of the product, heavily contaminated with ammonium chloride, is obtained. The recovery of the excess ammonia and of the methyl alcohol greatly reduces the cost of preparation by this method. The use of permutit in removing the last traces of ammonia was not found to be superior to precipitation with methyl alcohol alone.

Analysis of Product.—Molar solutions of five samples of glycine prepared by the above method showed no trace of ammonia with Nessler's reagent, nor of chloride with silver nitrate. Melting points and mixed melting points (with Eastman's ammonia-free glycine, No. 445) were determined by the capillary tube method. Both gave values of 236–239° (uncorrected), with decomposition and effervescence, after browning at 228°. Analyses for the nitrogen content, determined by the Kjeldahl method, gave values ranging from 18.44 to 18.76% (theoretical 18.67%).

Summary.—1. A simple, inexpensive method for the preparation of glycine from monochloroacetic acid and ammonia is outlined.

2. A 60–64% yield of glycine free from ammonia and chloride is obtained.

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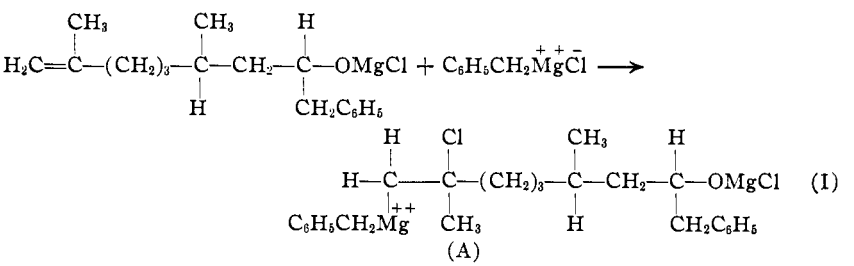
The Purported Addition of Benzylmagnesium Chloride to the Ethylenic Linkage in Citronellal.—It has been suggested[1] that the recent[2] indirect proof offered for the non-addition of benzylmagnesium chloride to the ethylenic linkage in citronellal is not decisive, and that a new possible mechanism is



(I)

(A)

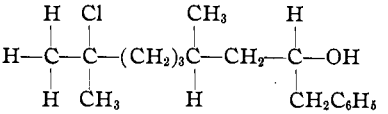
In this manner, "a complex molecule is obtained which is similar to that suggested by Rupe,[3] except that the second molecule of the Grignard reagent is attached in a slightly different manner."

[1] Kharasch, "Annual Survey of American Chemistry," 1930, Vol. V, p. 193.

[2] Gilman and Schulz, THIS JOURNAL, **52**, 3588 (1930).

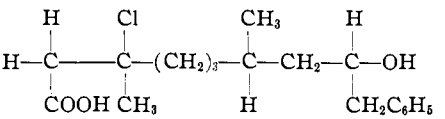
[3] Rupe, *Ann.*, **402**, 161 (1914).

Actually, this mode of addition is quite unlike that proposed by Rupe. On hydrolysis, one would expect Compound (A) to give



and toluene. However, Rupe's analysis shows his product to contain no chlorine, and to have in place of the chlorine the equivalent of a benzyl group. Furthermore, the same product is obtained with benzylmagnesium *bromide*. Accordingly, Compound (A) is without any experimental support.

Granting that Compound (A) is correct, it represents an unsymmetrical organomagnesium compound of the general formula R—Mg—R′. Although such compounds have not yet been prepared, it is known that the symmetrical R—Mg—R compounds on carbonation (followed by hydrolysis) yield the corresponding carboxylic acids, RCOOH. We do not know how R—Mg—R′ compounds would behave on carbonation, but it appears altogether reasonable to expect them to give the two carboxylic acids, RCOOH and R′COOH, in varying quantities depending on the nature of the R— groups. If this be true then Compound (A) on carbonation should give $C_6H_5CH_2COOH$ and



Actually, the latter acid is not obtained, because when the reaction mixture of citronellal and an excess of benzylmagnesium chloride is carbonated, only phenylacetic acid is obtained, as evidenced by melting point, mixed melting point and neutralization equivalent.

The possibility that RMgX adds to an ethylenic linkage to give an R—Mg—R′ compound which might undergo but partial carbonation to give RCOOH to the exclusion of R′COOH is rendered remote by other reported experimental evidence. First, a different RMgX compound (phenylmagnesium bromide) after reaction with citronellal and then carbonation gave presumably pure benzoic acid.[2] Second, if addition of RMgX to an ethylenic linkage did occur with olefins of a type to give rise to R—Mg—R′ compounds in which the R— and the R′— groups were closely related but not identical, then carbonation should give a mixture of acids, but no such mixtures have been obtained.[4]

[4] Gilman and McGlumphy, *Rec. trav. chim.*, **47**, 418 (1928). Earlier pertinent references are contained in this article.

Our unavoidable conclusion is that benzylmagnesium chloride does not add to the ethylenic linkage in citronellal.[5]

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COMMUNICATIONS TO THE EDITOR

THE STABILITY OF NITROGEN PENTOXIDE AT 1000 ATMOSPHERES OF OXYGEN IN THE PRESENCE OF NITROGEN TETROXIDE

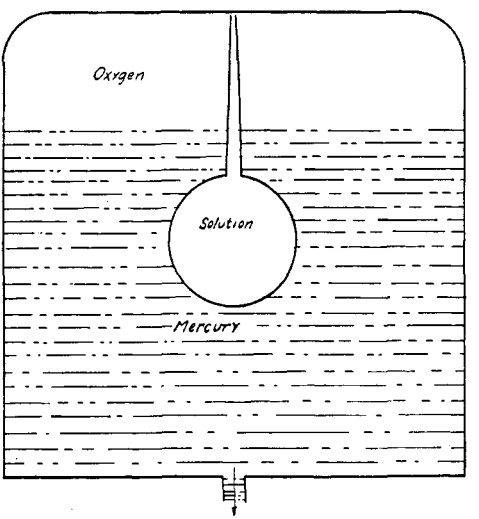
Sir:

The equilibrium

$$N_2O_5 = N_2O_4 + {}^1/_2O_2$$

has been investigated at 1000 atmospheres' pressure of oxygen by dissolving nitrogen tetroxide and nitrogen pentoxide in carbon tetrachloride in an apparatus shown schematically in Fig. 1.

It was found that at this pressure of oxygen the reaction goes completely to the right. With the gas evolution apparatus used for analysis it was possible to detect as little as 0.5 cc. of oxygen, which, with the volumes of nitrogen pentoxide solution used, is equivalent to a partial pressure of 0.00155 atmosphere of nitrogen pentoxide at 25°. The partial pressure of nitrogen tetroxide in one of the runs was 0.710 atmosphere, so that the equilibrium constant in atmospheres is greater than 1.48×10^4. The values given for the partial pressures depend on the assumption of a perfect solution of nitrogen tetroxide, nitrogen pentoxide and carbon tetrachloride and upon a solubility determination of nitrogen pentoxide in a solution of nitrogen tetroxide in carbon tetrachloride. This equilibrium constant gives a free energy change less



To pressure pump
and gage

Fig. 1.

[5] Professor Rupe is in agreement with this conclusion, and he is now engaged in a further study of the constitution of the product obtained from citronellal and benzylmagnesium chloride.