Identification and Determination of Millimolar C_6-C_8 Alkenes in the Corresponding Alkanes

Sir: An important problem in organometallic chemistry is "alkane activation" (1). Recently, the first soluble transition-metal catalysts have been reported for alkane dehydrogenation (2, 3). This has involved the evaluation of the relative merits of different catalysts by measuring millimolar amounts of the product alkene in the corresponding alkane. Typically a mixture of isomeric alkenes is formed, each of which must be identified and determined. The results give information on the selectivity of the catalyst.

Using direct injection of the mixture on a capillary GC column, we have found that the vast excess of alkane present leads to the obscuring of the peaks of interest. We have therefore turned to a method by which the alkenes are brominated and the resulting dibromides determined by capillary GC.

Alkene functionalization has often been employed, but usually in combination with GC-MS. For example, Francis et al. (4, 5) have used oxyselenation with RSeBr/NaOAc or bis thioetherification with Me_2S_2/I_2 to identify positional isomers of alkenes. These methods are not reported to give information about geometric isomers present, unlike the methods described here. We also considered chlorination, but this is less selective and less experimentally convenient.

Bromination has been used to identify which peaks in a complex GC trace are due to alkenes (6), but the resulting dibromides are said to elute so slowly that no peaks due to them are ever observed (7). We show in this paper how these dibromides can be eluted by using temperature programming techniques. This has led to a convenient and rapid analytical method for the problem at hand.

EXPERIMENTAL SECTION

Compounds were obtained from Aldrich and used as received. Procedure for Determining Alkenes. The crude reaction mixtures were evaporated in vacuo and the volatile components collected in a cold trap (liquid N_2). A convenient aliquot of the mixture was taken and added to a solution of $(C_5H_5NH)Br_3$ (0.4 g, 1.25 mmol) in CH_2Cl_2 (30 mL). The size of the aliquot should be chosen so that 1.0 mmol or less of the alkenes is present, but if need be, as little as 10^{-6} mol of alkenes can be quantified in this way. The reaction mixture is stirred for 2.0 h at 25 °C; excess saturated aqueous NaHSO₃ is added and the mixture shaken. The layers are separated and the organic layer washed with H_2O (3× 20 mL) and dried over anhydrous MgSO₄. At this point the volatiles can be removed in vacuo to obtain the dibromides as a volatile oil. Alternatively the original CH₂Cl₂ solution can be analyzed with a Varian Model 3700 GC using a 25-m Carbowax 20M capillary column. Ten microliters of PhEt is added to the CH_2Cl_2 solution as an internal standard, and 1 μ L of the resulting solution is injected onto the column. The peak areas were analyzed by use of a Varian 4270 integrator.

RESULTS AND DISCUSSION

In a typical alkane dehydrogenation experiment, the volatile alkane and alkene were separated from the involatile catalyst by distillation in vacuo and the products collected in a cold trap at liquid N_2 temperatures. The contents of the trap can then be warmed and added to a solution of the bromination reagent in CH_2Cl_2 .

The Br_2 adduct of pyridinium bromide ($[C_5H_5NH]Br_3$, 1) has been widely used by organic chemists for brominating alkenes (8). We find that it is very useful for routine analytical applications as well, being well-crystalline, of fixed composition, and commercially available. The brominations proceed at room temperature over 2 h to give overall trans addition to the C=C group in good and reproducible chemical yield (85-95%) depending on the alkene).

After the excess bromination reagent was reduced with aqueous NaHSO₃, the mixture was washed with water, and the organic layer was dried with anhydrous MgSO₄, the resulting dibromides can be determined by capillary GC. Previous workers have used mild elution conditions and have never observed the elution of dibromides from the heavier alkenes (9). We have used temperature programming over the 40–200 °C range with a Carbowax 20M capillary column and find that the C₆-C₈ dibromides survive the conditions unchanged and are readily eluted.

The dibromides formed from different isomers of C_6-C_8 alkenes are distinct and allow the determination of each positional and geometrical isomer present. We were unable to separate such isomers on a packed column. The products in the case of some of the hexenes are shown in eq 1-3. The



trans stereochemistry for the addition means that trans-2hexene gives the two enantiomers 2 and 3, which are not separable on an achiral substrate such as Carbowax. The isomeric *cis*-2-hexene, on the other hand, gives the pair of enantiomers 4 and 5. These are diasteromers of 2 and 3 and so have different physical properties and are well-separated under the analytical conditions used.

Certain analytes give slightly more complicated behavior. For example, 3-methylcyclohexene, an olefin having a cis configuration, gives two dibromides. The reason is shown in eq 4.



The 50:50 mixture of 6 and 9 that constitutes the analyte gives the products shown. Here, 7 and 10 are enantiomers and so cannot be separated and 8 and 11 constitute a second pair of enantiomers, which constitute the second peak. In view of the superior stability of 7 and 10, predicted by conformational analysis, these two products would be expected to predominate in the mixture. Experimentally the two peaks have an observed intensity ratio of 12:1, so we identify the major products with 7 and 10. Similarly 4-methylcyclohexene gives two different pairs of dibromides in a ratio of 6:1. In general, any alkene that is chiral is expected to give two peaks. Table I gives the retention times associated with the alkenes

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Table I. Retention Times of the Alkene Dibromides Studied

alkene	time, ^a min	alkene	time,ª min
PhEt (standard)	7.9	trans-3-hexene	13.61
t-BuCH=CH ₂	15.5	cis-3-hexene	14.10
cyclooctene cyclohexene	$22.6 \\ 17.72$	methylene- cyclohexane	18.17
$cyclohexene-d_{10}$ 1-hexene	$\begin{array}{c} 17.56 \\ 14.81 \end{array}$	1-methylcyclo- hexene	16.83
trans-2-hexene	13.75	2-methylcyclo-	16.52 (minor, 8%)
cis-2-hexene	14.02	hexene ^{b,c}	16.83 (major, 92%)
		3-methylcyclo-	16.53 (major, 86%
		hexene ^b	16.80 (minor, 14%

^aGC conditions: 25-m Carbowax 20 M column with temperature program: 5 min at 40 °C, then 10 °C/min to 200 °C, then 10 min at 200 °C, with a flow of 0.6 mL/min of He carrier gas (constant pressure). ^{b1}H NMR shows that the isomers formed from 2methylcyclohexene are not the same as formed from 3-methylcyclohexene, in spite of similarity in the retention times. ^c The dibromides from 1-methylcyclohexene and the major isomer from 2-methylcyclohexene were inseparable on Carbowax but were separated on a 50-m SE-30 column under the same conditions. Retention times were 24.34 and 24.56 min, respectively.

that were determined in this study.

The precision of the method is good (1% at 50 mM alkene), but good accuracy can only be obtained by using comparison samples of known concentration. This is because the chemical yields of the dibromides, although reproducible to $\pm 2\%$ are not quantitative but vary from 80 to 96% according to the exact alkene studied. In the case of cyclohexene, for example, the yield is 96%, but for the more complex olefins the yield tended to be less. The response factors of several different dibromides relative to ethylbenzene by flame ionization detection were accurately determined and lay in the range 0.75-0.9. In cases where exact response factors were not accurately determined, we calibrated the method by using standard samples containing a known concentration of alkene in alkane.

The dibromides have such a low volatility that, as Felkin (2) has shown, the alkanes can be evaporated in vacuo to leave the dibromides as an oil. The ¹H NMR spectrum of this oil gave further confirmation of the identity of these compounds by comparison with authentic materials prepared by bromination of the commercially available alkenes involved in the study. In particular the CH₂Br protons are strongly shifted to low field relative to the alkyl protons (δ 4.1–4.5), and this greatly helps chemical identification of the isomer(s) present.

Registry No. [C₅H₅N]Br₃, 39416-48-3; t-BuCH=CH₂, 558-37-2; cyclooctene, 931-88-4; cyclohexene, 110-83-8; cyclohexene-d₁₀, 1603-55-0; 1-hexene, 592-41-6; trans-2-hexene, 4050-45-7; cis-2hexene, 7688-21-3; trans-3-hexene, 13269-52-8; cis-3-hexene, 7642-09-3; 1-methylcyclohexene, 591-49-1; methylenecyclohexane, 1192-37-6; 3-methylcyclohexene, 591-48-0; 1,2-dibromo-3,3-dimethylbutane, 640-21-1; trans-1,2-dibromocyclooctane, 34969-65-8; trans-1,2-dibromocyclohexane, 7429-37-0; trans-1,2-dibromocyclohexane, 7429-37-0; trans-1,2-dibromocyclohexane, 624-20-4; 2,3dibromohexane (isomer 1), 58608-84-7; 2,3-dibromohexane (isomer 2), 58608-83-6; 3,4-dibromohexane (isomer 1), 16230-27-6; 3,4dibromohexane (isomer 2), 58608-89-2; 1-(bromomethyl)bromocyclohexane, 22690-21-7; trans-1,2-dibromo-1-methylcyclohexane, 16510-84-2; 1,2-dibromo-3-methylcyclohexane (isomer 1), 38795-14-1; 1,2-dibromo-3-methylcyclohexane (isomer 2), 35190-02-4.

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