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COLLEGE OF LIBERAL ARTS
EVANSTON, ILLINOIS

DEPARTMENT OF CHEMISTRY

November 29, 1939

Dr. Michael Heidelberger,
College of Physicians and Surgeons,
Columbia University, N.Y.

Dear Dr. Heidelberger:

My delay in answering your letter of the 8th has not been caused from lack of interest, I assure you. Thank you for writing me.

I agree with you that the work on cyclotetraene was carefully done. What is more, it reads convincingly, but it does seem to me that the argument has loop-holes, some of which I mentioned in the paper.

The narrow boiling range (0.5°) which you mentioned cannot be leaned on too heavily for isomeric dibromides should boil pretty closely together.

You mention that different effects might have been encountered at pyrolysis temperatures of 200-250° than at 100-150°. Perhaps so, but I doubt it because no comparable rearrangements occur with other unsaturated hydrocarbons till much higher temperatures are reached. 1-Butene is fairly stable at 500°, and rearrangement into 2-butene starts at 600-650° (Hurd and Goldsby, J. Am. Chem. Soc., 56, 1813 (1934)). Similarly, 600° is the temperature required to initiate the rearrangement of 1- into 2-pentene (Hurd, Goodyear, and Goldsby, *ibid.*, 58, 235 (1936)). Rearrangement of 1-alkynes into 1,2-alkadienes does not occur at 400°, but requires temperatures which are high enough to break the hydrocarbon otherwise into smaller molecules (Hurd and Christ, *ibid.*, 59, 2161 (1937)). These were experiments with 1-heptyne, 1-hexyne and 1-butyne. With the butyne, it was proven that no 1,3-butadiene came even at 560°. Hence I feel that anywhere between 100-300° would be safe temperatures insofar as subsequent rearrangements are concerned when dealing with 1,2-butadiene, 1,3-butadiene, or 1- or 2-butyne.

You point out that our X was a 1,2-diquaternary compound whereas Willstatter's VII (in our paper) was not. That is a good criticism and one that I had thought of. Nothing would be gained by taking the 1,4-isomer that you suggested, however, namely, $\text{HONMe}_3\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_3\text{OH}$, because 1,3-butadiene is the only possibility here. If the C_6 -analog were taken, $\text{CH}_3\text{CH}(\text{NMe}_3\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{NMe}_3\text{OH})\text{CH}_3$,

I feel sure it would pyrolyze to the mixture of 1,5-, 1,4-, and 2,4-hexadienes the last of which is the only conjugated one. Of

course this mixture would involve greater analytical difficulties than the C_4 -analogs. Also, the original synthesis would be harder.

There is one experiment more convincing than any of these that I would like to have tried, namely, the pyrolysis of $CH_3CH-CH=CH_2$.

With ^{NMe₃OH} one double bond already in place this would be quite analogous to Willstatter's VII. The difficulty here is the fact that the halide, $CH_3CHBrCH=CH_2$, from which the hydroxide would be made is so unstable, yielding $CH_3CH=CHCH_2Br$. The base corresponding to the latter should pyrolyze exclusively to methylallene, whereas the desired isomer might pyrolyze either to methylallene or 1,3-butadiene. The experiment, therefore, would be inconclusive.

The best escape from this dilemma, and it is an experiment I have planned to do for a long time, is to take the C_5 -analog. If $CH_3CHBrCH=CHCH_3$ rearranges, the product is still the same compound. Hence the base, $CH_3CH(NMe_3OH)-CH=CHCH_3$, should be obtainable pure. It should yield either 1,3- or 2,3-pentadiene, or both. A mixture of the two pentadienes could be separated by means of maleic anhydride, so the approach seems fairly definite.

I shall be pleased to keep you advised of further developments. Thank you ever so much for your helpful suggestions.

Very sincerely yours,

Charles D. Hurd
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