alcohol (12 ml.) was treated with an aqueous solution (10 ml.) of sodium hydrosulfite (2.0 g.). The precipitated triazole oxide was purified by repeated crystallization from dilute alcohol: m. p. 265–266° with decomposition; mixed with the isomer III, the triazole oxide, VII, melted at 225–228°.

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.7; H, 4.60. Found: C, 64.8; H, 4.62.

The triazole, VIII, was obtained from VII by reduction with stannous chloride in the manner already described for the conversion of III to VIII; melting point and mixed melting point with triazole obtained from III 217–218°.

Anal. Calcd. for $C_{13}H_{11}N_3O$: C, 69.3; H, 4.89. Found: C, 68.8; H, 5.08.

Summary

Evidence is introduced which proves the equivalence of positions 5 and 6 in the case of benzotriazoles which are substituted in position 2.

MINNEAPOLIS, MINN. RECEIVED OCTOBER 15, 1937

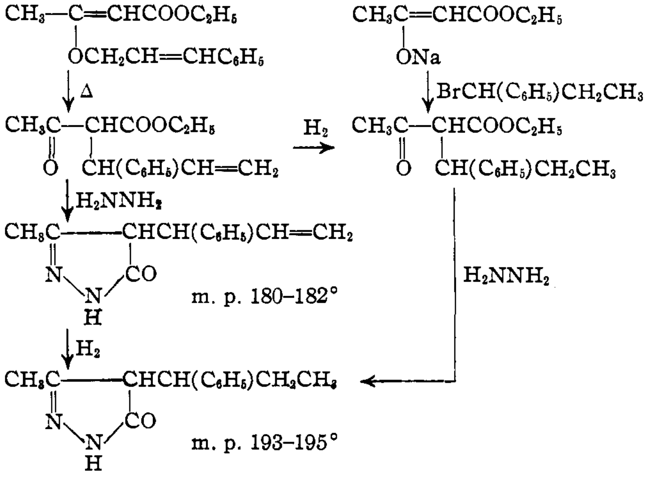
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Rearrangement of Some Beta-Allyloxycrotonic Esters

BY WALTER M. LAUER AND ELSIE I. KILBURN[1]

Alkylation of ethyl acetoacetate cannot proceed through the intermediate formation of a β-alkoxycrotonic ester, for it has been amply demonstrated that these β-alkoxycrotonic esters are far too stable to undergo rearrangement. There is a wide difference in the thermal stability of the simple alkyl and allyl phenyl ethers and inasmuch as the ethers of β-hydroxycrotonic acid bear a formal relation to the phenol ethers, it might be expected that the β-allyloxy-crotonates would rearrange under the influence of heat even though the β-alkoxy-crotonates do not. In fact, Claisen reported[2] that O-allylacetoacetic ester rearranged to the C-allyl derivative on distillation in the presence of ammonium chloride, but apparently he never published his experimental work in support of this claim. The case of the cinnamyl ether of β-hydroxycrotonic ester is of particular interest. As is well known, when sodium phenoxide is treated with cinnamyl bromide under certain conditions, a mixture of cinnamyl phenyl ether and *o*-cinnamylphenol is obtained. The rearrangement of cinnamyl phenyl ether yields not *o*-cinnamylphenol but *o*-(α-phenylallyl)-phenol, so that in this case it is clearly evident that the *o*-cinnamylphenol must result from some other process. The present paper deals with the rearrangement of ethyl β-cinnamyloxycrotonate and also in this case the rearrangement product differed from that obtained by the direct action of cinnamyl bromide on the sodium derivative of ethyl acetoacetate. Therefore, even though ethyl β-cinnamyloxycrotonate is capable of rearrangement, the course of the reaction between the sodium derivative of ethyl acetoacetate and cinnamyl bromide cannot involve ethyl β-cinnamyloxycrotonate since its rearrangement product is not identical with the product actually obtained.

Ethyl β-cinnamyloxycrotonate was prepared by the action of sodium cinnamyl oxide on a mixture of the stereoisomers, ethyl β-chlorocrotonate and ethyl β-chloroisocrotonate. Rearrangement was accomplished at a comparatively low temperature in the presence of ammonium chloride. The reactions outlined below indicate the evidence upon which the structure of the rearrangement product is based.



A similar series of reactions was carried out in the case of the product obtained by the action of cinnamyl bromide on the sodium derivative of ethyl acetoacetate and the corresponding derivatives were prepared.

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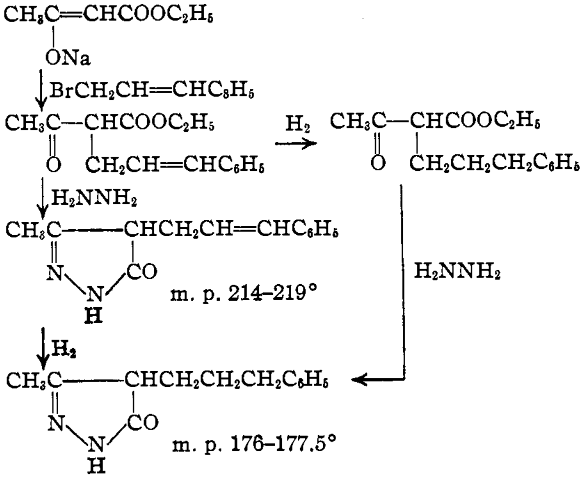
[1] Abstract of Ph.D. Thesis submitted October, 1935.

[2] Claisen, *Ber.*, **45**, 3157 (1912). See also private communications to Beilstein [4], Supp. Vol. III/IV, p. 256.



A recent study by Bergmann and Corte,[3] while not in entire agreement with our present findings, nevertheless affords also evidence for rearrangement of ethyl β-cinnamyloxycrotonate with transposition of the cinnamyl radical, for alkaline hydrolysis of their product yielded β-phenyl-β-vinylpropionic acid. Ethyl β-allyloxycrotonate also rearranges to yield ethyl α-allylacetoacetic ester, confirming the statement of Claisen.

Experimental

Ethyl α-cinnamylacetoacetate was prepared from cinnamyl bromide, ethyl acetoacetate and sodium ethoxide. Fractionation was carried out in an atmosphere of nitrogen under a pressure of 0.5–1 mm.; b. p. 156–158° at 0.5–1 mm.; d^{26}_4 1.0571; n^{26}_D 1.5263. One drop of the product in 1 ml. of alcohol produced a purplish black color with one drop of a dilute ferric chloride solution.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.21; H, 7.32. Found: C, 72.95; H, 7.17.

Ethyl α-(1-Phenylpropyl)-acetoacetate.—α-Bromopropylbenzene (25 g.), prepared from ethylphenylcarbinol and dry hydrogen bromide according to the method of Lepin and Reich,[4] ethyl acetoacetate (16.3 g.), sodium (2.9 g.) and absolute ethyl alcohol (50 ml.) were combined in the usual way and the product was fractionated carefully: b. p. 127–129° at 1 mm.; n^{27}_D 1.4934.

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.53; H, 8.12. Found: C, 72.48; H, 8.01.

Ethyl β-Chlorocrotonate (and Isocrotonate).—A mixture of the esters (b. p. 150–180°) was obtained in 50% yield by the method of Thomas-Mamert,[5] but it was not possible to separate the mixture easily into constant boiling fractions. Ethyl β-chloroisocrotonate (b. p. 154–157°) was obtained in 65% yield from pure β-chloroisocrotonic acid[6] by a method similar to that described by Scheibler and Vosz[7] for the methyl ester.

Ethyl β-cinnamyloxycrotonate was prepared from ethyl β-chloroisocrotonate and from a mixture of the two stereoisomers, ethyl β-chlorocrotonate and ethyl β-chloroisocrotonate with substantially the same result. In either case the yields were low.

Sodium cinnamyl oxide was prepared by the method of Beaufour[8] from sodamide (4.7 g.), cinnamyl alcohol (17 g.) and benzene (45 ml.). The mixture (20.6 g.) of ethyl β-chlorocrotonate and ethyl β-chloroisocrotonate (b. p. 150–180°), (or an equal amount of the isocrotonate, b. p. 154–157°), in dry benzene (25 ml.) was then added and the reaction mixture allowed to stand for several days, after which it was refluxed on the steam-bath for four hours, cooled and poured into water. The benzene layer, after drying over potassium carbonate, was distilled under high vacuum (mercury vapor pump). The yield of ethyl β-cinnamyloxycrotonate was low and there was considerable residue.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.21; H, 7.32. Found: C, 72.61; H, 7.25.

The Rearrangement of Ethyl β-Cinnamyloxycrotonate.—Ethyl β-cinnamyloxycrotonate (1.7 g.) was heated with ammonium chloride (0.2 g.) for four hours at 110° under nitrogen. The ammonium chloride was then removed by filtration, and washed with a small amount of alcohol.

The Formation of Pyrazolones.—(a) **Ethyl α-cinnamylacetoacetate** (2.46 g.) in alcohol solution treated with hydrazine hydrate formed 3-methyl-4-cinnamyl-5-pyrazolone. This pyrazolone was purified by crystallization from alcohol: a sample, introduced into the melting point bath at 198° and heated rapidly, darkened slowly and melted over a wide range; 214 to 219°.

Anal. Calcd. for $C_{13}H_{14}N_2O$: C, 72.85; H, 6.59. Found: C, 72.76; H, 6.79.

The same pyrazolone, together with hydrazine-N-N′-dicarboxylamide was also obtained by the reaction of ethyl α-cinnamylacetoacetate with semicarbazide hydrochloride and sodium acetate.

Hydrogenation of 3-Methyl-4-cinnamyl-5-pyrazolone.—Catalytic hydrogenation at room temperature and atmospheric pressure using the catalyst of Adams, Voorhees and Shriner[9] yielded 3-methyl-4-(3-phenylpropyl)-5-pyrazolone; m. p. 176–177.5°.

Anal. Calcd. for $C_{13}H_{16}N_2O$: C, 72.17; H, 7.45. Found: C, 71.75; H, 8.08.

These analytical values show better agreement with the formula $C_{13}H_{18}N_2O$. Nevertheless, since the same pyrazolone was obtained by the action of hydrazine hydrate on the hydrogenation product of ethyl α-cinnamylacetoacetate, the molecular formula $C_{13}H_{18}N_2O$ is preferred.

(b) **Ethyl β-cinnamyloxycrotonate** in alcohol solution did not yield a solid pyrazolone when treated at room temperature with hydrazine hydrate.

(c) **The rearrangement product of ethyl β-cinnamyloxycrotonate** yielded a crystalline pyrazolone (m. p. 180–182°) with hydrazine hydrate.

Anal. Calcd. for $C_{13}H_{14}N_2O$: C, 72.85; H, 6.54. Found: C, 72.80; H, 6.77.

The same pyrazolone (m. p. 182–184°, mixed m. p. with

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[3] Bergmann and Corte, *J. Chem. Soc.*, 1363 (1935).

[4] Lepin and Reich, *J. Russ. Phys.-Chem. Soc.*, **47**, 149–160 (1915); *Chem. Zentr.*, **87**, **I**, 787 (1916).

[5] Thomas-Mamert, *Bull. soc. chim.*, [3] **13**, 71 (1895).

[6] Michael and Schulthess, *J. prakt. Chem.*, [2] **46**, 236 (1892).

[7] Scheibler and Vosz, *Ber.*, **53**, 382 (1920).

[8] Beaufour, *Bull. soc. chim.*, [4] **11**, 650 (1912).

[9] Adams, Voorhees and Shriner, *Org. Syntheses*, **8**, 92 (1928).

product described above 181–183°) was obtained by the reaction of unheated ethyl β-cinnamyloxycrotonate with hydrazine hydrate and a few drops of hydrochloric acid. This pyrazolone was shown to be 3-methyl-4-(1-phenylallyl)-5-pyrazolone.

Catalytic hydrogenation of the pyrazolone $C_{13}H_{14}N_2O$ yielded the compound $C_{13}H_{18}N_2O$ (m. p. 193–195°). The same product ($C_{13}H_{16}N_2O$, m. p. 192.5–194) was obtained by the action of hydrazine hydrate on the hydrogenation product of the rearranged ester.

Anal. Calcd. for $C_{13}H_{16}N_2O$: C, 72.17; H, 7.46. Found: C, 72.32; H, 7.60.

Mixed melting point with the pyrazolone obtained from ethyl α-(1-phenylpropyl)-acetate, 193–194.5°.

(d) **Ethyl α-(1-phenylpropyl)-acetoacetate** in alcohol solution reacted with hydrazine hydrate to yield 3-methyl-4-(1-phenylpropyl)-5-pyrazolone. After several recrystallizations from alcohol, the colorless crystalline product melted at 193–195°.

Anal. Calcd. for $C_{13}H_{16}N_2O$: C, 72.17; H, 7.46. Found: C, 72.18; H, 7.61.

Ethyl α-allylacetoacetate was obtained in 40% yield by the method of Bruhl (b. p. 113–114° at 28 mm.).[10]

Ethyl β-allyloxycrotonate was prepared from equimolar amounts of sodamide, allyl alcohol and a mixture of ethyl β-chlorocrotonate and ethyl β-chloroisocrotonate in dry benzene. Distillation under reduced pressure (*ca.* 9 mm.) yielded a fraction which melted at 7–11°. No color change was observed upon treatment of an alcoholic solution with a drop of ferric chloride solution. (A red color developed when the mixture was allowed to stand overnight.) The compound did not give a solid pyrazolone upon treatment with hydrazine hydrate.

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.49; H, 8.30. Found: C, 63.50; H, 8.16.

The Rearrangement of Ethyl β-Allyloxycrotonate.—When heated to a temperature of 150–200°, ethyl β-allyloxycrotonate rearranged slowly to ethyl α-allylacetoacetate. In the presence of ammonium chloride, the rearrangement occurred more rapidly. The rearranged ester in alcoholic solution, treated with ferric chloride solution, gave a color identical with that obtained from ethyl α-allylacetoacetate. With hydrazine hydrate it formed a pyrazolone; m. p. and mixed melting point with 3-methyl-4-allyl-5-pyrazolone obtained from ethyl α-allylacetoacetate, 193–194°.

Summary

1. The mechanism for the cinnamylation of ethyl acetoacetate cannot proceed through the intermediate formation of ethyl β-cinnamyloxycrotonate for even though ethyl β-cinnamyloxycrotonate rearranges, it does not give ethyl α-cinnamylacetoacetate but its isomer.

2. Experimental evidence is presented for the rearrangement of ethyl β-allyloxycrotonate to ethyl α-allylacetoacetate.

MINNEAPOLIS, MINN. RECEIVED OCTOBER 15, 1937

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[10] Bruhl, *J. prakt. Chem.*, [2] **50**, 132 (1894); see also Philippi, *Monatsh.*, **51**, 277–299 (1920).

CONTRIBUTION FROM THE EASTMAN LABORATORY OF PHYSICS AND CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Crystalline Structure of Uranium

BY C. W. JACOB AND B. E. WARREN

Introduction

Uranium has been reported[1] to have a monoclinic structure with $a = 2.829$ Å., $b = 4.887$ Å., $c = 3.308$ Å., $\beta = 63°26'$. The unit cell contained two atoms and was side-centered on the "a" face. For a number of reasons this proposed structure is incorrect. In Wilson's calculated spacings he has overlooked the reflections 040 and 140, and he has incorrectly calculated the spacing for 102, which should be 1.633 rather than 1.433 as given. The agreement between his calculated and observed diffraction patterns is not satisfactory. A better diffraction pattern shows additional lines which are not predicted by his proposed structure.

Material Used.—Uranium in the form of small blocks obtained from Mackay gave satisfactory diffraction patterns. The best material[2] was obtained through the kindness of Dr. W. C. Lilliendahl. This material was in the form of a fused pellet and a wire. The drawn wire sample was of very great assistance in the structure determination because the preferred orientation in the wire showed up quite strongly in the diffraction pattern, and allowed one to distinguish weak uranium lines from possible impurity lines. A few weak lines which might otherwise have been overlooked were sufficiently enhanced by the preferred orientation to be readily seen and measured.

Experimental Methods.—The diffraction patterns were made in a cylindrical camera of radius 4.75 cm. The radiation was Cu K α filtered with nickel foil. To reduce the fluorescence M radiation of uranium, the film was covered with 0.002″ (0.05-mm.) aluminum foil. Exposures were of the order of six hours.

Several forms of sample were used. A sharp edge was filed on the pellet, and the edge used as the scattering sample. The wire was filed down to a diameter of about 0.4 mm. and used as a sample. On some of the patterns

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[1] T. A. Wilson, *Physics*, **4**, 148 (1933).

[2] F. H. Driggs and W. C. Lilliendahl, *Ind. Eng. Chem.*, **19**, 516 (1930).