proach of the functional group to the surface of the catalyst.

In contrast to 2,4-dimethylphthalazine-1,4-dione, phthalhydrazide was not attacked during a 20-hr. reaction (*cf.* Ref. 2). This is in accord with the observation that the former compound resembles a simple diacylhydrazine (*e.g.*, it undergoes hydrolysis easily[8]), whereas the latter seems to be a more highly stabilized aromatic ring system.

The last two examples show that hydrazones also are easily cleaved by refluxing with Raney nickel. Since phenylhydrazine[2] and phenylhydrazides[9] undergo cleavage, there is little question that phenylhydrazones can also be cleaved. This promises to be an important application of the method, and is under investigation in this laboratory.

EXPERIMENTAL

The reactions with Raney nickel were carried out by refluxing and stirring vigorously a mixture of 0.5–1.0 g. of the compound to be cleaved with ten times its weight of Raney nickel W-2[4] in 50 ml. of absolute ethanol. When commercial Raney nickel[5] was used, it was slurried several times with absolute ethanol before use. At the end of the reaction the catalyst was removed by filtration and the solvent was distilled under reduced pressure. The product was recrystallized from a suitable solvent and identified by mixed m.p. with an authentic specimen.

The reactions of 1,2-diacetylhydrazine, 1,2-dibenzoylhydrazine, and 1,2-dibenzoyl-1,2-dimethylhydrazine were carried out with Raney nickel W-2 and with commercial Raney nickel. No significant differences in yield were observed.

Iowa City, Iowa

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[8] J. C. E. Simpson, *Condensed Pyridazine and Pyrazine Rings*, Interscience Publishers, Inc., New York, N. Y., 1953, p. 175.

[9] C. Ainsworth, *J. Am. Chem. Soc.*, **78**, 1635 (1956).

[Contribution from the Department of Chemistry, Annex C Laboratories, Emory University]

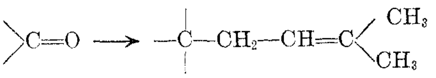
Addition of Isopentenyl[1] Magnesium Chloride to Cyclohexanone

LEON MANDELL

Received July 23, 1956

Isopentenyl magnesium chloride has been prepared and added to cyclohexanone. The alcohol produced, on the basis of its infrared spectrum, its ozonization products, and the ultraviolet absorption spectrum of its dehydration product, has been assigned formula III.

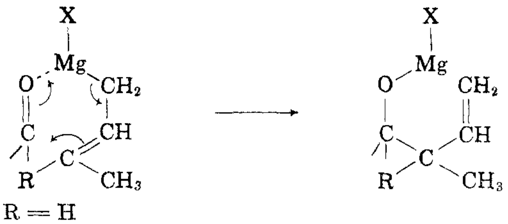
In the course of the syntheses of certain sesquiterpenes, being carried out in these laboratories, it became necessary to add to a ketone group an isopentenyl moiety, that is;



$$>C=O \longrightarrow -\overset{|}{\underset{|}{C}}-CH_2-CH=C\begin{matrix}CH_3\\CH_3\end{matrix}$$

As a possible route for this transformation, the addition of the Grignard reagent of 1-chloro-3-methyl butene-2 to cyclohexanone was studied make clear whether this allylic Grignard reagent adds *via* normal addition or with rearrangement.

The mode of addition of an unsymmetrical allylic Grignard reagent to ketones has been studied by Young and co-workers[2] who found that butenyl magnesium chloride added to ketones with rearrangement. Their extensive studies led them to postulate that both 3-chloro butene-1 and crotyl chloride give rise to the same Grignard reagent, namely the primary one, and that due to the favorable cyclic transition state possible, Ia, this primary Grignard adds with rearrangement.



Ia. R = H
b. R = CH$_3$

This situation may also obtain with isopentenyl magnesium chloride, the only difference being an extra methyl group substituted at the end of the allylic system. However, one could not predict *a priori* whether the analogy would here be valid, for the extra methyl group could so hinder the formation of the cyclic system, Ib, as to raise its energy over that of the transition state needed for normal addition.

The carbonation of the Grignard reagent of isoprene hydrobromide and hydrochloride has been in-

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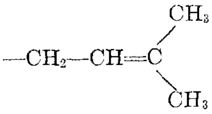
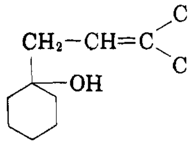
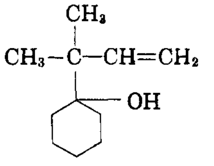
[1] For the sake of simplicity,  $-CH_2-CH=C\begin{matrix}CH_3\\CH_3\end{matrix}$, is referred to as isopentenyl.

[2] W. G. Young, A. N. Prater, and S. Winstein, *J. Am. Chem. Soc.*, **55**, 4805 (1933); W. G. Young, S. Winstein, and A. N. Prater, *J. Am. Chem. Soc.*, **58**, 289 (1936); J. F. Love, J. D. Roberts, and W. G. Young, *J. Am. Chem. Soc.*, **66**, 543 (1944); J. D. Roberts and W. G. Young, *J. Am. Chem. Soc.*, **67**, 148 (1945); W. G. Young and J. D. Roberts, *J. Am. Chem. Soc.*, **67**, 319 (1945); W. G. Young and J. D. Roberts, *J. Am. Chem. Soc.*, **66**, 1472 (1946).

vestigated and although the early workers[3] reported addition without rearrangement, recent work[4] has indicated this finding to be fallacious. Studies carried out[5] on the addition to open chain ketones indicated also a similarly to butenyl Grignard. In order to make more complete these investigations, the product of the reaction between isopentenyl magnesium chloride and cyclohexanone was carefully analyzed by spectral analysis and ozonization to distinguish between the two possible structures, II and III.



II

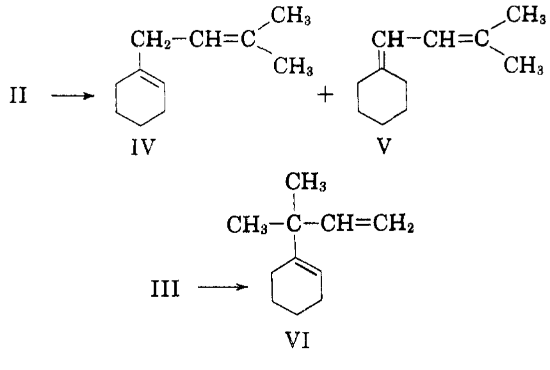


III

The infrared spectrum of the adduct clearly indicated the presence of a mono substituted olefin[6] and excluded any detectable amount of compound containing a trisubstituted double bond.[6] This would suggest that rearrangement had occurred and the alcohol has structure III.

This spectral evidence that rearrangement similar to the type mentioned above had taken place was confirmed by ozonization, from which formaldehyde (as the dimedone derivative) could readily be isolated whereas no acetone could be detected.

Final confirmation of the structure of the adduct was obtained by dehydration of the alcohol. It is seen that II can give rise to two dienes, IV and V, the latter being a substance which should exhibit



absorption in the ultraviolet. Structure III, on the other hand, can yield only one diene,[7] VI, a nonconjugated one, which therefore, would be transparent toward the ultraviolet. The ultraviolet spectrum of the total crude reaction product from dehydration of the adduct with thionyl chloride and pyridine (which was demonstrated to be dehydrated from its infrared spectrum) showed only end absorption and thus is in accord with the structure deduced from the infrared and ozonization data.

One may therefore conclude that the situation with isopentenyl magnesium chloride is much the same as the case of butenyl Grignard.

EXPERIMENTAL[8]

Grignard reaction of 1-chloro-3-methyl butene-2. With rapid stirring 9.5 g. of 1-chloro-3-methyl-butene-2[9] in 100 ml. dry ether was added to 7 g. magnesium suspended in 20 ml. dry ether. The addition was carried out over 3 hr., and the reaction mixture was stirred 30 min. after the addition was completed.

To the above solution was added 10 g. cyclohexanone in 50 ml. dry ether over a period of 0.75 hr.

The reaction mixture was cooled in an ice bath and decomposed with cold 10% hydrochloric acid and extracted with ether. The ether extract was washed with water to *p*H 6, dried over sodium sulfate, and distilled. A forerun of cyclohexanone was taken and the fraction boiling 93–95°/8 mm. collected. Yield, 6.75 g. (40%).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.5; H, 12.0. Found: C, 78.1; H, 11.9.

The infrared spectrum of the adduct exhibited, besides other absorptions, bands at 3095 cm.$^{-1}$ (m.), 1839 cm.$^{-1}$ (w.), 1642 cm.$^{-1}$ (m.), 1418 cm.$^{-1}$ (s.), 1300 cm.$^{-1}$ (m.), 1009 cm.$^{-1}$ (s.), and 915 cm.$^{-1}$ (s.). These bands are all associated with the monosubstituted ethylene grouping. Of particular interest is the absorption at 1009 cm.$^{-1}$ due to CH out of plane deformation, the higher than usual frequency for this absorption being associated with the vinyl double bond substituting a quaternary carbon atom.[10] The lack of absorption in the 840–790 cm.$^{-1}$ region precluded the presence of any trisubstituted double bond.

Ozonization of adduct. A 5% ozone-oxygen mixture was bubbled through a solution of 0.550 g. adduct dissolved in 20 ml. purified chloroform cooled by a dry-ice acetone bath, for 5 min. past the point where the solution became blue. Fifteen ml. water was then added and the chloroform and water were distilled off. The distillate was divided into two equal portions and one half treated with 0.5 g. dimedone in 10 ml. methanol and the other half added to a solution of 1 g. 2,4-dinitrophenylhydrazine in 100 ml. ethanol and 2 ml. concentrated hydrochloric acid.

The former solution was heated in a steam bath to drive off the chloroform and most of the methanol. Upon cooling fine needles separated which on filtration gave 0.122 g., m.p. 188–189°. Mixture melting point with authentic formaldehyde dimedone derivative showed no depression. This corresponds to 25% yield of formaldehyde.

The latter solution was concentrated so as to remove the chloroform and allowed to evaporate slowly at room temperature. From several fractions of crystals taken over a period of days only unchanged reagent could be isolated.

Dehydration of adduct. To a solution of 2.5 g. adduct in

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(3) H. Staudinger, W. Kreis, and W. Schilt, *Helv. Chim. Acta*, **5**, 743 (1922).

(4) H. Kwart and R. K. Miller, *J. Am. Chem. Soc.*, **76**, 5403 (1954); J. M. Rule, Senior Thesis, University of California at Los Angeles, 1944; also reference (5).

(5) B. L. Garner, Ph.D. thesis, University of California at Los Angeles, 1952.

(6) For a discussion of the infrared spectra, see Experimental.

(7) One could envisage a rearrangement involving ring expansion by which III could also give rise to a conjugated diene. However, as the results indicated no conjugated diene to be present at all, this possibility need not be considered.

(8) Melting points are uncorrected. Analyses are by Drs. G. Weiler and F. B. Strauss, Microanalytical Lab., Oxford, Great Britain.

(9) Prepared using the procedure of A. J. Ultee, *Rec. trav. chim.*, **68**, 125 (1949).

(10) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1954, Chapter 3.

10 ml. anhydrous ether and 3 ml. purified pyridine cooled in an ice bath, was slowly added with shaking, 2 g. thionyl chloride. The reaction mixture was allowed to warm to room temperature and then stand for 16 hr. It was then poured onto cracked ice and the mixture extracted with ether. The ether extract, after having been washed several times with water and then dried over sodium sulfate, was concentrated *in vacuo* to remove the ether.

An infrared spectrum of the total crude product revealed that the hydroxyl group, which appeared in the adduct at 3580 cm.$^{-1}$ as a sharp and intense bond, was completely lacking, thus indicating the completeness of the dehydration reaction.

The ultraviolet spectrum run on an ethanol solution whose concentration was 1.2 × $10^{-3}M$, showed only end absorption above 220 mμ.

EMORY UNIVERSITY, GA.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE U. S. NAVAL ORDNANCE TEST STATION]

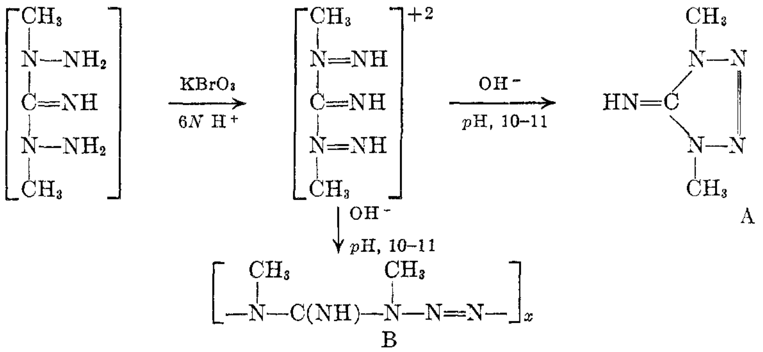
Preparation and Oxidation of 1,2-Diamino-1,2-dimethylguanidine

WILLIAM R. McBRIDE, WILLIAM G. FINNEGAN, AND RONALD A. HENRY

Received July 24, 1956

1,2-Diamino-1,2-dimethylguanidine has been synthesized and oxidized with bromate in acidic medium to 1,4-dimethyl-5-iminotetrazole.

It has recently been demonstrated[1] that the oxidation of 1,1-dialkylhydrazines with bromate or iodate in strongly acidic medium involves a two electron change and yields diazo-like intermediates, $[R_2N{=}NH]^+$, of varying stability. These intermediates are irreversibly converted to tetraalkyltetrazenes in basic medium. This sequence of reactions has now been applied to 1,2-diamino-1,2-dimethylguanidine. The coupling of the diazo-like intermediate can occur either intramolecularly to give the known 1,4-dimethyl-5-iminotetrazole[2] or intermolecularly to give a water-soluble polytetrazene.



Experimentally the substituted tetrazole (A) was recovered as its phenylthiourea derivative in 35–37% yield. The synthesis of the 1,4-dimethyl-5-iminotetrazole in this manner is further proof that the previously assigned positions[2] for the methyl groups are correct. In addition, this method offers a new route to this class of tetrazole compounds.

Since the phenylthiourea derivative of the 1,4-dimethyl-5-iminotetrazole is readily formed and is sparingly soluble, the results from this method of isolation should be a good indication of the total amount of tetrazole present in solution. However, a comparison of the molar absorbancy indices (A_M) for 1,4-dimethyl-5-iminotetrazole and the oxidized species from 1,2-diamino-1,2-dimethylguanidinium nitrate (A_M = 1980 and *ca.* 1750, respectively, at 258 mμ in basic aqueous solution) indicates that conversion to tetrazole or compounds with a similar nitrogen resonance system should be about 90%. This spectrophotometric procedure would probably not discriminate between the nitrogen system in the tetrazole and that found either in a polytetrazene (B) or conceivably in a 10-membered ring compound resulting from a dimerization of the diazo-like intermediate. Hence, the difference between the 36% and the 90% is best attributed to polytetrazene although it has not been isolated.

One other product that might result indirectly during the oxidation of 1,2-diamino-1,2-dimethylguanidine is 1,4-dimethyl-5-tetrazolone (from the hydrolysis of the corresponding imino-compound). This possibility is largely excluded, however, by the following: 1,4-Dimethyl-5-tetrazolone in aqueous solution has a maximum absorption at 223 mμ (A_M = 3185), which is similar to that for 1,4-dimethyl-5-iminotetrazole in acidic medium, but which is otherwise essentially independent of *p*H.

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(1) W. R. McBride and H. W. Kruse, Abstracts 129th National Meeting, AMERICAN CHEMICAL SOCIETY, 6Q, Dallas, April 1956. *J. Am. Chem. Soc.*, **79**, 572 (1957).

(2) R. A. Henry, W. G. Finnegan, and E. Lieber, *J. Am. Chem. Soc.*, **76**, 2894 (1954).