TABLE I

RELATIVE YIELDS OF RADIOACTIVE PRODUCTS (NORMALIZED TO 100 FOR ACTIVITY IN PARENT HYDROCARBON)

Molecules produced by mechanism described are boldface. Hydrocarbons are represented by appropriate symbols: thus /\/ butane; /=\ *cis*-butene, etc.

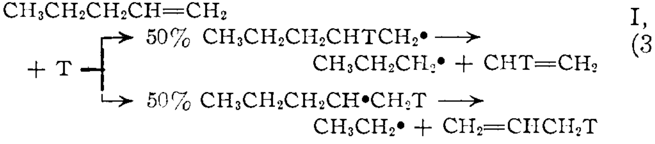
| Tritiated products / Hydrocarbon | $H_2$ | $CH_4$ | / | // | /\ | /\\ | /\/ | >— | /\// | /\\/ | /=\ | >= | /\/\ | /\/\\ | /\//\ + /\=/ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| /\// | 143 | 13 | 3 | **41** | 0 | **41** | 31 | 0 | 100 | 7 | 4 | 0 | 0 | 0 | 0 |
| /\\/ | 171 | 11 | 1 | 4 | 0 | **60** | 46 | 0 | 12 | 100 | 13 | 0 | 0 | 0 | 0 |
| /=\ | 191 | 15 | 1 | 5 | 0 | **69** | 58 | 0 | 14 | 13 | 100 | 0 | 0 | 0 | 0 |
| >= | 116 | 9 | 0 | 0 | 0 | **21** | 0 | 10 | 0 | 0 | 0 | 100 | 0 | 0 | 0 |
| /\/\\ | 178 | 9 | 6 | **33** | 0 | **42** | 0 | 0 | 4 | 0 | 0 | 0 | 24 | 100 | 9 |
| /\//\ + /\=/ | 184 | 13 | 2 | 0 | 0 | **23** | 0 | 0 | **22** | 2 | 0 | 0 | 30 | 6 | 100 |
| /\/ | 235 | 15 | 15 | 5 | 6 | 1 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| /\// + He(1:50) | 500 | 14 | 0 | **50** | 0 | **75** | 44 | 0 | 100[a] | 10 | 8 | 0 | 8 | 0 | 0 |
| /\// + $O_2$ (50:1) | 160 | 5 | 0 | **49** | 0 | **46** | 0 | 0 | 100 | 4 | 4 | 0 | 0 | 0 | 0 |

[a] Yield of butene-1 activity in this run reduced by order of magnitude compared to run containing no moderator.

alkane.[2,3,4] Only small amounts of labeled degradation products, apparently formed by displacement of alkyl groups instead of hydrogen atoms, are formed.

The present work on the reaction of recoil tritium with alkenes indicates the existence of an additional reaction mechanism. As with alkanes (see Table I, butane) about 60–80% of the tritium is found in HT and the labeled parent molecules. However, appreciable yields (10–20%) of labeled degradation products are also found. Table I shows that the yield pattern of these unsaturated fragments varies in a very specific manner with the alkene reagent.

The following mechanism for this "fragmentation" reaction is postulated. A tritium atom, having some residual recoil energy, adds on to the double bond of the alkene, forming a "hot" radical. This radical then decomposes by cleaving a carbon–carbon bond without rearrangement, to form a smaller radical and an olefin. Because the tritium atom carries excess energy, it will attack the double bond indiscriminantly and form approximately equal amounts of both possible "hot" radicals.



$$CH_3CH_2CH_2CH{=}CH_2 + T \rightarrow \begin{cases} 50\%\ CH_3CH_2CH_2CHTCH_2\bullet \longrightarrow CH_3CH_2CH_2\bullet + CHT{=}CH_2 \\ 50\%\ CH_3CH_2CH_2CH\bullet CH_2T \longrightarrow CH_3CH_2\bullet + CH_2{=}CHCH_2T \end{cases}$$

For example, the tritium atom will react with pentene-1 as shown, to give similar amounts of tritiated propylene and ethylene. From pentene-2, however, the same reaction will yield butene-1 and propylene.

This mechanism is in accord with results on the decomposition of deuterated butyl radicals at 500°.[5] Since addition of a hydrogen atom to a double bond is exothermic, the reaction probably could proceed at thermal energies. However, in the presence of an excess of helium as a moderator, the yields of the labeled fragments, as well as the yield of the parent molecule, are reduced greatly. On the other hand, these products are unaffected by the presence of a small amount of oxygen as scavenger. Therefore, this reaction to form labeled fragments apparently also takes place before the recoil tritium reaches thermal energies. Thus, while this is not a "hot-atom" mechanism occurring *only* at very high kinetic energies, it may be termed "epithermal" to denote that it competes effectively only at energies above the thermal range.

This mechanism accounts for the results so far at hand, some of which are shown in Table I. Work to demonstrate the further predictions of this model is continuing.

The authors wish to thank Professor W. Doering for his interest and criticism.

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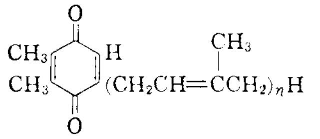
## COENZYME Q. VIII. STRUCTURE STUDIES ON A PLANT QUINONE

*Sir:*

We have isolated from alfalfa a quinone having coenzyme Q-like activity[1]; structural data support I, 2,3-dimethyl-5-[3′-methyl-2′-butenyl-oktakis-(3′-methyl-2′-butenylene)]-benzoquinone.



I. $n = 9$
II. $n = 3$

Crane and Lester[2,3] isolated from alfalfa a quinone (Q-254), m.p. 42–43°, which appeared to be a trimethylbenzoquinone with a fourth substituent of nine mono-unsaturated isoprenoid units. Kofler reported[4] a substituted benzoquinone, m.p. 48–49°, from alfalfa.

The coenzyme Q-like activity[2,3] of Q-254 and studies[5–8] on "unidentified factors" in alfalfa in

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(1) Kindly tested by Dr. F. L. Crane, University of Texas, Austin.

(2) F. L. Crane and R. L. Lester, *Plant Physiol.*, **33**, (Suppl.) VII (1958).

(3) F. L. Crane, *ibid.*, in press.

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animal nutrition, particularly in chicks, prompted us to examine the plant quinone.

Extraction of commercial alfalfa meal with petroleum ether followed by chromatography on Florisil and on Decalso yielded a crystalline yellow quinone, m.p. 48–49°.[9] Ultraviolet: $E^{1\%}_{1\,\mathrm{cm.}} = 247$ at 254 mμ and 226 at 262 mμ in isoöctane. Reduction with sodium borohydride gave the hydroquinone: $E^{1\%}_{1\,\mathrm{cm.}} = 48$ at 290 mμ in ethanol. The infrared spectrum in carbon disulfide differs from that of coenzyme $Q_{10}$ mainly in the absence of the intense 7.8 μ band associated with the methoxyl function; all other functional bands are similar.

The n.m.r. spectra[10] of I and its side-chain reduction product and of 2,3-dimethyl-5-farnesylbenzoquinone (II) and its side-chain reduction product when interpreted in comparison with the spectrum of $Q_{10}$[11] led to structure I for alfalfa quinone. It shows a ring proton as a triplet at 4.5, 6, and 7 c.p.s. and no methoxy protons. The latter are replaced by ring $CH_3$-functions which show at 178 c.p.s. in the side-chain reduction product which does not have the interference caused by the $=C{-}CH_2{-}CH_2{-}C=$ functions. The fact that the ring proton is a triplet and not a quartet signifies that its ortho group is the side-chain $-CH_2-$ and not $CH_3-$. Since the ring methyl protons are not spin-coupled, no ring proton is ortho to them. The ratio of the area of the doublet at 134, 141 c.p.s. to the ring proton triplet is 2 to 1. Thus, only one long side-chain is present ortho to the ring proton, and the two ring $CH_3-$ are ortho to each other. This is confirmed by the 6 to 1 area ratio of the ring $CH_3-$ resonance (178 c.p.s.) to the ring proton resonance in the quinone reduction product. All these deductions are quantitatively supported by the n.m.r. spectra of 2,3-dimethyl-5-farnesyl-1,4-benzoquinone and its side-chain reduction product.

2,3-Dimethyl-5-farnesylbenzoquinone (II) was synthesized from 2,3-dimethylhydroquinone and farnesol as a yellow oil; *anal.* Found: C, 81.39; H, 9.22; ultraviolet in isoöctane, $E_M = 18{,}000$ at 253 mμ, and 15,800 at 261 mμ. Combining this with the ultraviolet data of the alfalfa quinone leads to a value of 9 for *n* in I.

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(9) Crane's Q-254 and our quinone were not separated on Vaseline impregnated paper using dimethylformamide as the mobile phase.

(10) Proton resonances are in cycles per second relative to and on the high field side of benzene protons as external standard. All spectra run in carbon tetrachloride solutions at 40 mc.

(11) D. E. Wolf, C. H. Hoffman, N. R. Trenner, B. H. Arison, C. H. Shunk, B. O. Linn, J. F. McPherson and K. Folkers, THIS JOURNAL, **80**, 4752 (1958).

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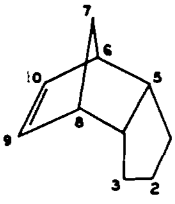
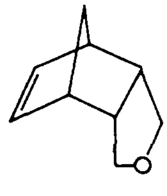
## A CYCLIZATION OF 2-AZA-1,2-DIHYDRO-*endo*-DICYCLOPENTADIENE

*Sir:*

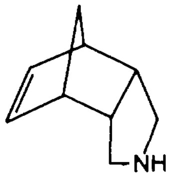
During an investigation of the effect of a hetero atom in the 2-position of 1,2-dihydro-*endo*-dicyclopentadiene (I) on the course of reactions with acidic reagents, we have found that 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene[1–3] (II) resists the rearrangement to the *exo*-configuration characteristic of its hydrocarbon analog.[4] Stabilization of the initial carbonium ion by the 2-oxa atom is proposed to explain the anomalous behavior. The steric possibility of such participation is proved by cyclization of 2-aza-1,2-dihydro-*endo*-dicyclopentadiene (III) with hydrobromic acid (48%) followed by 25% sodium hydroxide yielding the tertiary amine IV, the first member of a new heterocyclic ring system. Amine IV is identical with structure V.



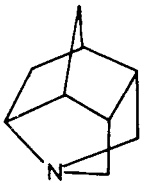
I



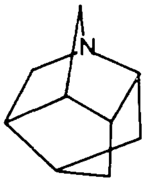
II



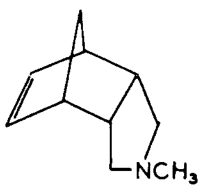
III



IV



V



VI

The secondary amine III (m.p. 117–119° with sublimation at about 55°. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69. Found: C, 79.84; H, 9.81), prepared by lithium aluminum hydride reduction of *endo*-bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid imide[5–7] by the method of Rice, *et al.*,[8] forms an alkali insoluble benzenesulfonamide (m.p. 107–108°. Calcd. for $C_{15}H_{17}NSO_2$: C, 65.42; H, 6.22. Found: C, 65.26; H, 6.24), and is reduced readily by catalytic hydrogenation to the saturated amine, isolated as the benzenesulfonamide (m.p. 168–168.5°. Calcd. for $C_{15}H_{19}NSO_2$: C, 64.95; H, 6.90. Found: C, 64.80; H, 6.76). The tertiary amine IV (m.p. 126–128° with sublimation at about 70°. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; mol. wt., 135. Found: C, 79.67; H, 9.51; 149) precipitates when a solution of the *endo* amine III in hydrobromic acid, heated under reflux for five hours, is made basic with 25% sodium hydroxide. The infrared spectrum of the new amine IV is in agreement with the saturated tertiary amine structure proposed. With benzenesulfonyl chloride the amine IV forms an alkali insoluble benzenesulfonamide of 9-chloro-2-azatetrahydro-

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