[*ibid.*, **235,** 200 (1897)] accomplished the separation by fractional crystallization of the hydrochlorides. A simpler procedure has now been developed.

The mixed alkaloids extracted from white lupine seeds were freed from residual solvent and impurities by vacuum distillation. Both forms distil at the same temperature, 220–226° at 12 mm. The distillate had n^{34}_{D} 1.5400; $[\alpha]^{25}_{D}$ 32.02 in alcohol (indicating 38% of *d*-lupanine). It solidified on standing, softened at 40°, became fluid at 67° and was completely melted at 81°; 105 g. was extracted with four 75-cc. portions of warm petroleum ether [Soldaini, *op. cit.*, states that *dl*-lupanine is insoluble in this solvent]. The undissolved material was dissolved in warm acetone and on cooling the solution deposited 20 g. of rhombic prisms, m. p. 98°, $[\alpha]_{D}$ 1.14° at 27° in alcohol. These were recrystallized from acetone and yielded optically inactive colorless prisms of *dl*-lupanine, m. p. 98°. Further crops were obtained from the mother liquors. The last mother liquor contained much *d*-lupanine which was recovered by the method used for the petroleum ether soluble fraction.

The petroleum ether solution was cooled and then deposited 7.5 g. of long needles melting above 90°. The solution was evaporated and left 31 g. of sirupy base that gradually crystallized; in water $[\alpha]^{25}_{D}$ 56.86° (indicating 67.4% of *d*-lupanine). The *d*-base was purified by adapting the method of Ingersoll [THIS JOURNAL, **47,** 1168 (1925)], which has been used successfully by Clemo, Raper and Tenniswood [*J. Chem. Soc.*, 429 (1931)] to resolve *dl*-lupanine: 24.3 g. of the mixed alkaloids in 25 cc. of acetone was added to a mixture of 23 g. of *d*-camphorsulfonic acid and 25 cc. of acetone. Heat was evolved and the whole went into solution. On cooling a good yield of crystals was obtained which when recrystallized from acetone yielded 23.5 g. of *d*-lupanine camphorsulfonate, m. p. 116–8°, $[\alpha]^{29}_{D}$ 44.76° (4.184 g. in acetone). The whole was dissolved in 35 cc. of water, and 7.7 g. of potassium iodide (1 mole) was added. Small needle crystals of the hydriodide were formed immediately, m. p. 183–184°, $[\alpha]^{25}_{D}$ 43.31° (5.084 g. in water). These dissolved in water, made alkaline with sodium hydroxide and extracted with chloroform yielded *d*-lupanine as a sirup that slowly crystallized. It distilled between 190 and 195° at 3 mm. The fluid distillate had n^{24}_{D} 1.5444 and, in alcohol, $[\alpha]^{25}_{D}$ 84.35°, $l = 2$, $c = 4.776$, $a = 7.782°$.

BUREAU OF ANIMAL INDUSTRY
WASHINGTON, D. C.
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RECEIVED APRIL 30, 1934

THE DEHYDROGENATION OF GITOGENIN

Sir:

The authors have recently studied the dehydrogenation of sarsasapogenin with selenium, a report of which is now in press [*Journal of Biological Chemistry*]. The reaction has yielded a low boiling fraction from which a semicarbazone was obtained which melted at 143–144° and analyzed as the derivative of a ketone $C_8H_{16}O$. This melting point does not agree with that (152°) reported for the same material by Ruzicka and van Veen [*Z. physiol. Chem.*, **184,** 69 (1929)] who concluded that it is the derivative of methyl isohexyl ketone. Through the kindness of Prof. I. M. Heilbron, we have obtained a sample of the semicarbazone of methyl isohexyl ketone (m. p. 152°) which, when mixed with our semicarbazone, melted at 130–133° after preliminary softening. The identity of this ketone is under further investigation. In addition, from the higher boiling fractions a crystalline hydrocarbon mixture was obtained which yielded after repeated fractionation by the triangle scheme an apparently homogeneous hydrocarbon of melting point 123.5–124°. This at once suggested identity with methyl-cyclopentanophenanthrene (Diels' hydrocarbon, $C_{18}H_{16}$). This conclusion was strengthened by the preparation of the trinitrobenzene and trinitrotoluene addition products.

We have since made a parallel study of the dehydrogenation of the digitalis sapogenin, gitogenin, with similar results. From the low boiling fraction of the reaction mixture the same semicarbazone was obtained which melted at 144.5–145°. In addition, a crystalline hydrocarbon resulted which after extensive fractionation gave a substance which melted at 123.5–124° and showed no depression when mixed with Diels' hydrocarbon. For confirmation of identity a study of its derivatives is in progress.

It would appear, therefore, in so far as the formation of Diels' hydrocarbon, $C_{18}H_{16}$, may be considered a characteristic of the sterol ring system, that sarsasapogenin and the digitalis sapogenins as well as the cardiac aglucones are alicylic derivatives of a cyclopentenophenanthrene ring system like the sterols and the bile acids.

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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.

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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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