-propyl-4-hexyltetralin
64	1-ethyl-4-heptyltetralin
65	unknown
66	1-ethyl-4-heptyltetralin
67	1-methyl-4-octyltetralin
68	1-methyl-4-octyltetralin

[a]LAB—Linear alkylbenzenes. Nuclear magnetic resonance analysis gives a ratio between aromatic and alkyl protons equal to, R = 1: 4.84.

[b]Tetralin (or indane) derivative coming from iso-paraffin (see text).

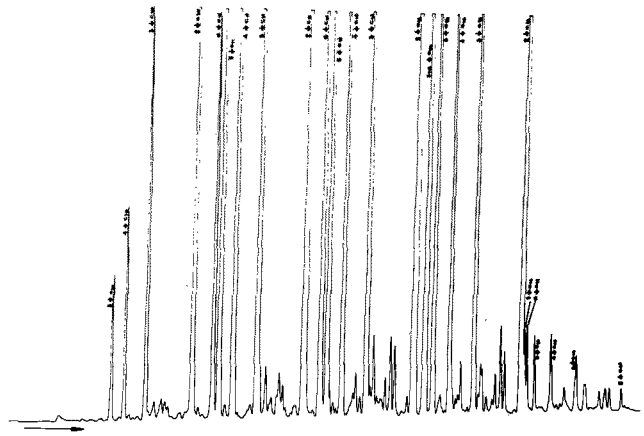


FIG. 7. Gas chromatogram of G linear alkylbenzene (LAB) using flame ionization detector.

TABLE VII

Comparison between Analytical Results of Industrial LABs[a] Investigated

Compound	Amount (%) G	H	K	I
Phenyl 2-C_{10}	4.9	4.3	1.1	0.8
Phenyl 3-C_{10}	2.2	3.0	0.9	0.7
Phenyl 4-C_{10}	1.1	2.7	1.0	0.8
Phenyl 5-C_{10}	0.8	2.7	1.3	1.1
Phenyl 2-C_{11}	9.1	6.5	7.6	7.8
Phenyl 3-C_{11}	5.6	4.9	6.8	7.9
Phenyl 4-C_{11}	4.9	4.9	7.5	9.2
Phenyl 5-C_{11}	5.3	6.4	10.2	12.3
Phenyl 6-C_{11}	2.7	3.3	5.0	6.1
Phenyl 2-C_{12}	8.3	5.2	4.9	5.2
Phenyl 3-C_{12}	5.7	3.9	4.7	5.2
Phenyl 4-C_{12}	4.7	3.7	5.1	6.0
Phenyl 5-C_{12}	5.0	5.1	7.1	8.3
Phenyl 6-C_{12}	5.0	4.9	7.1	8.9
Phenyl 2-C_{13}	6.2	4.8	2.6	0.5
Phenyl 3-C_{13}	4.0	3.2	2.9	1.3
Phenyl 4-C_{13}	3.4	3.3	3.2	1.7
Phenyl 5-C_{13}	3.7	4.0	4.3	2.4
Phenyl 6,7-C_{13}	6.4	6.5	7.5	4.3
Phenyl 2-C_{14}	0.1	1.8	0.1	-
Phenyl 3-C_{14}	0.2	1.5	0.1	-
Phenyl 4-C_{14}	0.3	1.3	0.1	-
Phenyl 5-C_{14}	0.4	1.6	0.2	-
Phenyl 6,7-C_{14}	0.4	3.4	0.5	-
Σ	90.4	92.9	91.8	90.5
Minor Components				
Phenyl iso-C_n	3.0	5.0	6.7	5.0
n-tetralin[b]	5.9	0.8	1.5	0.2
iso-tetralin	0.7	1.3	-	4.3
Σ	9.6	7.1	8.2	9.5
R[c]	4.84	5.15	4.80	4.63

[a]LAB = linear alkylbenzenes.

[b]See text.

[c]Number of alkyl protons respect to 1 aromatic proton.

groups (Fig. 4), is more complicated compared to the simple one displayed by the tetralins with linear side chain components, and the alkyl side chains cannot be firmly established. For this reason, we are also unable to define whether the structure of tetralins with branched side chain components is that of a tetralin or of an indane compound. However, because we failed to observe any trace of an indane derivative with linear side chains in all LABs investigated, the possibility of having indanes with branched side chains seems rather unlikely. In Table VI the tetralins with branched side chain components were indicated with their rough formula, and in Table VII, for simplicity, they were indicated as iso-tetralins. The same GC-MS analysis was also performed for the other commercial LABs, and the same conclusions, as far as the nature of the various components is concerned, were also achieved.

Quantitative analyses of the LABs were done independently by only the GC technique using the flame ionization detector. Figure 7 reports the chromatogram of the G LAB. Good GC resolution could be achieved under the conditions described above. The chromatographic pattern, as shown in Figure 7, is different from that shown in Figure 6 for the same sample. This is obvious considering the different, even if quite similar, chromatographic conditions. However, it was not difficult to reassign the various peaks of chromatograms such as that of Figure 7 on the basis of GC-MS work. The quantitative data obtained for G LAB are summarized in Table VII and compared with those of the other LABs. The distribution of the various phenyl isomers reveals the process of preparation of the different LABs. G LAB, which derives from the $AlCl_3$ catalyzed alkylation of benzene, has a high content of 2-phenyl isomers with decreasing quantities of internal isomers. The other LABs, H, K, and I, the alkylation step of which is catalyzed by HF, show a more equal distribution of all isomers. The total amount of minor components is nearly equal in all LABs investigated (7-10%). Their nature, however, appears significantly different. The branched alkylbenzenes content is small, particularly in G LAB. Tetralins with linear side chains have been found mainly in G LAB. Tetralins with branched side chains seem to be a peculiarity of I LAB. K LAB appears to be the product having the lesser content of phenyl disubstituted compounds (n-tetralins plus iso-tetralins). The quantitative data as reported in Table VII, however, have to be considered with caution and are only indicative of the LAB synthesis process. The data, in fact, are relative to only one sample for each LAB considered. This work, defining the nature and the structure of various minor components present in LABs, shows that a complete characterization of LABs is possible using the GC-MS system.

To summarize, on the basis of our work the following conclusions can be drawn. The minor components of the commercial LABs consists of: A) branched alkylbenzenes, B) 1,4-dialkyltetralins with linear alkyl groups, and C) 1,4-dialkyltetralins with branched alkyl groups. In such cases, however, 1,3-dialkylindanes with branched alkyl groups cannot be excluded. There is no evidence of dialkylindane structures with linear alkyl groups. There is no evidence of dialkylbenzene compounds. In such a case, according to our GC-MS identifications, we can only exclude those dialkylbenzenes which might have short alkyl chains coming from an homolytic bond-breaking of the original chloroparaffins. Some other GC investigations performed on the LABs considered in this work, on the other hand, did not give evidence of any product having an elution time greater than that of 2-phenyl-C_{14}. Consequently, we can also exclude the presence both of dialkylbenzene compounds with long alkyl chains and of diphenylalkanes.

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