derivatives of a cyclopentenophenanthrene ring system like the sterols and the bile acids.

FROM THE LABORATORIES OF
THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK CITY

WALTER A. JACOBS
JAMES C. E. SIMPSON
Commonwealth Fund Fellow

RECEIVED MAY 5, 1934

THE PEROXIDE EFFECT IN THE ADDITION OF REAGENTS TO UNSATURATED COMPOUNDS

Sir:

On the basis of a study of the addition of hydrogen bromide to pentene-1 and heptene-1 in glacial acetic acid, hexane and water, Sherrill, Mayer and Walter [THIS JOURNAL, **56**, 926 (1934)] conclude that the solvent is the dominant factor governing the direction of addition, and that the peroxide effect is insignificant or non-existent. They ignore the work of Kharasch, McNab and Mayo on the addition of hydrogen bromide to vinyl chloride, allyl and vinyl bromides and reject their work on the addition of hydrogen bromide to propylene on the ground that the small quantities of materials employed furnish yields which are "not very significant" [Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933); Kharasch, McNab and Mayo, *ibid.*, **55**, 2521 (1933); **55**, 2131 (1933)].

We have now repeated our earlier study of the addition of hydrogen bromide to propylene using larger quantities of reagents. Identification of the products was made by boiling points, refractive indices and the preparation of mercury derivatives. Using 1.4 mol (85 g.) of hydrogen bromide, 1 mol (31.5 g.) of propylene and 2 g. of ascaridole as peroxide or antioxidant we obtained, working at $-80°$, both without a solvent and using glacial acetic acid, an 80% yield of 100% *n*-propyl bromide, b. p. 70–71°, n_D^{20} 1.4340, and with a mercury derivative melting at 137.2°. With carbon tetrachloride as a solvent an 18% yield was obtained. Similar experiments using 2 g. of diphenylamine as peroxide or antioxidant gave, with no solvent, or glacial acetic acid or carbon tetrachloride, respectively, 61, 65 and 44% yields of 100% isopropyl bromide, b. p. 59–60°, n_D^{20} 1.4250 (± 0.0001) and a mercury derivative melting at 92.6°. These results confirm our earlier observations and conclusions in every detail.

We would also point out that recently published work on butene-1 and isobutylene [Kharasch and Hinckley, Jr., THIS JOURNAL, **56**, 1212, 1243 (1934)] and unpublished work on the addition of hydrogen bromide to pentene-1 are also completely in accord with our earlier observations. Finally, in view of the possibility of interpreting the work of Whitmore and Homeyer [*ibid.*, **55**, 4555 (1933)] as in disagreement with our observations, we would say that Professor Whitmore in a private communication assures us that he has confirmed our recent findings as to the effects of peroxides and antioxidants in the addition of hydrogen bromide to 4,4-dimethylpentene-1 [Kharasch, Hannum and Gladstone, *ibid.*, **56**, 244 (1934)]. Professor Whitmore has generously withheld publication of his note in order to accord us priority.

JONES CHEMICAL LABORATORY
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M. S. KHARASCH
M. C. MCNAB

RECEIVED MAY 7, 1934

THE ACTION OF THE GRIGNARD REAGENT ON α,β-UNSATURATED ALDEHYDES

Sir:

Up to the present time the reaction of the Grignard reagent with α,β-unsaturated aldehydes has been considered as taking place solely through the carbonyl group, *e. g.*, 1,2-addition. It has now been found that *t*-butylmagnesium chloride reacts with crotonic aldehyde yielding both 1,2- and 1,4-addition products in about equal amount (about 25%). Moreover, preliminary experiments with ethyl-, propyl- and isopropylmagnesium bromides and crotonic aldehyde indicate that here, too, some 1,4-addition takes place though to a very much less extent.

The aldehyde, $C_8H_{16}O$, semicarbazone: m. p. 166°, arising from *t*-butylmagnesium chloride and crotonic aldehyde was easily oxidized by Tollens' solution to an acid, $C_8H_{16}O_2$, amide: m. p. 163–4°. Bromination of this acid by the Hell, Volhard and Zelinsky method followed by treatment with methyl alcohol led to an α-bromo ester, $C_9H_{17}O_2Br$, which when heated with diethylaniline yielded an α,β-unsaturated ester, $C_9H_{16}O_2$. Ozonolysis of this ester produced pinacolone identified as the semicarbazone: m. p. 155°. The original aldehyde was therefore β,γ,γ-trimethylvaleric aldehyde.

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