Double Bond Migration and Dehydrogenation of Squalene on Hydrogenation Catalysts *

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From infrared spectroscopic evidence it has been concluded that considerable double bond migration takes place during the catalytic hydrogenation of squalene. Dehydrogenation has been observed after treating the olefin with catalysts, in particular with Raney nickel. Ultraviolet spectra indicate the presence of chromophores consisting of 2, 4, and 6 conjugated double bonds, but none with 3, 5, or 7, which suggests a reversed 1,4-addition as a possible mechanism.

Catalytic dehydrogenation has also been achieved with esters of oleic acid.

In the course of a study of the catalytic hydrogenation of the triterpenoid hydrocarbon squalene,
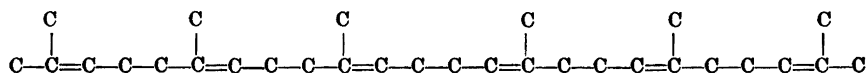
it was observed that the partially hydrogenated product showed infrared absorption bands that were not present either in the starting material, natural squalene, or the completely saturated product, squalane. Thus, in the $C=C$ double bond stretching region a new band had developed at 6.07 μ in addition to the original band at 6.01 μ. Stronger bands had developed at 10.35 μ and at 11.27 μ (only weak in natural squalene); also a weak band appeared at 14.4 μ. These latter bands are generally attributed to the out-of-plane deformation vibrations of ethylenic C—H bonds [2] and are characteristic for the various types of alkyl substitution at a double bond, as indicated in Fig. 1. The obvious conclusion was therefore that the double bonds had in part migrated from the trisubstituted position (absorption at 12.0 μ) and along the chain to give *trans*- or *cis*-disubstituted double bonds, or to the methyl groups to give asymmetrically disubstituted double bonds.

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* This work has been preliminarily mentioned in a survey article on squalene [1].
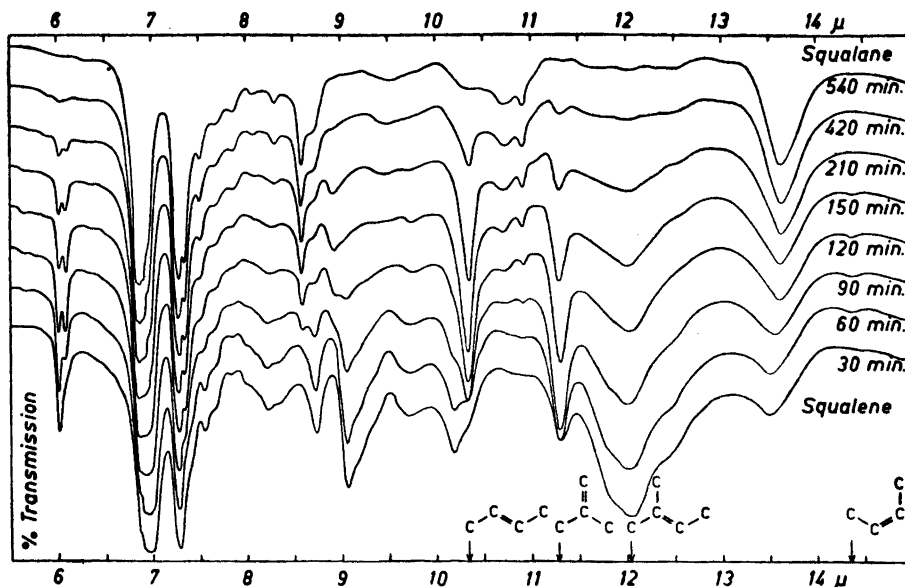
*Fig. 1. Infrared spectra taken at intervals during an ordinary hydrogenation of squalene
with Raney nickel. Cell thickness: 0.055 mm.*

Further systematic studies revealed that this *double bond migration* is quite general and always takes place during the hydrogenation of squalene, irrespective of reaction velocity, temperature, pressure, and of activity and type of catalyst used (nickel, platinum, palladium). Fig. 1 shows the gradual change in the infrared spectrum that occurs during a typical hydrogenation experiment using Raney nickel as a catalyst. The variation in the amount of
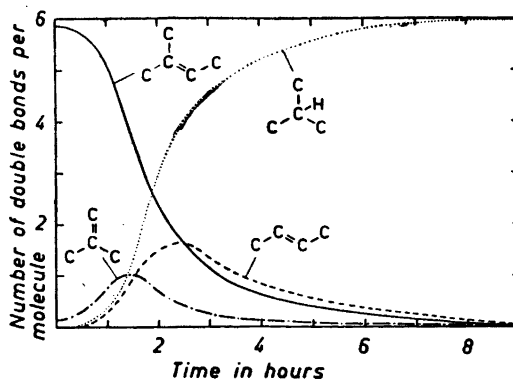

*Fig. 2. Approximate amounts of the various types of double bonds during hydrogenation of
squalene as estimated from the spectra in Fig. 1. The increase of tertiary hydrogen (absorp-
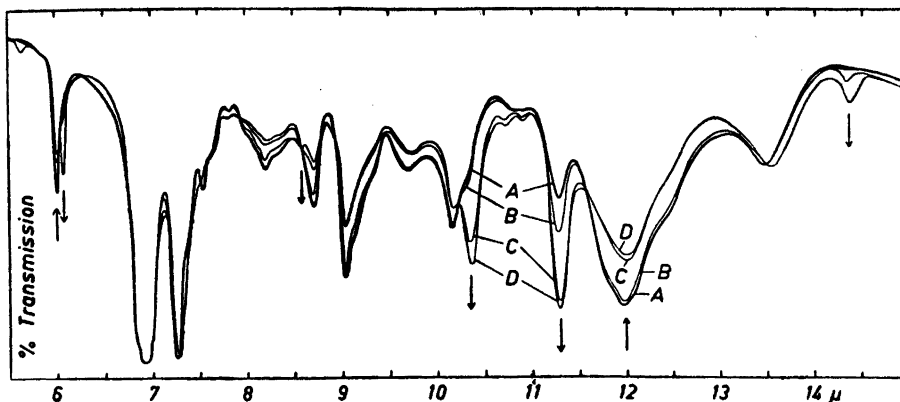tion at 8.57 μ) has been included for comparison.*

Fig. 3. Changes in the infrared spectrum of squalene during treatment with a Raney nickel catalyst (no hydrogen).

Curve A: heavy line: starting material.
Curve B: after 15 hours.
Curve C: 72 hours.
Curve D: 158 hours. Cell thickness: 0.055 mm.

the various types of double bonds during hydrogenation has been estimated from these spectra using approximate extinction values known from other systems [3], and the results are given graphically in Fig. 2. As can be seen from these curves the *trans*-disubstituted bonds tend to lag behind and are the last ones to become saturated.

It is here interesting to note that Heilbron, Hilditch and Kamm concluded, from the course of the hydrogenation of squalene, that it was strongly selective [4]. From our results, however, it is more likely that the change in reaction velocity is merely a secondary effect, and not due to real differences in hydrogenation velocity of the original double bonds. That these authors have actually had to do with double bond migration is shown by the oxidation products which were obtained from partially hydrogenated squalene (5/6 saturation) [5]. Together with reasonable cleavage products, there were also isolated C_{19}- and C_{24}-ketones and C_6- and C_{11}-acids which cannot be expected from ozonization of the original double bonds. Furthermore, the corresponding products were not obtained by oxidation of squalene itself [6].

Dehydrogenation has also been observed on hydrogenation catalysts. In one case, evolution of hydrogen started immediately after mixing squalene with a Raney nickel catalyst that had been prepared in a somewhat abnormal manner (see Experimental Part). When the gas evolution slowed down, heat, vacuum, and stirring were applied, and the reaction was made to proceed for many days. The colourless oil became yellow, then orange, and eventually red, and a greenish fluorescence developed. The corresponding changes in the infrared spectrum are shown in Fig. 3, and are strikingly similar to the changes observed during hydrogenation.

The red oil was chromatographically separated into fractions that, when examined for ultraviolet absorption, showed the maxima characteristic for two, four, and six conjugated double bonds, the yields decreasing rapidly in the given order. There was no indication of the formation of chromophores consisting of three, five, or seven conjugated bonds.

Considering the structure of squalene, it may be seen that the exclusive formation of chromophores with an even number of double bonds must result if the assumption is made that the dehydrogenation proceeds as a sort of reversed 1,4-addition; that is, the hydrocarbon may be adsorbed on the catalyst *via* the double bond, and then desorbed, while one hydrogen atom on each side of the double bond is retained by the catalyst. This idea receives some support from the observation that chemisorption of ethylene on nickel films is accompanied by dehydrogenation to give an acetylene complex [7]. In squalene acetylene formation is not possible and may be replaced by diene formation.

By comparing the number of double bonds ($\sim$10 %) that are in conjugation, as estimated from ultraviolet absorption, and the decrease in trisubstituted double bonds estimated from infrared absorption ($\sim$30 %), it is evident that the main effect is still double bond migration. This is confirmed by the appearance of an absorption band at 8.57 μ which is due [3] to the grouping

$$\begin{array}{c} C \quad\quad H \\ \backslash \quad\quad / \\ C \\ / \quad\quad \backslash \\ C \quad\quad C \end{array}$$
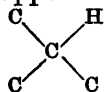
. Also, no significant increase in iodine number, determined by hydrogenation [8], could be detected, so apparently most of the hydrogen released is used for the saturation of other double bonds.

At first it was found surprising that there was no detectable displacement or doubling of the new infrared absorption bands due to conjugation, like that reported for the simpler conjugated olefins [2,9]. However, recently reported spectra of polyenes with a similar isoprenoid skeleton, show that the bands have in many cases reverted to the isolated position [10-12]. Also, a slight displacement might be obscured by the strong absorption of isolated double bonds.

When *ethyl oleate* was tried, and later *triolein*, to make possible the use of higher temperatures and lower pressure, the main effect was a rapid elaidinization. Whether it was accompanied by migration, could not be decided from the infrared spectra, but migration is known to occur during hydrogenation [13]. An increase in ultraviolet absorption at 232 mμ, due to the diene chromophore, indicated that some dehydrogenation had taken place, in accordance with the results of Forbes and Neville [14]. In the infrared spectrum the stretching frequency underwent a normal displacement from 6.05 μ to 6.22 μ.

It is an open question, which deserves consideration, whether double bond migration on contact with catalysts might actually proceed *via* dehydrogenation and subsequent partial hydrogenation (1,2-addition) of the diene formed. One indication of such a mechanism is the fact that the double bonds of squalene migrate from trisubstituted to disubstituted positions. The general tendency is for double bonds to migrate towards higher substitution. Furthermore, alkali treatment is quite ineffective in conjugating the double bonds of squalene [15].

Unfortunately, it was not possible to reproduce a catalyst with such a high activity as the Raney nickel catalyst we first tried. A systematic search revealed that there is some dehydrogenating effect with all types of hydrogenation catalysts. However, even the least active catalyst in this respect caused extensive double bond migration when used for hydrogenation. This is in accord with earlier findings that the presence of adsorbed hydrogen promotes isomerization [16] and disproportionation [17].

EXPERIMENTAL

Materials. The squalene used for the experiments was prepared from a concentrate obtained by technical distillation of basking-shark liver oil. Ethyl oleate and triolein were prepared by esterification of oleic acid that had been carefully purified through its urea adduct.

For most of the hydrogenations and dehydrogenations a W-6 Raney nickel catalyst [18] was used. In cases where washing with water had to be interrupted, the catalyst could not later be washed free from alkali in the continuous apparatus without too much loss, and a discontinuous process was used. In one particular case several days were needed, and this was the one catalyst that proved to be especially efficient for dehydrogenation.

Hydrogenation experiments. These were usually performed with about 2.5 litres of purified squalene and 50 g Raney nickel in an autoclave fitted with stirrer and cooling coil. With a hydrogen pressure of 90 atm and initial temperature of 155° C, complete saturation was obtained within 3 minutes, whereby the temperature rose to 210° even with full cooling. At 10 atm and 170° C, saturation was obtained in about 3 hours.

Sometimes the hydrogen uptake ceased before complete saturation. This we believe is a poisoning effect due to CO, and can be avoided by repeatedly expelling the gas with fresh hydrogen. When working at atmospheric pressure by bubbling hydrogen through the oil-catalyst mixture, the hydrogenation was always complete.

Dehydrogenation experiments. These were performed on 100 g squalene and 20 g Raney nickel under a vacuum of 1 mm Hg and with vigorous shaking. The temperature was gradually increased to keep the gas evolution constant, and stayed at 140—150° C most of the time. After 160 hours there was little further change in the infrared spectrum (Fig. 3), and the oil was chromatographed from petrol ether on zinc carbonate. Most of the oil passed through the column; it showed a strong U. V. maximum at 238 mμ (diene). The lower part of the column contained a broad colourless, blue-fluorescent zone with U. V. maxima at 334, *317*, and 302 mμ (tetraene). Above this was a narrow yellow, blue-fluorescent zone with U. V. maxima at 397, *379*, and 352 mμ (hexaene), and on the top were several coloured zones without distinct spectral maxima. The eluted polyene fractions were very easily autoxidized.

Ultraviolet spectra were measured in hexane with a Beckman spectrophotometer, Model DU. Infrared spectra were recorded in a Perkin-Elmer instrument, Model 21.

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