precipitate is obtained. The analyses[3] support the formula for bistrichlorostibine-triscarbonmonoxide iron, $\mathrm{Fe(CO)_3(SbCl_3)_2}$: Fe, 10.4 (calcd. 9.37); Sb, 39.3 (calcd. 40.83); Cl, 34.4 (calcd. 35.70). The presence of carbon monoxide was shown qualitatively and a rough qualitative estimate of the gas evolved on thermal decomposition of the compound agrees with the other analyses. Like iron pentacarbonyl, the antimony trichloride complex is photosensitive, darkening on exposure to light, and consequently the reactions were carried out in absence of light.

Both the nickel and iron complexes are amorphous powders, insoluble in organic solvents such as benzene, pentane, cyclohexane and carbon tetrachloride. Carbon disulfide reacts, liberating carbon monoxide and leaving dark colored residues. With alcohols and acetone, decomposition occurs, carbon monoxide is evolved, and solutions of divalent nickel and iron result, leaving a precipitate of antimony oxychloride. With water, dilute acids and alkalies, similar rapid reactions occur with loss of carbon monoxide, giving nickelous or ferrous solutions or hydroxides, antimony oxychloride or antimonate. The compounds are decomposed on heating to give carbon monoxide and, in the case of the iron compound, some metal carbonyl together with antimony trichloride. On treating the compounds with phosphorus trichloride, there is a vigorous reaction evolving carbon monoxide and it is possible that further substitution occurs; the color of the residue is darker but no analyses have been made.

The great difference in properties between the antimony trichloride substitution compounds of nickel and those formed by the phosphorus halides may be due to the increasing inertness of the electron pair in the antimony halides compared with the phosphorus halides. Presumably there is also a lowered tendency to form π bonds with nickel which operate to stabilize metal complexes. Efforts to identify further antimony trichloride substitution products were without success.

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The Propargylic Rearrangement. IV. The Carbonation Products of Propargylmagnesium Bromide

BY JOHN H. WOTIZ, JOSEPH S. MATTHEWS AND JOHN A. LIEB

Recently it was found that primary propargylic bromides,[1] $\mathrm{R{-}C{\equiv}C{-}CH_2Br}$ (I), where R signifies the normal propyl, butyl or amyl group, can be converted to Grignard reagents by means of amalgamated magnesium using a newly developed high dilution technique.[2] These Grignard reagents on low temperature carbonation yielded stable solid allenic acids, $\mathrm{R{-}\underset{\underset{\displaystyle CO_2H}{|}}{C}{=}C{=}CH_2}$ (II), liquid acetylenic acids, $\mathrm{R{-}C{\equiv}C{-}CH_2CO_2H}$ (III) and unidentified dimeric acids. Secondary and tertiary propargylic bromides[3] were also converted into stable solid allenic acids by a similar procedure.

Prévost, *et al.*,[4] recently reported the conversion of propargyl bromide into a Grignard reagent which they carbonated at −80°. Upon hydrolysis they isolated a solid acid melting at 73° to which they assigned the structure $\mathrm{H{-}C{\equiv}C{-}CH_2CO_2H}$ (IV) (*e.g.*, III where R equals H). They also found a liquid acidic portion and resins thought to be derived from the unstable butadienoic acid, $\mathrm{CH_2{=}C{=}CH{-}CO_2H}$ (V) (*e.g.*, II where R equals H). Since these workers did not state the method used in assigning of structure of the solid acid, we thought they might be in error because: (a) the acid IV was previously prepared[5] by the oxidation of 3-butynol-1 and found to melt at 83°, (b) they regarded allenic acids (II) as unstable which is contrary to our findings.

We have repeated some of the above-described work treating propargyl bromide with amalgamated magnesium in the cyclic reactor,[2] and poured the formed Grignard reagent on Dry Ice. The yield of the crude acidic portion was 28% which is lower than the yields obtained (52 to 72%)[1] from I. On distillation a semi-solid was obtained which on repeated crystallization yielded 3-butynoic acid (IV), m.p. 83–84°, in form of white plates. Its structure was established by elementary analysis and infrared spectrum, Fig. 1, curve A. The spectrum shows a strong absorption band near 3270 cm.$^{-1}$ characteristic for the $\mathrm{H{-}C{\equiv}}$ structure, and the absence of isomeric compounds. The mother liquor from IV was freed of solvent by redistillation. The distillate, b.p. 75–80° at 5 mm., had the same elementary analysis as IV. Its spectrum (Fig. 1, curve B) showed it to be a mixture of IV, the allenic

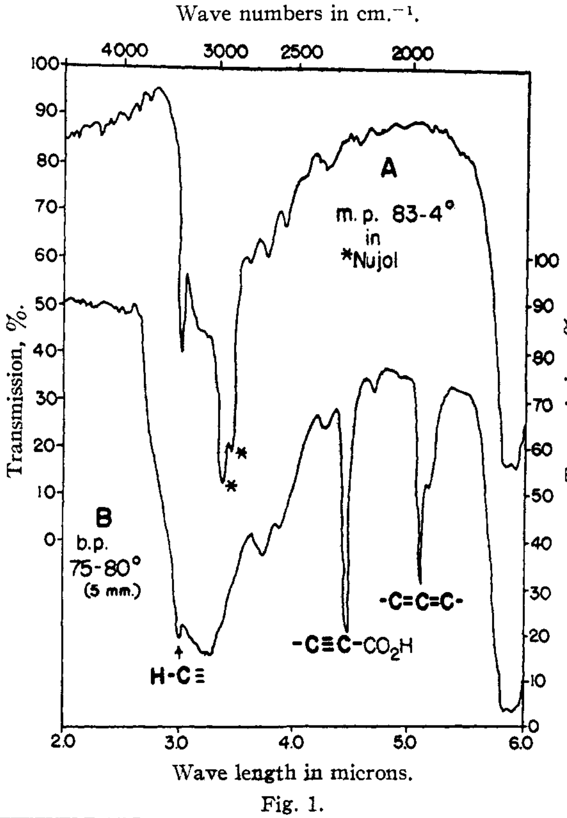

Fig. 1.

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[1] J. H. Wotiz, THIS JOURNAL, **72**, 1639 (1950).

[2] D. C. Rowlands, K. W. Greenlee and C. E. Boord, Abstracts of the 117th A. C. S. Meeting, Philadelphia, April, 1950.

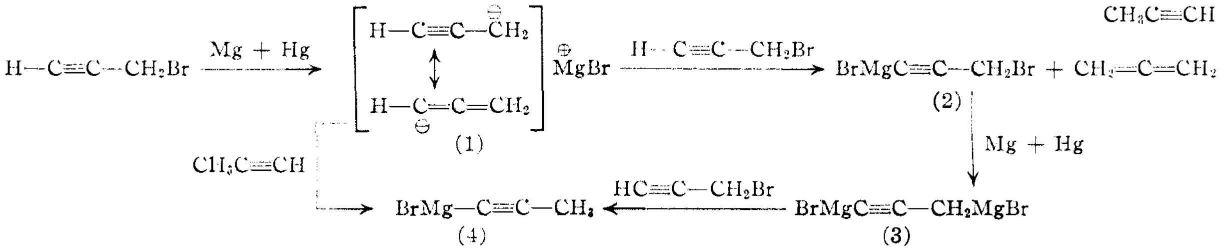
[3] J. H. Wotiz and R. J. Palchak, THIS JOURNAL, **73**, 1971 (1951).

[4] C. Prévost, M. Gaudemar and J. Honigberg, *Compt. rend.*, **230**, 1186 (1950); *C. A.*, **45**, 1497 (1951).

[5] I. Heilbron, E. R. H. Johnes and F. Sondheimer, *J. Chem. Soc.*, 604 (1949).

acid V and of 2-butynoic acid, $CH_3—C≡C—CO_2H$ (VI).[6] Aside from the mentioned band near 3270 cm.$^{-1}$, the spectrum contains a strong band near 2240 cm.$^{-1}$ characteristic of the triple bond conjugated with a carboxy group (—C≡C—CO_2H), and the strong 1950 cm.$^{-1}$ allenic bond (C=C=C—) absorption band. The positions and intensities of the mentioned bands are consistent with the ones of similar compounds previously described.[1,7]

The formation of the found acids could be explained on the basis of the equations



Acids derived from forms 2 and 3 are not isomeric with the one derived from forms 1 and 4. Their presence or absence was not established as only a product boiling over a limited range was analyzed. The presence of the Grignard reagent 3 in the reaction product of propargyl bromide and magnesium was favored by Gaudemar[8] who also found glycols of the type R—CHOH—C≡C—CH_2—CHOH—R in the reaction product of "propargylmagnesium bromide" and aldehydes.

On the basis of our findings, we conclude that the French workers[4] were dealing with an impure sample of IV and that they were incorrect in thinking that V is unstable. Since we were not successful in separating V from IV and VI we were not able to characterize this compound.

Experimental

Propargyl bromide was prepared from propargyl alcohol[9] and phosphorus tribromide in the presence of pyridine. Since there are several different constants recorded in the literature, we rectified the bromide through a column till a constant boiling point and refractive index were reached; b.p. 81°, $n^{25}D$ 1.4875.

Anal.[10] Calcd. for C_3H_3Br: C, 30.2; H, 2.5. Found: C, 30.2; H, 2.6.

Preparation and Carbonation of the Grignard Reagent.—A solution of 36 g. (0.3 mole) of propargyl bromide in 300 ml. of dry ether reacted with amalgamated magnesium as previously described.[1] A solid which adhered to the side of the boiler separated during this reaction and was loosened with a spatula before the ether solution (suspension) was poured upon a Dry Ice–ether mixture and allowed to come to room temperature overnight. The hydrolysis with a saturated solution of ammonium chloride was accompanied by an evolution of a gas. The acidic portion (7 g., 28% yield) was dark colored. On a one-plate distillation, 4 g. (b.p. 75 to 80° at 5 mm.) of a colorless semi-solid was collected. On four crystallizations from a mixture of petroleum ether (30–60°) and benzene, a product comprising 2.5 g. of white plates was isolated, m.p. 83–84°.

Anal. Calcd. for $C_4H_4O_2$: C, 57.1; H, 4.8. Found: C, 56.8; H, 4.9.

Its infrared spectrum[11] in Nujol is described by curve A in Fig. 1. The mother liquor was redistilled and the portion boiling at 67–68° at 4 mm. partly solidified. The solid was removed by filtration and the filtrate analyzed.

Anal. Calcd. for $C_4H_4O_2$: C, 57.1; H, 4.8. Found: C, 56.7; H, 5.3.

Its infrared spectrum is described by curve B in Fig. 1.

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[6] W. L. German, G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 1604 (1937), list it to melt at 76–78°.

[7] J. H. Wotiz and F. A. Miller, THIS JOURNAL, **71**, 3441 (1949).

[8] M. Gaudemar, *Compt. rend.*, **233**, 64 (1951).

[9] We gratefully acknowledge the General Aniline and Film Co. for their generous sample.

[10] Microanalyses by the Microanalytical Laboratory of the University of Pittsburgh.

[11] Infrared analyses by Dr. F. A. Miller and co-workers at the Mellon Institute, Pittsburgh, Pa.

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1-Nitromethylcyclohexanol and Homologs

BY THOMAS F. WOOD AND RICHARD J. CADORIN

Recently there have appeared four papers by different investigators[1–4] in which the preparation of 1-nitromethylcyclohexanol from the condensation of nitromethane and cyclohexanone by several methods is described. This compound was first prepared and described by Fraser and Kon[5] in 1934. Since that time other investigators[1,4,6] have encountered difficulties in reproducing the results of these workers. Nightingale and coworkers[1] advocated the use of freshly prepared sodium ethoxide catalyst for carrying out the condensation which was conducted at 50° for 1.5 hours and 36 hours at room temperature; they reported a yield of 33.7% by this modification in contrast to the 45% yield claimed by Fraser and Kon.[5] Grob and von Tscharner[2] satisfactorily effected the condensation of nitromethane and cyclohexanone at room temperature in absolute alcohol using a molar equivalent of sodium ethoxide as condensing agent and with exclusion of moisture; after the mixture was allowed to stand overnight the insoluble sodium salt of the resulting nitroalcohol was isolated and decomposed with acetic acid to yield the desired nitroalcohol in 75% yield. Dauben and co-workers[4] mentioned the difficulties encountered by others[1,6] in effecting the condensation and described a slight improvement in yield (78 to 82%) by the use of a 50% excess of nitromethane in the Grob–von Tscharner procedure.[2] This improved yield was apparently calculated on either the sodium ethoxide or the cyclohexanone used. They further summarized their experiences

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[1] D. V. Nightingale, F. B. Erickson and N. C. Knight, *J. Org. Chem.*, **15**, 782 (1950).

[2] C. A. Grob and W. von Tscharner, *Helv. Chim. Acta*, **33**, 1070 (1950).

[3] G. A. R. Kon, *J. Chem. Soc.*, 843 (1951).

[4] H. J. Dauben, Jr., H. J. Ringold, R. H. Wade and A. G. Anderson, Jr., THIS JOURNAL, **73**, 2359 (1951).

[5] H. B. Fraser and G. A. R. Kon, *J. Chem. Soc.*, 604 (1934).

[6] H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 384 (1943).