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Metal Acetate- and Alcohol-catalyzed Retropropargyl Rearrangement

Fumio TODA, Masahiro HIGASHI and Katsuhiko AKAGI

Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama

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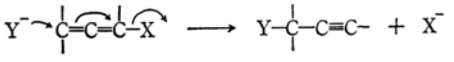
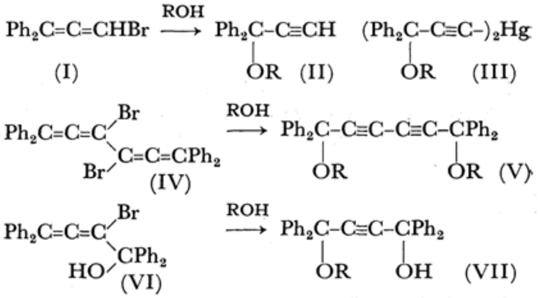
A few lithium aluminum hydride-,[1,2] cuprous bromide-,[3] potassium iodide-[3] and silver nitrate-[4] catalyzed retropropargyl rearrangements*1 (Eq. (1)) have been reported. In all these cases, however, the rearrangement was accompanied by isomerization to allene or by reduction to ethylene. It has also been reported that the alkylation of haloallene increases the proportion of the allenic isomer[5] or of the reduction product.[2] We have found that some metal acetates in alcohol and, surprisingly, alcohol itself also act as catalysts for the retropropargyl rearrangement of phenyl-substituted bromoallenes, thus affording alkoxy-acetylenes in moderate yields. This is the first finding of the alcohol-catalyzed displacement of a relatively unreactive halogen atom on an unsaturated carbon.



$$Y^- \rightarrow \underset{|}{\overset{|}{C}}=C=\overset{|}{C}-X \longrightarrow Y-\underset{|}{\overset{|}{C}}-C\equiv C- + X^- \quad (1)$$

The treatment of 1,1-diphenyl-3-bromopropadiene[6] (I) in methanol with an equimolar amount of AgOAc at room temperature for 1 hr afforded 1,1-diphenyl-1-methoxyprop-2-yne[7] (IIa) in a 71% yield. By the procedure employed for I, 1,1,6,6-tetraphenyl-3,4-dibromohexa-1,2,4,5-tetraene (IV)[8] was then reacted with methanol in the presence of twice the molar amount of AgOAc; this afforded 1,1,6,6-tetraphenyl-1,6-dimethoxyhexa-2,4-diyne (Va)*2 in a 94% yield. A similar rearrangement was observed with 1,1,4,4-tetraphenyl-3-bromobuta-1,2-diene-4-ol[9] (VI), where the reaction was faster than those of I and IV. The treatment of VI with methanol in the presence of AgOAc for 30 min at room temperature afforded 1,1,4,4-tetraphenyl-1-methoxybut-2-yne-4-ol (VIIa) in a 95% yield. The structure of VIIa was identified by comparing its mp and infrared spectrum with those of an authentic specimen prepared according to the literature.[7]



a: $R=CH_3$ b: $R=H$

When the AgOAc-catalyzed rearrangements of I, IV, and VI were carried out in aqueous acetone, the corresponding acetylenic alcohols, IIb, Vb, and VIIb, were obtained in quantitative yields.

All of the rearrangements described above were also catalyzed by $Hg(OAc)_2$, whereas the acetates of Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cr^{2+}, Co^{2+} and Ni^{2+} were all inert. The treatment of I in methanol with an equimolar amount of $Hg(OAc)_2$ afforded the mercuric acetylide IIIa, whereas the same treatment of IV gave Va. Since IIIa was easily formed by the reaction of IIa and $Hg(OAc)_2$, IIa may be produced initially. The mercuric acetylide IIIa was identical with that prepared according to the usual method.[10] In the case of VI, an unidentified mercuric compound, $C_{30}H_{23}O_3BrHg$, was obtained in a 14% yield in addition to VIIa (54% yield).

The most striking rearrangement was the alcohol-catalyzed one. After standing for a long time at room temperature, a mixture of IV and methanol afforded Va quantitatively. Although the metal acetate-catalyzed rearrangement was done for 1 hr,

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[1] T. L. Jacobs and W. L. Petty, *J. Org. Chem.*, **28**, 1360 (1963).

[2] T. L. Jacobs and R. D. Wilcox, *J. Am. Chem. Soc.*, **86**, 2240 (1964).

[3] T. L. Jacobs and W. F. Brill, *ibid.*, **75**, 1314 (1953).

[4] Y. R. Bhatia, P. D. Landor and S. R. Landor, *J. Chem. Soc.*, **1959**, 24.

*1 For a recent review, see D. R. Taylor, *Chem. Revs.*, **67**, 317 (1967).

[5] T. L. Jacobs, E. G. Teach and D. Weiss, *J. Am. Chem. Soc.*, **77**, 6254 (1955).

[6] P. Martinet and H. Doupeux, *Compt. rend.*, **261**, 2498 (1965).

[7] J. Godineau, P. Cadiot and A. Willemart, *ibid.*, **246**, 2499 (1958).

[8] F. Toda, M. Higashi and K. Akagi, unpublished results.

*2 An authentic sample of Va was prepared by the oxidative coupling of IIa which had been obtained according to the reported method.[7]

[9] F. Toda, T. Komoda and K. Akagi, This Bulletin, **41**, 1493 (1968).

[10] B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.*, **1951**, 893

a similar reaction without a catalyst afforded unreacted bromoallene. However, the reaction was accelerated by heating; for example, the heating of a mixture of IV and methanol under reflux for 5 hr afforded Va in a 93% yield. The heating under reflux of a solution of I in methanol for 1 hr afforded IIa and 1,1-diphenylprop-1-en-3-al (VIII) in 43 and 46% yields respectively. The latter was identical with that prepared according to the reported method.[11] The same treatment of VI in methanol afforded, quantitatively, 1,1,4,4-tetraphenyl-1,4-dimethoxybut-2-yne (IX), which was identical with that prepared according to a different method.[12] Since the treatment of VIIa in methanol containing a catalytic amount of hydrogen bromide afforded IX quantitatively, it is clear that VIIa was formed initially and that it then reacted further with methanol. The acid-catalyzed replacement of hydroxyl with the alkoxyl group will be reported in a separate paper.

Experimental[*3]

Silver Acetate-catalyzed Rearrangements in Methanol of Several Bromoallenes. I) A solution of I (2.71 g, 10 mmol) and AgOAc (1.67 g, 10 mmol) in methanol (100 m*l*) was stirred at room temperature for 1 hr. The reaction mixture was then decomposed with water and extracted with ether. The ether layer was washed with water and dried over sodium sulfate. The crude oil remaining after the evaporation of the solvent was distilled to afford IIa, 1.58 g (71%), bp 109°C/3 mmHg. The infrared spectrum was identical with that of an authentic sample prepared according to the literature.[7]

IV) A solution of IV (270 mg, 0.5 mmol) in methanol (10 m*l*) was treated with AgOAc (160 mg, 1 mmol) by the procedure employed for I. The crude crystals obtained by adding water to the reaction mixture were recrystallized from methanol to yield Va as colorless needles, 208 mg (94%), mp 196°C. IR: 2160 ($\nu_{C\equiv C}$) and 1090 cm^{-1} (ν_{C-O}). NMR: a multiplet centered at 2.65 (phenyl, 20H) and a singlet at 6.62τ (methyl, 6H). These spectral data were identical with those of an authentic sample prepared by the oxidative coupling of IIa.

Found: C, 87.15; H, 5.77%. Calcd for $C_{32}H_{26}O_2$: C, 86.88; H, 5.92%.

VI) A solution of VI (453 mg, 1 mmol) in methanol (10 m*l*) was treated with AgOAc (167 mg, 1 mmol) by the procedure employed for I. The curde crystals obtained by adding water to the reaction mixture were recrystallized from petroleum ether (bp 70—80°C) to afford VIIa as colorless needles, 380 mg (95%), mp 112—113°C. IR: 3350 (ν_{OH}) and 1060 cm^{-1} (ν_{C-O}).

Found: C, 85.83; H, 6.12%. Calcd for $C_{29}H_{24}O_2$: C, 86.14; H, 5.94%.

Silver Acetate-catalyzed Rearrangements in Aqueous Acetone of I, IV, and VII. A solution of the bromoallene (I, IV or VII) in 80% aqueous acetone was treated with an equimolar amount of AgOAc by the procedure employed for the rearrangement in methanol. The reaction mixture was decomposed with water and extracted with ether. The ether layer was washed with water, dried over sodium sulfate, and evaporated to dryness to give the corresponding acetylenic alcohol, IIb, VIb, or VIIb, in a quantitative yield in all cases. Each product was recrystallized from acetone to afford the corresponding complex with acetone; each product was identical with the respective authentic sample.[13]

Mercuric Acetate-catalyzed Rearrangements in Methanol of the Following Bromoallenes. I) A mixture of I (271 mg, 1 mmol), $Hg(OAc)_2$ (319 mg, 1 mmol), and methanol (10 m*l*) was stirred at room temperature for 2 hr. Crystals collected by filtration were recrystallized from benzene-petroleum ether (bp 70—80°C) to afford IIIa as colorless needles, 232 mg (72%), mp 211°C. IR: 2160 ($\nu_{C\equiv C}$), and 1185 and 1075 cm^{-1} (ν_{C-O}). NMR: a multiplet centered at 2.63 (phenyl, 20H) and a singlet at 6.64; (methyl, 6H). Those spectral data were identical with those of an authentic sample prepared according to the usual method.[10]

Found: C, 59.72; H, 4.01%. Calcd for $C_{32}H_{26}O_2Hg$: C, 59.76; H, 4.08%.

IV) The same treatment of IV for 5 hr gave Va in a 53% yield.

VI) The treatment of VI (453 mg, 1 mmol) in methanol (10 m*l*) with $Hg(OAc)_2$ (320 mg, 1 mmol) at room temperature for 30 min afforded a crystalline solid. The solid was collected by filtration, washed with methanol, and recyrstallized from acetone to yield an unidentified mercuric compound, 100 mg, (14% as $C_{30}H_{23}O_3BrHg$), mp>270°C.

Found: C, 50.11; H, 3.02%. Calcd for $C_{30}H_{23}O_3$-BrHg: C, 50.63; H, 3.23%.

The combined methanol layer was decomposed with water and extracted with ether. The ether layer was washed with water and dried over sodium sulfate. Crystals obtained by the evaporation of the solvent were recrystallized from petroleum ether (bp 70—80°C) to yield VIIa as colorless needles, 220 mg (54%), mp 112—113°C. A mixed-melting-point determination with an authentic sample prepared by the AgOAc-catalyzed reaction showed no depression.

Alcohol-catalyzed Rearrangements of Several Bromoallenes. I) A solution of I (135 mg, 0.5 mmol) in methanol (10 m*l*) was heated under reflux for 1 hr. After the addition of water, the reaction mixture was extracted with ether. The ether layer was washed with water, dried over sodium sulfate, and

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[11] H. Lorenz and R. Wizinger, *Helv. Chim. Acta*, **28**, 600 (1945).

[12] R. Kuhn and H. Trischmann, *Chem. Ber.*, **94**, 2258 (1961).

[*3] All the melting points were uncorrected. The infrared spectra were recorded in Nujol mull on a grating spectrophotometer IR-G of the Japan Spectroscopic Co. The NMR spectra were recorded on a Japan Electron Optics Laboratory C-60 Spectrometer, in $CDCl_3$, using TMS as the internal standard. The vpc analysis was performed on a Hitachi Perkin-Elmer model F6-D instrument at 200°C, using a column containing PEG 6000/Diasolid M.

[13] F. Toda and K. Akagi, *Tetrahedron Letters*, **1968**, 3695.

evaporated to dryness to leave an oil, 96 mg. The oil was identified as a mixture of IIa (43% yield) and 1,1-diphenylprop-1-en-3-al[11] (VIII) (46% yield) by vpc analysis using authentic samples.

IV) A solution of IV (135 mg, 0.25 mmol) in methanol (5 m*l*) was heated under reflux for 5 hr to give Va, 103 mg (93%).

VI) The same treatment of VI with methanol for 1 hr afforded IX in a quantitative yield, mp 112—113°C (lit.[12] mp 113—114°C). A mixed-melting-point determination with an authentic sample prepared according to the literature[12] showed no depression. The heating of VIIa with methanol in the presence of a catalytic amount of hydrogen bromide also gave IX in a quantitative yield.