We wish to thank Dr. D. A. Long for sending us a sample of his material to aid in the establishment of the biological assay. We are indebted to Mr. R. N. Boos and his associates for the microanalyses and to Mr. R. W. Walker for the determination and interpretation of the infrared absorption spectra.

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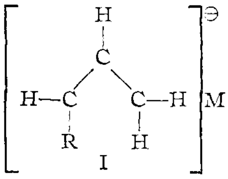
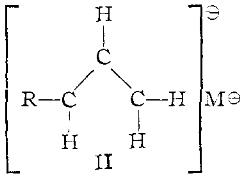
STRUCTURE OF ALLYLIC ANIONS

Sir:

The vibrational spectra of a large number of allylic organoalkali compounds are consistent with the proposition that these ions have a planar structure (C_{2v} symmetry) with angles of approximately 120° about the carbon atoms of the allylic system. That is, the ions have sp^2 hybridization as might be expected from a simple molecular orbital treatment if the double bond is considered to be completely delocalized.[1] On the basis of the observed spectra, the allylic ions of potassium, sodium and lithium have the same structure which may be represented approximately by I and II. Considerable evidence has been presented indicating Grignard reagents to be essentially covalent[2,3] (dicyclopentadienylmagnesium however, is reported to be ionic[4]) but the spectra of allylic magnesium compounds differ little from those of allylic organoalkali compounds.



I



II

Alkenylsodium and potassium compounds were prepared by metalation of olefins with amylsodium and amylpotassium.[5] Alkenyllithiums were prepared by interchange of sodium compounds with lithium chloride and by addition of butyllithium to butadiene. Magnesium compounds were prepared from reaction of allylic halides with magnesium in ether and by interchange with sodium compounds and subsequent extraction. Grignard reagents prepared in ether were heated at reduced pressure to free them of ether.[6] Solvent-free Nujol mulls were prepared under dry-box conditions and spectra were determined on a Perkin-Elmer infrared spectrophotometer. Except for the regions obscured by Nujol, excellent spectra were obtained with most of the allylic compounds studied.

Allylic ions should have a considerable energy barrier to rotation about the allylic carbon–carbon bonds, hence the existence of two distinct isomers, I and II, is possible. None of the compounds examined had bands in the normal double bond stretching region, but all the compounds investigated did show very strong bands in the 1500–1560 cm.$^{-1}$ range. Those ions where R = H should have only one isomer but where R is some alkyl substituent configurations I and II are possible. Symmetrical compounds such as allyl-, isobutenyl- or cyclohexenylsodium show only one very strong band at 1535, 1520 and 1522 cm.$^{-1}$, respectively. Compounds such as pentenylsodium have two very strong bands, one about 1525 cm.$^{-1}$ and the other about 1560 cm.$^{-1}$. No evidence has been found for structures of the type (R—CH$\doteq$CH$\doteq$CHCH$_3$)$^{\ominus}$M$^{\oplus}$ (III). Carbonation of allylic organoalkali compounds yields acids derivable from structures I and II.[5] Indeed, attempts to prepare a system like III by metalation of heptene-3 gave a spectrum identical with that from heptene-2. Although heptene-1 was not available, the spectra of heptenylsodium prepared from heptene-2 and -3 showed only minor differences when compared with compounds prepared from pentene-1 and -2, hexene-1 and -2 or octene-1 and -2. However, since olefins are easily isomerized by organoalkali compounds it is rather difficult to determine which isomeric olefin is actually metalated.[7]

From a fairly complete analysis of the vibrational spectra of allyl- and perdeuteroallylsodium, the band at 1535 cm.$^{-1}$ in allylsodium has been assigned to the carbon–carbon unsymmetrical stretching frequency.[8] Analogy with substituted olefins suggests that the band around 1525 cm.$^{-1}$ in the substituted allylic ions belongs to structure I and the band around 1560 cm.$^{-1}$ belongs to structure II.[9] This assignment is supported by the position of the band in cyclohexenylsodium at 1522 cm.$^{-1}$ since this ion can exist only in a form geometrically equivalent to structure I.

Acknowledgment.—This work was performed as a part of the research project sponsored by the National Science Foundation, Office of Synthetic Rubber.

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TRANSFER OF MOLECULAR OXYGEN BY PEROXIDASE

Sir:

The metabolic function of peroxidase is unknown. We wish to report observations, based upon the use of O^{18} as a tracer, which support the view that ferroperoxidase activates molecular oxygen.

The system consisting of horseradish peroxidase, dihydroxyfumarate and oxygen, catalyzes non-