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THE CHEMISTRY OF ALLENIC ACIDS. II.[1] SOME REACTIONS OF 1,2-HEPTADIENE-3-CARBOXYLIC ACID

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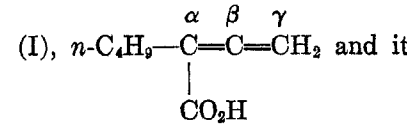
Allene, $CH_2{=}C{=}CH_2$, was isolated and characterized as early as 1888 (1). However, the chemistry of allene and its derivatives was not a subject of extensive research. Some of the allenic compounds described in the earlier literature were prepared using reactions where the products were of questionable purity. This is especially true in case of liquid products. Since the properties attributed to allenic compounds many times were based on such reaction products, they were often erroneous. For example, Prévost, *et al.* (2) who carbonated the Grignard reagent from propargyl bromide thought that the resinous portion of the products was derived from the "unstable" allenecarboxylic acid. That this acid is not the source of resins, under such experimental conditions, has since been established (3).

In our laboratory we have recently prepared a number of alkyl-substituted allenic acids (4, 5) in a high state of purity. These compounds revealed properties which were in many instances contrary to those in the literature. In this paper we are reporting some properties of 1,2-heptadiene-3-carboxylic acid



(I), and its methyl ester (II), which were selected as representatives of these allenic compounds. The reactions studied were: (A) The stability toward heat; (B) The possibility of polymerization; (C) The reaction as a diene or dienophile in a Diels-Alder type of reaction. This work was especially concerned with finding the conditions for such reactions, rather than the identification of products when a reaction occurred.

HEAT STABILITY

The stability of I toward heat was determined and the results are summarized in Table I, experiments one through six. The extent of reaction was measured indirectly by the quantity of original acid that was recovered by recrystallization. This method offered no means of distinguishing between decarboxylated and polymerized material, and the solubility of I in the recrystallization solvent was neglected. Since, in many cases 90 % or more of I was recovered, the latter factor was not extensive.

Experiment 1 confirmed our previous findings (4) that the acid I can be

[1] The Chemistry of Allenic Acids. I. *J. Am. Chem. Soc.*, **74**, 2559 (1952).

[2] Abstracted from a portion of the M.S. dissertation of N. C. B., University of Pittsburgh, 1953.

TABLE I

THE DECARBOXYLATION AND POLYMERIZATION OF 1,2-HEPTADIENE-3-CARBOXYLIC ACID (I) AND OF METHYL 1,2-HEPTADIENE-3-CARBOXYLATE (II)

EXPERIMENT NO.	COMPOUND			SOLVENT	CATALYST	REACTION		PRODUCT				
	No.	Grams	Quantity, moles			Temp., °C.	Time, Hrs.	Recovery, %	Decarboxylation, Moles	CO_2 %	Color	Viscosity
1	I	0.8073	0.0058	None	None	100	5	99	0	0	—	—
2	I	1.0290	.0074	None	None	150	5	0	0.0008	10	Str.	+++
3	I	1.8584	.0133	None	None	150	48	0	.0019	15	Br.	++
4	I	.9842	.0070	None	None	200	5	0	.0024	33	D. Br.	+++
5	I	.5481	.0039	None	None	200	15	0	.0017	44	D. Br.	++
6	I	.4079	.0028	None	None	260	5	0	.0009	36	D. Br.	+++
7	II	1.0941	.0071	None	None	100	5	[f]	0	0	—	—
8	II	1.1642	.0075	None	None	150	5	[f]	.0001	2	Str.	+
9	II	1.0909	.0070	None	None	200	5	[f]	.0002	2.5	Str.	++
10	II	1.010	.0064	None	None	150	168	[f]	[f]	[f]	Lght. Br.	+++
11	II	1.010	.0064	None	None	200	168	[f]	[f]	[f]	Br.	++
12	I	1.0542	.0075	Ether	BF_3	25	24	105	0	0	—	—
13	I	.9478	.0067	None	BF_3	100	5	0	.0011	16	D. Br.	+++
14	I	.9612	.0060	Benzene	BF_3	Reflux	5	96	.0003	4	—	—
15	I	.9811	.0070	Benzene	$AlCl_3$	Reflux	5	93	.0009	12	—	—
16	I	1.0451	.0075	Ether	$AlCl_3$	25	24	100	0	0	—	—
17	I	.9374	.0067	Benzene	Na[a]	Reflux	5	96	.0005	7	—	—
18	I	1.0642	.0076	Benzene	Na[b]	25	24	89	.0006	8	—	—
19	I	1.0295	.0073	Benzene	Peroxide[c]	Reflux	5	102	.0004	5	—	—
20	I	.9345	.0067	Benzene	Peroxide[d]	Reflux	5	98	.0005	8	—	—
21	I	1.1036	.0070	Benzene	CH_3ONa	Reflux	5	95	.0007	9	—	—
22	I	.9072	.0065	Ether	$NaNH_2$	25	24	95	0	0	—	—
23	I	.9481	.0068	Benzene	$NaNH_2$	Reflux	5	102	.0006	8	—	—
24	I	.7673	.0055	Cyclohexane	U.V.[e]	25	24	99	.0003	5	—	—

25	II	1.0312	.0067	None	BF_3	100	5	*f*	.0005	7	Br.	+
26	II	1.0740	.0070	Benzene	BF_3	Reflux	5	*f*	.0002	3	Br.	−
27	II	2.0382	.0132	Ether	$AlCl_3$	25	24	*f*	0	0	Str.	−
28	II	1.0423	.0068	Benzene	$AlCl_3$	Reflux	5	*f*	.0008	13	Str.	−
29	II	.8328	.0054	Benzene	CH_3ONa	Reflux	5	*f*	.0007	13	Str.	−
30	II	1.0807	.0070	Benzene	$NaNH_2$	Reflux	5	*f*	.0006	8	Str.	−
31	II	.8555	.0055	Benzene	Peroxide[c]	Reflux	5	*f*	.0004	7	Str.	−
32	II	1.1368	.0074	Benzene	Peroxide[d]	Reflux	5	*f*	.0006	7	Str.	−
33	II	.4093	.0027	Cyclohexane	U.V.[e]	25	24	*f*	.0005	2	Str.	−
34	II	1.0575	.0068	Benzene	Na[a]	Reflux	5	*f*	.0001	2	Lght. Br.	+

Symbols; color and viscosity: − unchanged; + slightly; ++ moderately; +++ greatly; Br. = brown; Str. = straw; Lght. = light; D. = dark. [a] A 2% sodium dispersion in kerosene. [b] A 50% sodium dispersion in kerosene. [c] Benzoyl peroxide. [d] Methyl amyl ketone peroxide. [e] Ultraviolet light source directly in contact with the quartz vessel. [f] Not determined.

distilled without decomposition, b.p. 102° at 2 mm. Decomposition occurred at a somewhat higher temperature; see experiments 2 and 3. Decarboxylation at 150° was not extensive, being about 10 to 15% depending on the time of heating. Since none of the starting acid was recovered polymerization was the main reaction as also evidenced by the formation of a light-brown viscous product. The infrared spectrum[3] of the polymer exhibited very broad bands which we attribute to the presence of a mixture. The characteristic strong absorption bands of the allenic linkage near 1930 and 1950 cm^{-1} (6) of I were no longer present in the product, indicating that any reaction involved the allenic linkage. There was a strong absorption band near 1600 cm^{-1}, characteristic of a double bond conjugated with the carbonyl group. There was no spectroscopic evidence for the presence of a terminal double bond. We conclude that these reactions involved the β,γ-double bond in the allenic acid. This is different from the reactions of I with a Grignard reagent where the formation of the product involved an apparent addition to the α,β-double bond (7).

Experiments 4, 5, and 6 showed again the dependence of the extent of decarboxylation on the time and temperature. The conditions used in experiment 6 are especially noteworthy because they parallel the ones used by Arnold, *et al.* (8) when they studied the mechanism of thermal decarboxylation. They found 75% decarboxylation with 2,2-dimethylbuten-3-oic acid which is significantly higher than that of our allenic acid. Arnold's mechanism assumes that an α,β-unsaturated acid rearranges first to its β,γ-isomer which eliminates carbon dioxide through a cyclic transition state. In our allenic acid I which has the α,β, and γ-carbon atoms colinear such a transition state is not formed readily as can be observed using "Fisher-Hershfelder-Taylor Molecular Models." Thus, the relative stability of such an allenic acid over an olefinic acid can be explained in a manner which supports the cyclic mechanism of decarboxylation.

The effect of heat on the ester II is listed in Table I, experiments 7 through 11. Since the ester is a liquid and quantities of one gram were used, we were not able to determine accurately the extent of polymerization during heating. An apparent change in viscosity was observed. In all cases the amount of decarboxylation was negligible. Polymerization was the major reaction at temperatures above 150°. The spectroscopic analysis of the viscous product in experiment 10 was similar to the analysis of the product formed by heating the free acid.

POLYMERIZATION

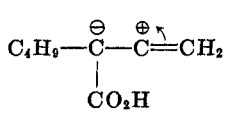
Since the experiments cited in section A showed that no change occurred when the acid I or ester II were heated below 100°, attempts were made to effect polymerization below this temperature using catalysts known to initiate such reactions. The literature showed no instances in which an allenic acid or its ester had been polymerized. There were a number of reasons for believing

[3] All infrared spectra were determined using a Baird double beam spectrometer and were interpreted by Dr. Foil A. Miller and co-workers at the Mellon Institute.

that a catalyst-initiated polymerization might occur. Allene was polymerized by heating at 140° in a sealed tube (9). Tetramethylallene was polymerized by heating at 150° (10), and 4-hydroxy-1,2-butadiene by heating at its boiling point for 24 hours (11). The polymerization of the acrylic acid type of compounds is well known. Since such substituted ethylenes polymerize more readily than ethylene, we expected that our allenic acid or ester would polymerize more readily than allene.

The catalysts, and conditions used for the polymerization are listed in Table I. Experiments 12 through 24 used the allenic acid as monomer. In most cases about 90% of the acid was recovered. Decarboxylation was not extensive. Such findings show that the allenic acid is not only stable toward polymerization and decarboxylation, but also to certain catalyzed-rearrangements. Experiments 25 through 34 used the ester II. The extent of reaction was estimated by noting an increase in viscosity. In some cases the infrared spectrum of the "product" was determined. In cases where there was no visible change in the viscosity, the allenic group absorption band also did not change in intensity and *vice versa*. In cases where there were signs of reaction, spectroscopic analysis again showed that interaction was at the β,γ-unsaturation. We like to offer three possible explanations for our findings:

(a) In a study of molecules of our monomer units, built from "Fisher-Hirshfelder-Taylor Molecular Models," in which the α,β-double bond was activated (polarized), we found that there are a limited number of positions in which the monomers can be oriented, so that a "collision" would bring about the addition of one unit to another. It can therefore be expected that the entropy of activation of such monomer units would be very low. As a result one would find a low rate constant, and polymerization would proceed at a very slow rate. (b) A molecular model of a polymer formed through activation at the α,β-double bond, shows that groups within the chain are very restricted in their movements. However, this is not the case for a polymer formed from monomers reacting at the β,γ-double bond. The entropy of formation may be represented as ΔS = S polymer − S monomer. The entropy of a polymer which is rigid, is less than for a polymer in which the groups within the chain are not restricted in their movements. The entropy of formation of the former would therefore be less than the entropy of formation of the latter. The free energy of formation of a rigid polymer $\Delta F = \Delta H - T\Delta S$ would therefore be less negative than for an unrestricted one. Hence, the polymer formed from molecules reacting at the α,β-double bond would be less stable than a polymer formed through reaction at the β,γ-double bond. (c) When the α,β-double bond is polarized there might be a simultaneous shift of electrons from the β,γ-double bond.



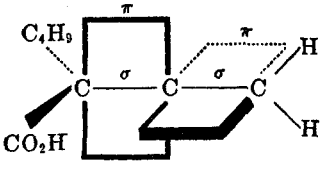
The net effect of this would be a "smearing out" of the positive center over the

beta and *gamma* positions. The *beta* carbon atom would therefore be relatively electron "rich" when compared to the *beta* carbon atom in acrylic acid. This "increase" in the electron density might be enough to discourage the attack of the negative portion of another molecule in an attempted catalyst-initiated polymerization.

DIELS-ALDER REACTIONS

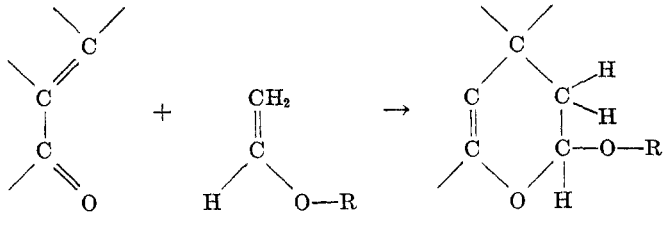
It has not been established whether the double bonds in allenic hydrocarbons possess dienophile properties (12). Since acrylic acid derivatives react readily with conjugated dienes we expected similar reactivity of our allenic acid (I) or its ester (II). However, no reaction took place between the ester (II) and an excess of butadiene at its reflux temperature (−4°). The acid (I) was also completely recovered when dissolved in butadiene at room temperature (under pressure) for one week.

The valence bond structure clearly shows:



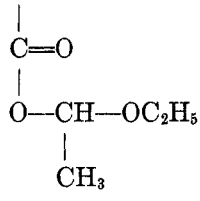
that the p orbitals which form the bond between the *alpha* and *beta* carbon atoms are in a plane perpendicular to the butyl and carboxyl group. Such an orientation does not sterically hinder additions and we do not think that steric hindrance is the reason for lack of reactivity. We considered therefore, other possible factors: lack of polarization for which we presented arguments in section B, and too mild reaction conditions. To test the latter possibility we heated the allenic acid (I) with an excess of butadiene, and a catalytic amount of hydroquinone, in a steel autoclave at 100° for 18 hours. In this experiment we formed an acidic product but none of the original acid I was recovered. Most of the product was a colorless neutral fraction which showed rubber-like properties. Analysis (elementary and spectroscopic) showed it to be a copolymer of butadiene and the allenic acid. A more thorough investigation of this product and copolymerization of allenic compounds is in progress.

We have also considered the possibility that our allenic compounds could react as dienes, especially since various α,β-unsaturated carboxyl compounds were successfully condensed with vinyl ethers (13) yielding six-membered heterocyclic compounds.



We have therefore heated at 100° in a sealed tube the allenic acid (I) with an

excess of ethyl vinyl ether and have obtained a quantitative yield[4] of a one to one mole addition product which we identified as ethoxyethylidine-1,2-heptadiene-3-carboxylate (III), $C_4H_9—C(=C=CH_2)—C(=O)—O—CH(CH_3)—OC_2H_5$. This neutral compound showed



strong allenic group absorption bands at 1930 and 1950 cm.$^{-1}$ It was not a Diels-Alder type of reaction product but a product formed by the addition of the carboxy group across the double bond according to Markovnikov rule. Saturated acids are known to react in that manner with vinyl ethers (14, 15).

Because of the quantitative conversion of the allenic acid (I) into the ester (III) in the presence of a large excess of vinyl ethyl ether, it was inferred that the ester (II) would also not react as a diene. We have also tried to condense the allenic acid (I) with maleic anhydride in dioxane at its reflux temperature, but all of the starting acid was recovered.

EXPERIMENTAL

A number of experiments listed in Table I were run as duplicates with results in agreement with the ones cited. To save space we have also omitted the listing of experiments where we used milder conditions.

Decarboxylation and polymerization of 1,2-heptadiene-3-carboxylic acid (I). A 25-ml. round-bottom flask containing about one gram of the acid, 20 ml. of solvent, and the catalyst (when used) were fitted with a reflux condenser. A U-tube filled with Caroxite[5] was connected to the top of the condenser. The flask was heated to the desired temperature while a gentle stream of dry, carbon-dioxide-free stream of nitrogen was passed over the reaction mixture. The increase of weight of the U-tube was noted. The product was cooled, dissolved in ether, and the catalyst was removed by washing with water. The ether layer was dried with sodium sulfate, and evaporated to dryness in a vacuum. The residue was redissolved in petroleum ether and the acid I was recovered as large crystals by permitting the solvent to evaporate at room temperature over a period of days. The crystals were washed free from the polymerized product with a stream of cold petroleum ether. There was no depression of the melting point of a mixture of these crystals with an authentic sample of I.

The decarboxylation and polymerization of methyl 1,2-heptadiene-3-carboxylate (II) was performed as described above for the acid I. There was no attempt made to recover quantitatively the starting ester. The color and viscosity of the residue was also noted.

Reaction of 1,2-heptadiene-3-carboxylic acid with butadiene-1,3. Compound I (5 g., 0.035 mole) was dissolved in 25 ml. of dry ether and placed in a high pressure autoclave. The bomb was cooled in a Dry Ice-acetone slurry and 200 ml. of butadiene was condensed into it. The container was sealed and the mixture was kept at room temperature for one week. The unreacted butadiene was permitted to boil off and 5 g. of the original acid was recovered.

In another experiment 5 g. (0.035 mole) of the acid (I) was kept with an excess of butadiene and 0.1 g. of hydroquinone at 100° for 18 hours. The bomb was then cooled in Dry Ice and the unreacted butadiene was permitted to escape. The residue (10 g.) was diluted with ether and extracted with a sodium carbonate solution. Three layers appeared. The lowest aqueous layer upon acidification yielded 2.5 g. of an oily acid which resisted crystallization.

[4] The yield at the boiling temperature of the mixture was only 20%.

[5] A carbon dioxide absorbent from Eimer and Amend.

The two ether layers were combined and were evaporated to dryness yielding 7.2 g. of residue which was elastic. Its infrared spectrum showed absorption bands characteristic of a carbonyl group, an unconjugated double bond, a terminal double bond, and the absence of an allenic group absorption band. Its elementary analysis[6] was 73.3% of carbon and 9.9% of hydrogen.

Ethoxyethylidene-1,2-heptadiene-3-carboxylate (III). A glass tube containing 1.0075 g. (0.0072 mole) of the acid (I), 15 ml. of freshly distilled vinyl ethyl ether, and 0.01 g. of hydroquinone was sealed and heated for 510 minutes in an oil-bath at 100°. The tube was then cooled, opened, and the excess of the ether was removed at room temperature under reduced pressure, leaving 1.6038 g. of a colorless liquid. The hydroquinone was removed by adding a little cold petroleum ether (30–60°) and filtering. The solvent-free filtrate weighed 1.4914 g, b.p. 94° at 4 mm., n_D^{25} 1.4530.

Anal. Calc'd for $C_{12}H_{20}O_3$: C, 67.9; H, 9.9.
Found: C, 67.6; H, 9.6.

A sample of the product was saponified with dilute sodium hydroxide. The basic solution upon acidification yielded an acid which did not depress the melting point of an authentic sample of the acid (I).

SUMMARY

1. The allenic acid, 1,2-heptadiene-3-carboxylic acid (I), and its methyl ester (II) do not rearrange, polymerize, or decarboxylate even in the presence of certain catalysts at temperatures below 100°. At higher temperatures polymerization is more extensive than decarboxylation.

2. The acid (I) is more stable toward thermal decarboxylation than are olefinic acids.

3. Possible explanations for such an inertness have been offered.

4. The compounds I and II did not react as dienes or dienophiles in Diels-Alder type of reactions. At 100° the acid (I) copolymerized with butadiene.

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[6] Microanalyses by G. L. Stragand of the Microanalytical Laboratory of the University of Pittsburgh.