Composition of the C_nH_{2n-8} Fraction from an Alkylation Reaction

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Abstract

The C_nH_{2n-8} distillation cut from the alkylation of benzene with tridecyl chlorides using $AlCl_3$ catalysis has been examined. Spectroscopic techniques (mass spectra, infrared, ultraviolet and nuclear magnetic resonance) were not able to resolve the question of whether these compounds are indans or tetralins. Aromatization of the distillation cut using a Pd/C catalyst gave a mixture of 1,4-dialkylnaphthalenes, showing that the starting material was almost completely of the tetralin structure.

Introduction

During the course of an extensive investigation of the products resulting from the $AlCl_3$ catalyzed alkylation of benzene with purposely overchlorinated tridecane, a distillation cut that is predominantly C_nH_{2n-8} compounds was isolated. Spectroscopic examination showed that these compounds are $C_{19}H_{30}$ species with a saturated ring fused to the benzene nucleus. Such compounds apparently originate from alkylation of benzene with dichlorotridecane. They would be expected to be either 1,3-dialkylindans (Scheme I) or 1,4-dialkyltetralins (Scheme II).

A recent publication (1) indicates that lower molecular weight phenylalkyl chlorides will ring-close under the influence of $AlCl_3$ to give tetralins rather than indans. An even more recent paper indicates, however, that the alkylation of benzene with dichlorodecane gives dialkylindans (2). Alkylation of benzene with 3,4-dichlorohexane gives 1,4-dimethyltetralin as the 1:1 addition product (3). Much early work indicates that phenylalkyl ketones will ring-close to give an indanone rather than a tetralone (4). 4-Methyl-4-phenyl-1-penetene ring-closes to give a mixture of 1,1,3-trimethylindan and 1,1-dimethyltetralin (5). Reaction of 1,3-dichlorobutane and benzene with $AlCl_3$ reportedly gives 1-methylindan (6).

The work reported here is intended to show unequivocally the structure of the C_nH_{2n-8} compounds resulting from the $AlCl_3$ catalyzed alkylation of benzene with chlorotridecane containing some dichlorotridecane. Preliminary results of a spectroscopic study of alkylindans and alkyltetralins are presented. An explanation for the spectroscopic anomalies originally encountered is advanced.

Experimental

Chlorination and Alkylation Reaction

A sample of pure tridecane was chlorinated to a level of 16.9 wt % chlorine. The resulting material was alkylated with benzene (8 moles) using 5 wt % $AlCl_3$. The alkylation was run for 90 min at 65C.

Nuclear Magnetic Resonance. All nuclear magnetic resonance (NMR) data were obtained on a Varian Associates HR-60 spectrometer. The samples were examined as approximately 25% solutions in CCl_4 using tetramethylsilane as an internal standard. The sample temperature was 35C. Line position measurements were made by the usual sidebanding technique.

Mass Spectra. All mass spectra (MS) were obtained on a Consolidated Electrodynamics Corporation model 21–103C mass spectrometer. Modifications to the mass spectrometer include a heated inlet system (7) and a 40-liter getter-ion exhaust vacuum system. Spectra were recorded on a CEC Mascot digitizer. Normal 70 electron volt instrument conditions were used.

Instrument performance was checked by reference to *n*-hexadecane standard for which a m/e 226/57 peak ratio of 3.50 was obtained. Complete mass spectra for all calibration compounds employed in this study will be submitted for publication by API Research Project 44 and will be distributed under the matrix serial numbers.

Infrared Spectra. Infrared (IR) spectra were obtained with Perkin-Elmer models 21 and 521 recording spectrophotometers. The samples were examined neat using standard instrumental operating parameters.

Ultraviolet Spectra. Ultraviolet (UV) spectra were obtained with an Applied Physics Cary model 14 recording spectrophotometer. The samples were diluted with spectral grade isooctane and examined in 1.0 cm absorption cells.

Dehydrogenation Reactions

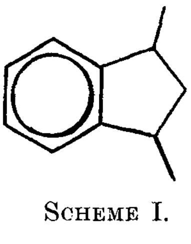
The dehydrogenation reactions were run by contacting the sample with 10% Pd/C at 285C for 9 hr.

Discussion

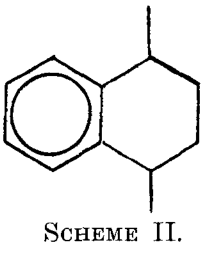
The sample of tridecyl chlorides used in the alkylation reaction contained about 20% dichlorotridecane. The alkylation product was distilled and the fraction boiling at 195–196C at 10 torr was studied by MS, IR, UV, and NMR. Comparisons were made with two standard compounds, 1-ethyl-3-heptylindan and 1-methyl-4-heptyltetralin.

The NMR spectrum of 1-methyl-4-heptyltetralin shows a closely spaced multiplet centered at 1.70 ppm. This signal is from the beta-CH_2 groups of the saturated ring and appears to be the most diagnostic feature of the spectrum. The beta-CH_2 of the saturated ring of the 1-ethyl-3-heptylindan gave a multiplet signal spread throughout the region from about 1.4 to 2.7 ppm. Examination of the C_nH_{2n-8} distillation cut using the criteria of the shape and intensity of the signal around 1.70 ppm indicated that the sample was a mixture containing only about 50% dialkyltetralin.

Typical MS of tetralins show that these compounds



Scheme I.



Scheme II.

undergo electron-impact fragmentation equivalent to a "retro-Diels-Alder reaction" (8). The standard compound, 1-methyl-4-heptyltetralin, gave a stabilized even-number positive ion at m/e 118 corresponding to a C_9H_{10} fragment ion of an intensity nearly equal to the molecular ion (2.3% compared to 3.4%). Corresponding peaks of similar intensities are not found in the spectra of indans, thus providing a means of differentiating tetralins from indans. Based upon these spectral-structural correlations, the C_nH_{2n-8} distillation cut was indicated to be about 37% dialkyltetralin.

The IR and UV spectra for 1-methyl-4-heptyltetralin and 1-ethyl-3-heptylindan show absorption maxima characteristic of 1,2-dialkylbenzenes. Distinguishing features from the IR spectra are changes in the absorbance ratio $A_{1600\ cm^{-1}}/A_{1580\ cm^{-1}}$ and the frequency of the absorption maxima in the 755 to 740 cm^{-1} region. These changes are shown for the standard samples (A and B) in Table I.

Distinguishing features from the UV spectra are changes in the calculated molar absorptivities for the 250 to 280 mμ absorption maxima. These data are shown in Table I.

The C_nH_{2n-8} fraction is shown as sample D in Table I. A comparison of the IR parameters would lead to the conclusion that the fraction possessed a negligible indan content. The UV data, however, are more consistent with an 85/15 tetralin-indan ratio.

The discrepancies between the spectroscopic methods were resolved by subjecting the C_nH_{2n-8} distillation cut to an aromatization reaction. Dehydrogenative aromatization reactions are known to proceed smoothly to give 1,4-dialkylnaphthalenes from 1,4-dialkyltetralins (3,9). When contacted with 10% Pd/C for 9 hr at 285C, the C_nH_{2n-8} sample gave 94% 1,4-dialkylnaphthalenes and 6% unchanged tridecylbenzene. The 1,4-dialkylnaphthalenes were separated by GLC and the structures proven by NMR, MS, UV, and IR. Under the same dehydrogenation conditions, 1-ethyl-3-heptylindan gave no naphthalenic compounds. This shows definitely that the C_nH_{2n-8} compounds formed in the alkylation reaction are dialkyltetralins and not dialkylindans.

Treatment of 1-ethyl-3-heptylindan with Pd/C produces two new, but non-naphthalenic, compounds. One of these is a corresponding indene, and the other is a different 1-ethyl-3-heptylindan, evidently a *cis-trans* isomer of the original dialkylindan. Considering the method of preparation (hydrogenation of the indene), the starting material is almost certainly the *cis*-isomer (10), and the new indan formed by treatment with Pd/C is the *trans*-isomer. The NMR spectrum of the *trans*-isomer shows a well-resolved triplet at 1.87 ppm for the beta-CH_2 group. This is in contrast to the broad multiplet seen in the spectrum of the *cis*-isomer.

The *trans*-1-ethyl-3-heptylindan species is shown as sample C in Table I. The IR data indicate the structure to be some hybrid between A and B. A similar analogy could be drawn from the UV data. However, the molar absorptivity data confirm the indan structure even though there is an inversion in the magnitudes of the two absorption maxima.

TABLE I

Infrared and Ultraviolet Spectral Data for Dialkyltetralins and Dialkylindans

	A	B	C	D
Infrared absorbance ratio;				
$A_{1600\ cm^{-1}}/A_{1580\ cm^{-1}}$	1.8	2.9	2.4	1.5
Infrared absorption maximum (cm^{-1})	754	740	748	751
Ultraviolet molar absorptivity;				
$\epsilon_{266m\mu} \times 10^2$	4.32	13.8	13.3	5.78
$\epsilon_{273m\mu} \times 10^2$	4.28	14.7	12.6	5.46

A = 1-methyl-4-heptyltetralin; B = 1-ethyl-3-heptylindan (cis); C = 1-ethyl-3-heptylindan (trans); D = C_nH_{2n-8} fraction.

The mass spectrum of the *trans*-1-ethyl-3-heptylindan isomer shows a molecular ion peak of an intensity of 2.6% of total ion yield, while the *cis* isomer gives a molecular ion peak of 3.1% intensity. The lower molecular ion intensity of the *trans* isomer is not in satisfactory agreement with the general observation that the relative abundances of molecular ions are greater for the ionized *trans* isomers than *cis* isomers (11,12). Another spectral difference between the *cis* and *trans* isomers is that the *trans* isomers have a much more intense C_nH_{2n-8} peak below the molecular ion than the *cis* isomers. The unexpected high intensity of the C_nH_{2n-8} peak below the molecular ion for the *trans* isomer could result in difficulties in differentiating tetralins from indans by mass spectrometry.

The stereochemistry of the 1-methyl-4-heptyltetralin is not known (MS data support the *cis* isomer), but the sample appears to be homogeneous. The tetralins formed during an $AlCl_3$ catalyzed alkylation reaction would be expected to be both *cis* and *trans,* since stereochemically pure 1-methyl-3-phenylindan gives a mixture of *cis* and *trans* forms when treated with $AlCl_3$ (13). Judging from the 1-ethyl-3-heptylindan case, gross differences would be expected in the spectra of *cis* and *trans*-dialkyltetralins. Thus attempts to identify or to estimate quantitatively such materials should be based on both *cis* and *trans* standard compounds.

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