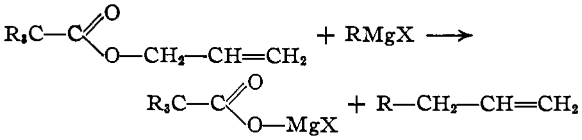
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

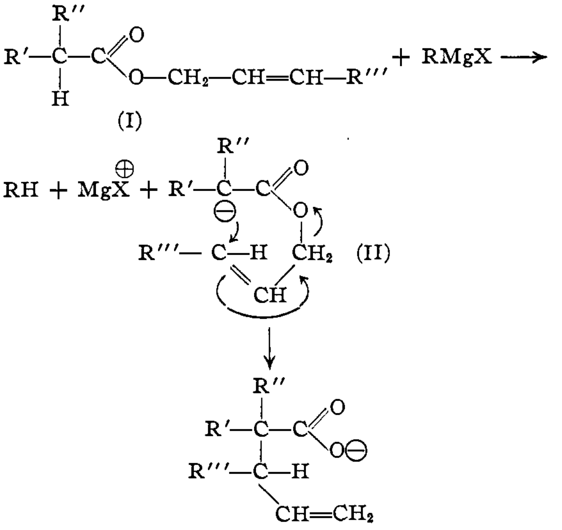
A New Rearrangement of Allylic Esters

BY RICHARD T. ARNOLD AND SCOTT SEARLES, JR.[1,2]

In an earlier study[3,4,5,6] it was demonstrated that allylic esters of hindered, tertiary carboxylic acids react with the Grignard reagent to give olefins and halomagnesium salts according to the following equation.

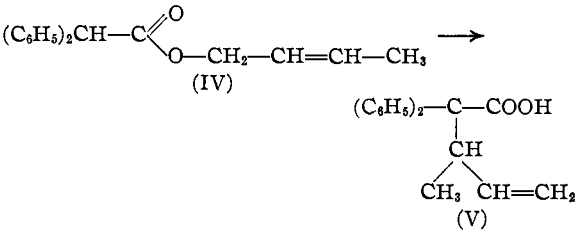


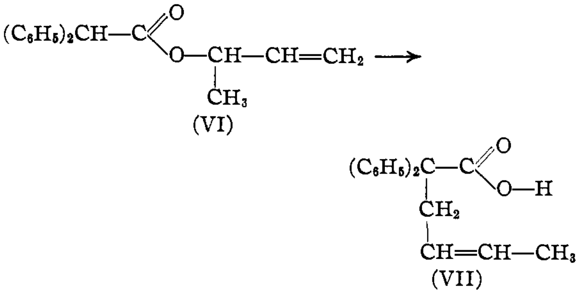
In the event that the allylic ester (I) contains at least one alpha hydrogen atom, the Grignard anion (R^-) can act as a base and bring about formation of the anion (II). An intramolecular rearrangement can then occur to produce a thermodynamically more stable anion (III).


(I)
(II)
(III)

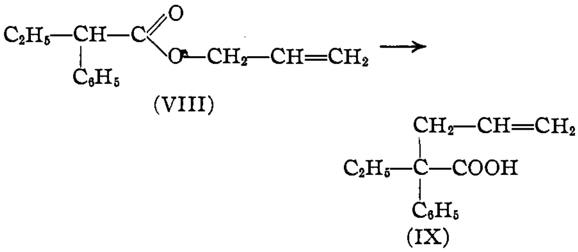
Several examples of this new intramolecular rearrangement have now been observed.[7]

In support of a mechanism involving the transient ring intermediate (II), it has been demonstrated that the allylic system undergoes an alpha-gamma shift during the course of this reaction. Thus, *n*-crotyl diphenylacetate (IV) yields 2,2-diphenyl-3-methylpenten-4-oic acid (V) and isocrotyl diphenylacetate (VI) is transformed into 2,2-diphenylhexen-4-oic acid (VII).


(IV)
(V)


(VI)
(VII)

A wide variety of basic reagents (RMgX, NaH, and R_2N-MgX) have been employed with varying degrees of success. When R' and R'' (in I) are aromatic, very satisfactory yields were obtained by the use of Grignard reagents or pulverized sodium hydride. To date, poor results have been observed when R' = alkyl and R'' = aryl. However, by employing a base of the type R_2N-MgX, allyl α-phenylbutyrate (VIII) was converted into 2-ethyl-2-phenylpenten-4-oic acid (IX) in low yields.


(VIII)
(IX)

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Experimental

Allyl Diphenylacetate.—A solution containing allyl alcohol (10 g.) and dry pyridine (15 g.) was added dropwise into a solution of diphenylacetyl chloride (35 g., prepared by means of thionyl chloride on the acid) and chloroform (30 ml.) at 30–50°. After standing several hours at room temperature, the solution was washed with dilute alkali and with water and the chloroform layer was then dried with sodium sulfate. Direct distillation gave allyl diphenylacetate; b. p. 161–162° (3 mm.); yield 28.6 g.

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[1] Most of the work reported here has been taken from the Ph.D. thesis of Scott Searles, Jr., University of Minnesota, July, 1947.

[2] Present address, Department of Chemistry, University of Illinois.

[3] Arnold, Bank and Liggett, THIS JOURNAL, **63**, 3444 (1941).

[4] Arnold and Liggett, *ibid.*, **64**, 2875 (1942).

[5] Arnold and Liggett, *ibid.*, **67**, 337 (1945).

[6] Unpublished results by Scott Searles, Jr.

[7] A patent application covering this reaction was filed at the United States Patent Office on December 31, 1947.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.82; H, 6.15.

2,2-Diphenylpenten-4-oic Acid.—(a) A Grignard solution prepared from bromomesitylene (25 g.), magnesium (3.1 g.) and ether (75 ml.) was allowed to react for fifteen hours at 25–35° with a solution composed of allyl diphenylacetate (25 g.) and anhydrous ether (25 ml.). After decomposition of the reaction mixture with slightly acidified ammonium chloride solution, the ether layer was extracted thoroughly with sodium hydroxide solution (5%). Distillation of the ether layer gave mesitylene (9.5 g., 63%) and unchanged allyl diphenylacetate (5.4 g.).

Acidification of the aqueous layer gave 2,2-diphenylpenten-4-oic acid (11.9 g.); m. p. 141.5–141.9°.[8]

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39; neut. equiv., 252.3. Found: C, 80.73; H, 6.57; neut. equiv. 252.9.

(b) Allyl diphenylacetate (149 g.) was allowed to react with sodium hydride (18 g.) in boiling toluene in a nitrogen atmosphere for about twenty hours. The cooled mixture was poured into water and the whole shaken vigorously. From the toluene layer there was obtained, by distillation, unused allyl diphenylacetate (56 g.).

Acidification of the alkaline layer gave 2,2-diphenylpenten-4-oic acid which after recrystallization weighed 83.5 g. (56%) and melted at 142–142.5°.

β-Methylallyl Diphenylacetate.—Diphenylacetyl chloride (prepared by the action of thionyl chloride on diphenylacetic acid (159 g.)) was dissolved in chloroform (300 ml.). To this was added, at 0–10°, β-methylallyl alcohol (54 g.) dissolved in pyridine (59.5 g.). The solution stood overnight at room temperature and was worked up as described above for the allyl ester. Distillation of the chloroform layer gave the required ester; yield 163 g.; b. p. 153° (1.3 mm.).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.11; H, 6.82.

2,2-Diphenyl-4-methylpenten-4-oic Acid.—β-Methylallyl diphenylacetate (163 g.) was allowed to react with pulverized sodium hydride (24 g.) in boiling toluene (1100 ml.) for twenty-two hours. The cooled mixture was decomposed with water and the aqueous alkaline layer was acidified. Recrystallization of the solid so formed gave pure 2,2-diphenyl-4-methylpenten-4-oic acid; yield 121.5 g. (76%); m. p. 120.5–121.5°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.99; H, 6.81.

Isocrotyl Diphenylacetate.—This ester was prepared by the above described method from methylvinylcarbinol (6 g.), pyridine (7 g.) and diphenylacetyl chloride (15.3 g.) in carbon tetrachloride (30 ml.) as solvent. When the reaction was complete, the mixture was poured into cold water and the organic layer was extracted with sodium hydroxide (5%). Removal of the solvent gave a solid residue which when crystallized from petroleum ether melted at 57–58°; yield 16.4 g. (93%).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.19; H, 6.81. Found: C, 81.30; H, 7.11.

2,2-Diphenylhexen-4-oic Acid.—A solution of mesitylmagnesium bromide was prepared from bromomesitylene (10.75 g.), magnesium (1.3 g.) and ether (50 ml.). To this was added isocrotyl diphenylacetate (11.5 g.) dissolved in ether (50 ml.). A slightly exothermic reaction ensued and after refluxing for thirty minutes, the solution remained at room temperature for forty hours. Decomposition with ammonium chloride solution was followed by extraction of the ether layer with sodium hydroxide (5%). Distillation of the ether solution gave mesitylene (4.6 g., 88.4%) and unused isocrotyl diphenylacetate (0.9 g.).

Upon acidification, the alkaline layer gave 2,2-diphenylhexen-4-oic acid (8.5 g., 74%); m. p. 122.2–122.6°. A mixed melting point determination with diphenylacetic acid gave 108–111°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.19; H, 6.81; neut. equiv., 266.3. Found: C, 81.47; H, 6.88; neut. equiv., 266.6.

Ozonization of the above unsaturated acid gave acetaldehyde identified as its dimedon derivative.

***n*-Crotyl Diphenylacetate.**—This compound was prepared from *n*-crotyl alcohol (13 g.), pyridine (14.5 g.), diphenylacetyl chloride (34.7 g.) and chloroform (50 ml.) at 0°. The ester boiled at 155–162° (0.1 mm.); yield 22.6 g. (56.5%).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.19; H, 6.81. Found: C, 80.84; H, 7.10.

2,2-Diphenyl-3-methylpenten-4-oic Acid.—This ester (12.5 g.) was treated with a solution of mesitylmagnesium bromide prepared from bromomesitylene (12.0 g.), magnesium (1.5 g.) and ether (75 ml.).

The mixture was refluxed for twelve hours and then allowed to stand at room temperature overnight. Decomposition with ammonium chloride solution gave an ether layer which was extracted with sodium hydroxide solution. From the ether layer, mesitylene (5 g.) was obtained by careful fractionation. Acidification of the alkaline aqueous layer gave a solid acid which was recrystallized from aqueous alcohol; yield 8.2 g. (65.5%); m. p. 138–138.5°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.19; H, 6.81; neut. equiv., 266.3. Found: C, 81.34; H, 7.10; neut. equiv., 266.5.

Ozonization of the above acid gave formaldehyde which was isolated as its dimedon derivative; yield 52.3%; m. p. 187–188°.

2-Ethyl-2-phenylpenten-4-oic Acid.—An ethereal solution of ethylmagnesium bromide (114 ml. of 1.76 *N*) was treated with diethylamine (14.6 ml.). To this was added allyl α-phenylbutyrate (40.8 g.). Heat was evolved and the solution was stirred for three days at room temperature before decomposition with dilute ammonium chloride.

Bicarbonate extraction of the ether layer followed by acidification gave a carboxylic acid which after recrystallization from aqueous methanol gave 2-ethyl-2-phenylpenten-4-oic acid; yield 3.1 g. (7.8%); m. p. 78.5–80°.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90; neut. equiv., 204.3. Found: C, 76.81; H, 7.99; neut. equiv., 204.8.

Summary

1. It has been shown that allylic esters having at least one aryl group and one hydrogen atom attached to the alpha carbon atom undero intramolecular rearrangement in the presence of many strong basic reagents to give α-allylic substituted acids.

2. The allylic group undergoes an alpha-gamma shift during the course of the reaction.

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(8) Ramart, *Compt. rend.*, **178**, 396 (1924).