Tetrahedron Letters No. 30, pp. 2137-2143, 1963. Pergamon Press Ltd.
Printed in Great Britain.

TETRACYCLOSQUALENE AND ITS BEARING ON THE STRUCTURE OF CYCLIZED RUBBER

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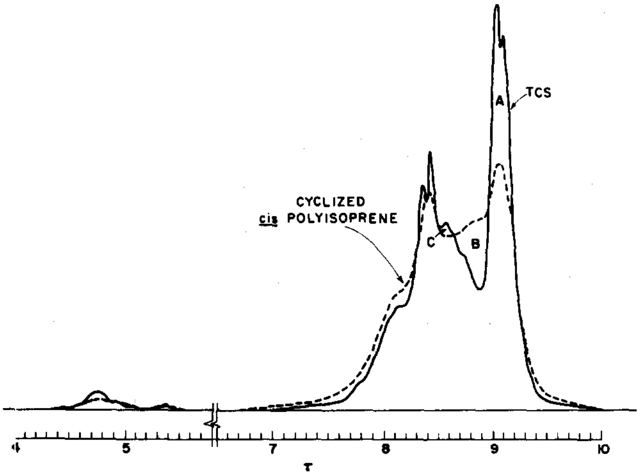
(Received 7 October 1963)

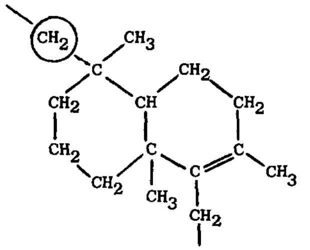
Recently we reported that cyclized rubber consists of six-membered rings fused into predominantly bicyclic structures which are connected by methylene groups and/or uncyclized isoprene units (1). Each of the fused ring structures is presumed to contain a single tetra-, tri- or di-substituted double bond, the relative amounts of which are in the order, tetra- > tri- > di-substituted. The predominantly bicyclic structure was not rigorously established, but it was considered reasonable on the basis of a comparison of the n.m.r. spectra of cyclized cis polyisoprene and cyclized cis poly(2-methyl-$\underline{d}_3$-1,3-butadiene-1,1-$\underline{d}_2$). However, although a predominantly monocyclic structure was clearly excluded, it was not possible to rule out a structure in which the average number of rings per fused segment ("cyclicity") exceeds two and may even be as high as three. In an effort to determine this cyclicity more accurately, we now compare the n.m.r. and i.r. spectra of cyclized cis and trans polyisoprenes with the corresponding spectra of tetracyclosqualene (TCS). The latter is known to have a structure consisting of two bicyclic segments connected by two methylene groups (2).

The preparation of TCS was based on that of cyclized polyisoprene (1) and involved refluxing a solution of benzene (120 ml.), 30 ml. (0.063 mole) of squalene, and 0.002 mole $TiCl_4$ under nitrogen for 68 hrs. Following addition of a few ml. of methanol, the reaction mixture was filtered and the benzene evaporated. The dark brown crude product was then worked up by the procedure of Van Duuren and Schmitt (2). The physical properties of our product were virtually identical to those obtained by these workers for TCS.

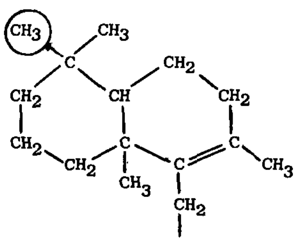
A superposition of the n.m.r. spectra of cyclized cis polyisoprene and TCS in CCl_4, adjusted to the same total area (or proton content) by controlling the gain of the (Varian HR-60) spectrometer, is shown below. These



spectra are evidently quite similar, both showing peaks at around 8.4 and 9.1 τ (protons on CH_3 groups attached to olefinic and saturated carbon atoms, respectively). If cyclized rubber is considered to have the bicyclic structure I, analogous to TCS (II), area A can be identified with the encircled CH_3 in II and area B identified with the encircled CH_2 in I.

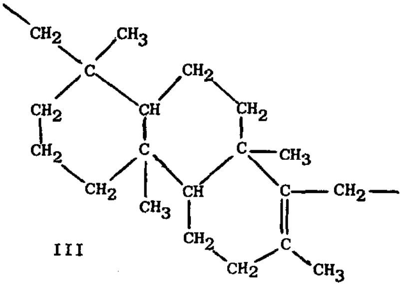


I



II

Accordingly, the areas of A and B should be in the ratio of 1.45:1 (i.e., $3/25 \div 2/24$), but the actual ratio is around 1.65:1. This is not a serious discrepancy since the spectra do not superimpose too well in the region of B and C. More serious, however, is the fact that A comprises only 9% of the total area of the TCS spectrum, whereas a value of 11% is calculated on the basis of the difference in saturated methyl content of I and II (i.e., 9/25 or 36% in II minus 6/24 or 25% in I). Because the n.m.r. spectra give satisfactory superposition in the saturated methyl region, area A can nevertheless be taken as a measure of the difference in percent saturated methyl protons of TCS and cyclized rubber, irrespective of the latter's cyclicity. For the tricyclic structure III, in which the saturated CH_3 protons comprise 9/32 or 28.1% of all the protons, the difference between this value and the corresponding value in TCS (36%) is about 8%, or somewhat

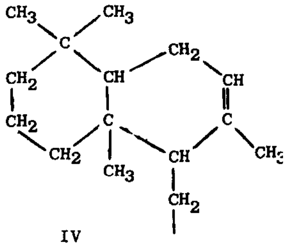


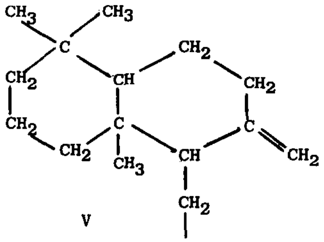
III

less than the proton content (9%) of area A. We are thus forced into revising our earlier estimate of the cyclicity of cyclized rubber from a predominantly bicyclic structure to one approaching an average tricyclic structure. Actually, cyclized rubber cannot be considered to have a unique structure, but must contain an assortment of mono-, bi-, tri- and tetracyclic segments and possibly also segments of even higher cyclicity. Such a point of view has already been advanced by Wallenberger (3). However, on the basis of the present work, the average number of rings per fused segment appears to be somewhere between two and three but probably closer to three.

This latest finding can be reconciled with our earlier results on the grounds that the analysis of the n.m.r. spectrum of cyclized rubber (1) was arbitrary and, although favoring a predominantly bicyclic structure, could admit also of a predominantly tricyclic structure. Unfortunately, the i.r. spectra, even on partially deuterated polyisoprenes, are of little help in determining the cyclicity, although they do show the pronounced loss of unsaturation in the course of cyclization and definitely rule out a monocyclic structure. Furthermore, while the residual unsaturation of the completely cyclized rubber, if known accurately, would help define the cyclicity, there has been no agreement among the workers in the field on a reliable chemical method for unsaturation. Also, a knowledge of the amount of unreacted or "widowed" isoprene units, if any, is important in relating the unsaturation to the cyclicity. It is our view that the ultimate resolution of the old question concerning the structure of cyclized rubber will have to involve the examination of the n.m.r. spectra of the cyclized products of appropriately deuterated polyisoprenes. Towards that end, work is in progress here on the preparation and cyclization of cis polyisoprene-1,1,4,4-$\underline{d}_4$ and -1,1,3,4,4-$\underline{d}_5$. Meanwhile, it appears very interesting to call attention to the close similarity of the n.m.r. spectra of cyclized polyisoprene and TCS, and also to examine the latter in somewhat greater detail.

As noted by Van Duuren and Schmitt (2), TCS displays peaks at around 4.9 $(-C\underline{H}=\overset{|}{C}-)$ and 8.1 τ $(-C\underline{H}_2-\overset{|}{C}=)$, in addition to those at 8.4 $(C\underline{H}_3-\overset{|}{C}=)$ and 9.1 τ $(C\underline{H}_3-\overset{|}{\underset{|}{C}}-)$, mentioned above. Moreover, each of the latter two peaks consists of two component peaks: the pair at 8.4 τ corresponds to methyl protons on tri- and tetra-substituted double bonds, the assignments being probably 8.33 $(-C(C\underline{H}_3)=CH-)$ and 8.42 τ $(-C(C\underline{H}_3)=C\langle)$; the pair at 9.05 and 9.12 τ undoubtedly correspond to the gem-dimethyl protons and those on the other saturated CH_3 group in II. There is also a peak at 4.75 τ which, like that at 4.9 τ, is due to olefinic protons of $-C(CH_3)=CH-$ units located in cyclized and uncyclized segments, respectively. The small peak at 5.4 τ, as with cyclized rubber (1), can be assigned to $\rangle C=C\underline{H}_2$ protons. These n.m.r. results indicate that our TCS consists of a mixture of II and the isomeric structures IV and V. It was estimated that about 2.1% of the total


IV


V

protons are in trisubstituted double bonds and 0.44% in disubstituted ones. The TCS obtained in the $TiCl_4$-catalyzed cyclization thus consists of approximately 42% II, 52% IV and 6% V, disregarding the minor widow content. This distribution of tetra-, tri- and di-substituted double bonds differs somewhat from that noted above for cyclized rubber. It is important to mention here that the superposition of the n.m.r. spectra of TCS and cyclized rubber leaves no doubt that the latter contains some widowed double bonds. This is indicated by the peak at 4.9-5.0 τ which is also the location for $-C(CH_3)=C\underline{H}-$ protons in the original polyisoprene. It is worth noting, too, that cyclized *trans* polyisoprene gave a very similar n.m.r. superposition to that shown above for the *cis* polymer. Also, the i.r. spectrum of TCS was found to be practically the same as those of the cyclized polyisoprenes, differing from them only to the extent that it contains a relatively stronger band at around 12.3 μ (due to cyclic $-C(CH_3)=CH-$ units) and a relatively weaker band at 11.3 μ (due to $>C=CH_2$ units).

Very recently, Lee, Scanlan and Watson (4a), re-examining the cyclization of natural rubber, claimed that the cyclicity was markedly dependent on reaction temperature, varying from as low as 1.5 at 110°C. to 6 at 60°C. They also reported (4b) that the cyclicity could exceed 10 at reaction temperatures below 30°C. Their results are evidently in partial disagreement with those of Van Veersen (5) which, although also favoring a polycyclic structure for cyclized rubber, indicate that the reaction temperature does not affect the ultimate cyclicity but only the rate of cyclization. Moreover, contrary to the findings of Van Veersen and other workers, as well as our own results described above, the British workers reported that there were no widowed isoprene units left in their cyclized rubber. They reached this conclusion on the grounds that the i.r. spectrum of their fully cyclized material showed *complete* disappearance of the 12 μ band, associated with the original double bonds. Since their spectrum was admittedly rather diffuse, such that they could not estimate the exo-methylene content, for example, this claim appears unsubstantiated, and, in any case, is contradicted by our previous i.r. evidence on cyclized polyisoprenes (1) which show unmistakably the presence of residual absorption at 12 μ. And, as indicated in the present paper, the existence of some widowed units in cyclized rubber is strongly supported by the n.m.r. evidence. It may be noted in passing that the British workers used perbenzoic acid titrations for determining the unsaturation of their product. Although this method works well on cyclized dihydromyrcene (4), it remains to be established that it is quantitative for a cyclized high molecular weight compound. Thus, for example, Van Veersen (5) cites the observations of Ruzicka (6) concerning the difficulty of reacting the double bond in a cyclic terpene like α-amyrin with peroxy acids.

Finally, we may note that for the temperature at which our $TiCl_4$-catalyzed cyclization of polyisoprene was carried out, 80°C., Lee, Scanlan and Watson obtained a cyclicity of about 3.7 for their $SnCl_4$-catalyzed reaction. Notwithstanding the possible effects of different catalysts, and the various assumptions involved in our respective studies, it is interesting to find that this value of 3.7 agrees qualitatively with our revised tricyclic picture of cyclized rubber.

Acknowledgments: The authors wish to thank Charles B. Kingsley and Mrs. Judith A. Black for experimental assistance, and William R. Anderson, Jr., for obtaining the n.m.r. spectra. They are also indebted to Stanford Research Institute for supporting this work.

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