322. *Migration of Allyl Groups in the Ethyl Acetoacetate Series.*

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The starting point of our experiments was Claisen's observation (Beilstein, Ergänzungsband 3, p. 135) that the interaction of ethyl β-methoxycrotonate and allyl alcohol in presence of ammonium chloride gives ethyl *C*-allylacetoacetate :

$$\begin{tikzcd}
CH_3\cdot C(O\cdot CH_3){:}CH\cdot CO_2Et \arrow[r] & CH_3\cdot C(O\cdot CH_2\cdot CH{:}CH_2){:}CH\cdot CO_2Et \arrow[d] \\
 & CH_3\cdot CO\cdot CH(CH_2\cdot CH{:}CH_2)\cdot CO_2Et
\end{tikzcd}$$

The hypothetical intermediate ethyl allyloxycrotonate was supposed to suffer a rearrangement analogous to that of phenyl allyl ether into *o*-allylphenol (see, *inter al.*, Claisen, *Annalen*, 1919, **418**, 78). Although in the phenol series the rearrangement is accompanied by a transposition * of the migrating allyl group, nothing is known regarding the reaction in the ethyl acetoacetate series, which is of particular interest because the rearrangement of allyl thiocyanate does not follow the same course as that of phenyl allyl ether (see preceding paper).

The available evidence in the ethyl acetoacetate series is conflicting, and in order to elucidate the matter we have used the cinnamyl group as an unsymmetrically substituted allyl group.

(a) The interaction between cinnamyl chloride and ethyl sodioacetoacetate in benzene under anhydrous conditions, which, according to Claisen, usually produce *C*-alkylation (*Annalen*, 1925, **442**, 210; Busch and Knoll, *Ber.*, 1927, **60**, 2243), affords two products: The higher-boiling one was *ethyl dicinnamylacetoacetate* (I), the formation of which is due to the same circumstances as " direct " dibenzylation of ethyl acetoacetate or malonate (Schlenk and Bergmann, " Lehrbuch d. organ. Chemie," 1932, Vol. I, p. 433), the cinnamyl and the benzyl group being very similar. The lower-boiling and main product, $C_{15}H_{18}O_3$, was the required *monocinnamyl* ester (II), which was decomposed by heating with dilute alcoholic potash into γ-benzylidenebutyric acid (Erlenmeyer and Kreutz, *Ber.*, 1905, **38**, 3503) and also a ketone, $C_{13}H_{14}O$, proved to be α-phenyl-Δ^{α}-hexen-ε-one (III) by hydrogenation to α-phenylhexan-ε-one (Borsche, *Ber.*, 1911, **44**, 2594). Moreover, the compound (II) absorbs 3·4 atoms of bromine, owing to addition at the cinnamyl double bond and nearly complete substitution of the mobile hydrogen atom (cf. Arndt and Martius, *Annalen*, 1932, **499**, 228).

(I.) $CH_3\cdot CO\cdot CR_2\cdot CO_2Et$ (II.) $CH_3\cdot CO\cdot CHR\cdot CO_2Et$
(III.) $CH_3\cdot CO\cdot CH_2R$ (IV.) $CH_3\cdot C(OR){:}CH_2$
(V.) $CH_3\cdot C(OR){:}CH\cdot CO_2Et$ (VI.) $CH_3\cdot C(OR){:}CR\cdot CO_2Et$
($R = \cdot CH_2\cdot CH{:}CHPh.$)
(VII.) $CH_2{:}CH\cdot CHPh\cdot CH_2\cdot CO_2H$

(b) Interaction between ethyl β-ethoxycrotonate and cinnamyl alcohol also gave two products. The main product had the formula $C_{15}H_{18}O_3$, but was not identical with (II). It was proved to be *ethyl β-cinnamyloxycrotonate* (V) because alkaline hydrolysis afforded a non-acid compound, $C_{12}H_{14}O$, which contained no carbonyl group but two double bonds (bromine absorption), and was therefore *cinnamyl* iso*propenyl ether* (IV), which could readily arise from (V).

The second product has the same composition as (I), *viz.*, $C_{24}H_{26}O_3$, and the b. p.'s are nearly identical, but as it absorbs 5·6 atoms of bromine its formula is (VI), and we have to assume that its formation occurs in two stages (see below). (Separate experiments have shown that in ethyl β-ethoxycrotonate the double bond absorbs 1 mol. of bromine.) Consequently, the interaction between cinnamyl alcohol and ethyl β-ethoxycrotonate

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* The term "transposition" means that the atoms connecting the "migrating group" with the trunk of the molecule before and after migration are not identical.

is primarily an *O*-cinnamylation, thus affording support for Claisen's view that the first stage in the allylation of ethyl β-methoxycrotonate involves the " enolic " oxygen. [The possibility is not excluded that in compounds (IV)—(VI), the " cinnamyl " group has the structure $CHPh{\cdot}CH{:}CH_2$, but such a transposition has never been observed in *O*-alkylations.]

(c) The alkaline hydrolysis of (V) gave not only the ether (IV), but also an oily acid, $C_{11}H_{12}O_2$, which on hydrogenation afforded β-phenylvaleric acid and was therefore *β-phenyl-β-vinylpropionic acid* (VII). Evidently the alkali treatment of ethyl β-cinnamyloxycrotonate to some extent leads to a rearrangement, which is accompanied by a " transposition " of the allyl group as in the case of phenyl allyl ethers; subsequently, degradation occurs as usual.

(d) Ethyl β-cinnamyloxycrotonate (V) is also isomerised when heated at 260° for several hours, the compound (II) being formed; therefore, the rearrangement of (V) need not be accompanied invariably by a transposition in the allyl group—both types of reaction are possible, one occurring on treatment with alkalis and the other on heating. The thermal conversion of (V) into (II) is the reason for the formation of (VI) in reaction (b) : in the first stage, (V) is formed, this is rearranged into (II), and the enolic form of the latter is again cinnamylated on the hydroxyl group.

EXPERIMENTAL.

(a) *Reaction between Cinnamyl Chloride and Ethyl Sodioacetoacetate.*—To ethyl sodioacetoacetate (prepared from 5 g. of sodium and 30 g. of ethylacetoacetate in 100 c.c. of dry benzene), cinnamyl chloride (35 g.; Klages and Klenk, *Ber.*, 1906, **39**, 2552; Emde, *Ber.*, 1909, **42**, 2593) was added. After 48 hrs.' boiling, water was added, and the benzene solution dried and evaporated. The remaining oil (15 g.) on fractionation afforded (i) *ethyl* C-*cinnamylacetoacetate* (II), b.p. 200°/14 mm. [Found : C, 73·0; H, 7·1. $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·3%. 0·1690 G. absorbed 0·1800 g. (= 3·4 atoms) of bromine]; (ii) *ethyl dicinnamylacetoacetate* (I) (2 g.), b. p. 258°/14 mm. (Found : C, 79·9; H, 7·3. $C_{24}H_{26}O_3$ requires C, 79·6; H, 7·2%).

Hydrolysis of (II). 7 G. of the ester were boiled for 2 hours with 10% alcoholic potash (50 c.c.) and poured into water. The oil which separated was extracted with ether; b. p. 160°/12 mm.; semicarbazone, m. p. 130° (from benzene–light petroleum). It was proved to be α-phenyl-Δ^{α}-hexen-ε-one (III) by hydrogenation in alcoholic solution by means of palladised barium sulphate; the resulting α-phenylhexan-ε-one was converted into its semicarbazone, m. p. 143° (from benzene), identified by mixed m. p. with a sample prepared according to Borsche (*loc. cit.*) (Found : C, 67·5; H, 8·2. Calc. for $C_{13}H_{19}ON_3$: C, 67·5; H, 8·2%).

The alkaline mother-liquor was acidified and extracted with ether. The residue from the ether (1·2 g.) crystallised immediately and was identified (m. p. and mixed m. p.) as γ-benzylidenebutyric acid.

(b) *Reaction between Cinnamyl Alcohol and Ethyl β-Ethoxycrotonate.*—Cinnamyl alcohol (30 g.), ethyl β-ethoxycrotonate (30 g.) (Koll, *Annalen*, 1888, **249**, 324), and ammonium chloride (10 g.) were heated for 1 hour at 150°, during which ethyl alcohol and some of the ester distilled off. The resulting oil was dissolved in ether and washed with water, the ether evaporated, and the residue distilled in a vacuum. *Ethyl β-cinnamyloxycrotonate* (18 g.) (V), b. p. 162°/12 mm. (Found : C, 73·3; H, 7·4. $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·3%), was first obtained; the residue distilled at about 250°/12 mm. with marked decomposition, and on redistillation at 200—210°/5 mm., it afforded *ethyl β-cinnamyloxy-α-cinnamylcrotonate* [Found : C, 79·7; H, 7·0. $C_{24}H_{26}O_3$ requires C, 79·6; H, 7·2%. 0·0862 G. absorbed 0·1060 g. (5·6 atoms) of bromine].

Hydrolysis of (V). 10 G. of the ester (V) were added to 5 mols. of alcoholic potash solution (10%) and boiled for one hour. Addition of water precipitated *cinnamyl* iso*propenyl ether* (IV) as an oil, which was extracted by ether and recovered; b. p. 120—122°/12 mm. [Found : C, 82·1; H, 8·0. $C_{12}H_{14}O$ requires C, 82·7; H, 8·0%. 0·1562 and 0·1048 G. absorbed 0·2380, 0·1580 g. (3·4, 3·3 atoms) of bromine].

(c) The alkaline mother-liquor from the hydrolysis was acidified and extracted with ether. The oily residue (1·2 g.) was *β-phenyl-β-vinylpropionic acid* (VII), b. p. 162°/12 mm. (Found : C, 74·6; H, 6·9. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%).

Oxidation gave only benzoic acid. Hydrogenation of 1 g. in 10 c.c. of alcohol in presence of palladised barium sulphate took place readily, and the oil obtained (1 g.) crystallised on standing; it was easily soluble in methyl alcohol and light petroleum, so was purified by sublimation in a vacuum. The acid melted at 63°, unaltered on admixture with β-phenylvaleric acid (Reynolds, *Amer. Chem. J.*, 1910, **44**, 316).

(d) Ethyl β-cinnamyloxycrotonate (4 g.) (V) was heated for 6 hours at 260°. From the dark brown oil, which was fractionated in a vacuum, only 0·8 g. of a constant-boiling product could be isolated; b. p. 170—172°/12 mm. It was identified as (III) by treatment with alcoholic potash (10%) as above, and conversion of the oily ketone into its semicarbazone, identical (m. p. and mixed m. p.) with that derived from α-phenyl-Δ^{α}-hexen-ε-one.

The alkaline liquid, on acidification, gave traces of an acid melting at 87°, but different from γ-benzylidenebutyric acid. It seems possible that, by a not unusual isomerisation (migration of the double bond and subsequent ring closure), 1 : 2 : 3 : 4-tetrahydro-1-naphthoic acid had been formed, for which Baeyer and Schoder (*Annalen*, 1891, **266**, 184) give m. p. 85° (compare Bogert and co-workers, *J. Amer. Chem. Soc.*, 1934, **56**, 248, 959; 1935, **57**, 151, and the similar observation of Hoermer and Schenck in the case of α-benzyloxy-γ-phenylbutyric acid, *Ber.*, 1928, **61**, 2312).

The above experiments were partly carried out in the laboratory of the Friedrich Wilhelm University, Berlin.

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