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73. Tyunosin Ukita,* Hiroshi Watanabe, and Michiyasu Ichige**: Studies on Azulenes. VI.[1] Synthesis of Azulenes from Hydrindeneglycol Diacetate without Dehydrogenation.

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Although the dehydrogenation reaction is generally used in the last step of azulene synthesis, it usually gives the products in a poor yield. Several results of investigations on the synthesis of azulenes without this reaction have been reported. Thus, Ziegler and Hafner[2] synthesized azulene from cyclopentadiene sodium and pyridinium salt in a good yield, while Nozoe, *et al.*[3] reported that azulene was obtained by the condensation of a five-membered ring to tropone derivatives.

In a previous paper of this series,[4] it was shown that attempted synthesis of azulene by bromination of octahyroazulene with N-bromosuccinimide (NBS) and subsequent dehydrobromination did not give the azulene but several bromine-substituted azulenes.

In this paper a new method of azulene synthesis without dehydrogenation step will be reported. The starting material, *trans*-hydrindeneglycol (*trans*-1,2-hydrindanediol) diacetate (I), was condensed with diazoacetate by Buchner's reaction, the products containing seven-membered ring gave azulenes by subsequent dehydration. In Buchner's ring-expansion reaction, after reaction of ethyl diazoacetate with *trans*-hydrindeneglycol diacetate (I) at 125°, the product was heated at 140° under the irradiation of ultraviolet ray.

Several reports on the catalytic effect of heavy metals[5] or their salts for this reaction have appeared. However, the most profitable condition in this reaction in our case was to irradiate the reaction mixture with ultraviolet ray without adding heavy metals or their salts.

The reaction products were distilled in nitrogen atomsphere to give three fractions: (1) b.$p_{1.5}$ 60~90°, (2) b.$p_{1.5}$ 120~124°, and (3) b.$p_{0.04\sim0.05}$ 105~120°.

Fraction (1), a colorless oil, was a mixture of decomposition products of diazoacetate, fraction (2) consisted of unreacted diacetate of *trans*-hydrindeneglycol which could be used repeatedly as starting material, and fraction (3), a blue oil, contained the desired azulene-carboxylates.

On passage of the solution of fraction (3) dissolved in petroleum ether through an alumina (Wako) column and elution with a mixed solvent (benzene : ether=1 : 1), three fractions ((1′), (2′), (3′)) were obtained. The colorless fraction (1′) was the starting material (I), the fraction (2′) and (3′) were blue and orange-yellow colored oils, respectively.

The fraction (2′) was further fractionated by repeated chromatography through an alumina (Brockmann) column using benzene—ether (1:1) as elution solvent, whereby a part of the blue colored products remained adsorbed at the top of the column, and

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2) K. Ziegler, K. Hafner : Angew. Chem., **67**, 301(1955).
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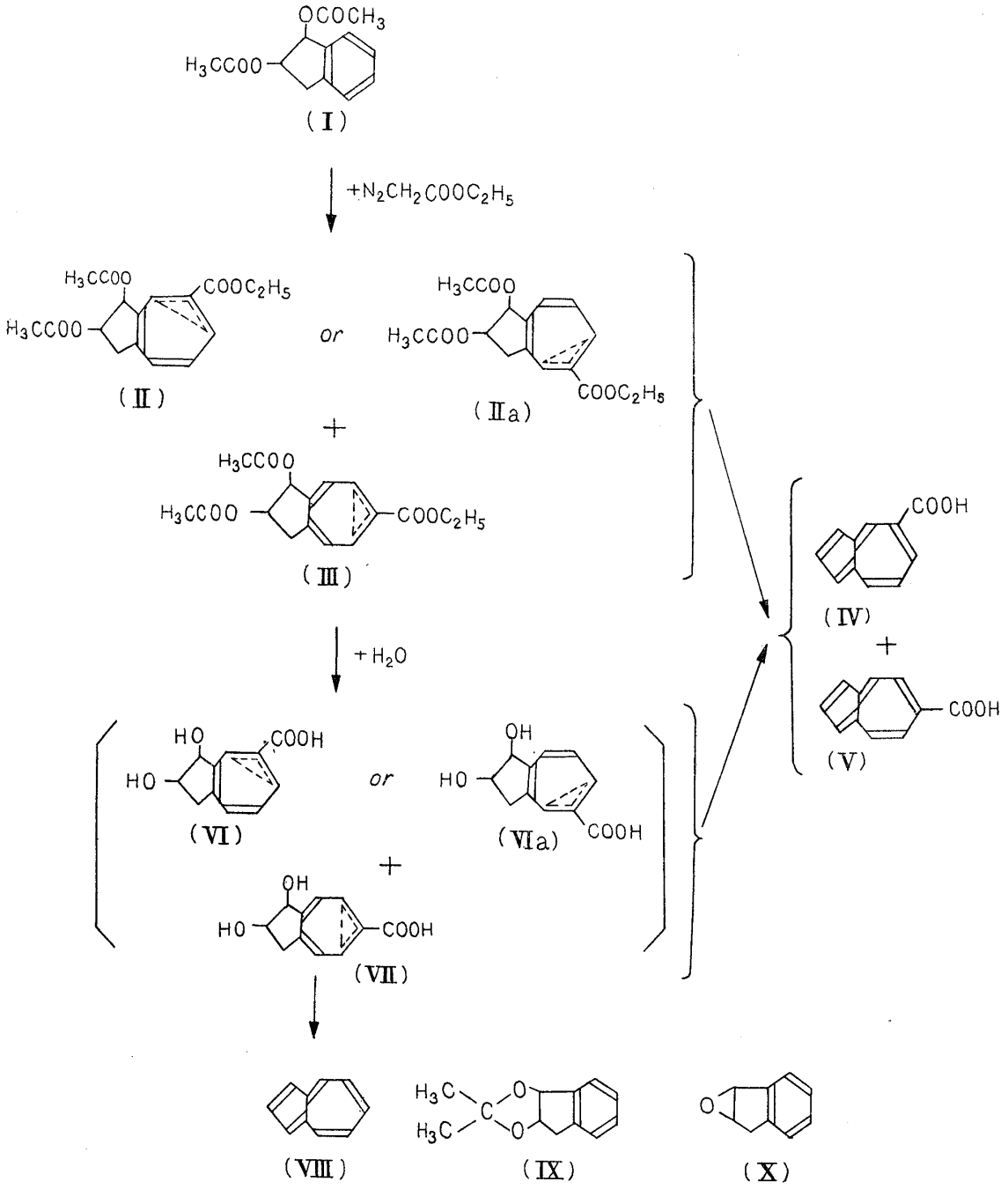
4) T. Ukita, M. Miyazaki, H. Watanabe : This Bulletin, **3**, 199(1955).
5) A. Loose : Prakt. Chem., [2], **79**, 509(1909); C. Grundmann, G. Ottmann : Ann., **582**, 163(1953)

another part of the blue oil eluted out. After removal of the solvent and hydrolysis with *N* sodium hydroxide solution, the latter gave azulene-5-carboxylic acid (IV), m.p. 205~207°,[6] in 14% yield, calculated from the condensation product (2′).

The blue product remaining on Brockmann's alumina was eluted out with 0.5*N* sodium carbonate solution. This product was proved to be azulene-6-carboxylic acid (V) with m.p. 224~226°(decomp.)[6] (yield, 1.7%). The melting point of both azulene-carboxylic acids obtained this time as well as those of their trinitrobenzene (TNB) complexes agreed with those of azulene-5- and -6-carboxylic acids and their TNB complexes reported by Plattner, *et al.*[6] The absorption spectra of (IV) and (V) were also in good agreement with those of authentic specimens.



6) Pl. A. Plattner, A. Fürst, A. Müller, A.R. Somerville : Helv. Chim. Acta, **34**, 971(1951).

After alkaline hydrolysis and lyophilization of the neutralized hydrolysate, the orange-yellow fraction (3′) gave both azulene-5- and -6-carboxylic acids in a yield of 6% and ca. 1% calculated from (3′). Thus, this fraction evidently contained precursors of these acids, norcaradiene or tropilidene derivatives (II and III or VI and VII), which on hydrolysis should form azulene ring by simultaneous dehydration of glycolic hydroxyl groups.

From the acidified solution obtained after alkaline hydrolysis of fraction (3′), azulene (VIII) was obtained by steam distillation. The observation can be explained by that the glycolcarboxylic acids contained in fraction (3′) suffered dehydration and simultaneous decarboxylation by steam distillation.

As for the yield of the two azulene-carboxylic acids, that of azulene-5-carboxylic acid was predominant than that of azulene-6-carboxylic acid, thus in the Buchner's condensation of diazoacetate with *trans*-hydrindeneglycol diacetate the main product seemed to be (II) or (IIa) instead of (III).

Other derivatives of hydrindeneglycol, O-isopropylidene-*cis*-hydrindenglycol[7] (IX) and indene epoxide[8] (X), did not give any sufficient amounts of condensation products with diazoacetate.[9]

When diazomethane instead of diazoacetate was used as a condensation agent, azulene was not obtained from (I).

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Experimental

Preparation of Hydrindeneglycol Diacetate (I)—To a suspension of indene (b.p. 176~182°) in water, Br_2 was added dropwise under vigorous stirring to give *trans*-hydrindene bromohydrin,[10,11] (m.p. 126~128°) in 80% yield. When the bromohydrin was treated with AcONa and Ac_2O, it gave *trans*-hydrindeneglycol diacetate,[8,12] $b.p_{10}$ 162~163°, in a 75% yield.

Reaction of Hydrindeneglycol Diacetate (I) with Ethyl Diazoacetate—52.5 g. of hydrindeneglycol diacetate (I) was kept at 120~125° in N_2 and 10 g. ethyl diazoacetate was added dropwise under irradiation of U.V. rays during 4 hrs. After addition, the temperature was slowly raised to 140° during 2 hrs. The reaction product was distilled in N_2 and fractionated into three parts: (1) 5 g. of a colorless oil, $b.p_{1.5}$ 60~90°, (2) 49.0 g. of a yellow oil, $b.p_{1.5}$ 120~124°, (3) 4.0 g. of a blue green oil, $b.p_{0.05}$ 105~120°, and the residue remaining in the flask weighed 1 g. The blue-colored fraction (3) was dissolved in petr. ether and poured into the top of alumina (Wako) column. The column was eluted with a mixed solvent (benzene : ether = 1:1) giving three fractions. On removal of solvent from each fraction, three oils: (1′) 1.5 g. of a colorless oil, (2′) 1.1 g. of a blue colored oil, (3′) 1.2 g. of a orange-yellow oil, were obtained.

Preparation of Azulene-5-carboxylic Acid (IV) and -6-carboxylic Acid (V)—1.1 g. of the fraction (2′) was rechromatographed through an alumina (Brockmann) column using benzene + ether (1:1) as elution solvent. A part of blue-colored material remained adsorbed on alumina, but another part passed through. When the solvent was removed from the blue-colored eluate 0.75 g. of a blue oil was obtained. 5 cc. of ethanolic solution of the blue oil was boiled with 10 cc. of *N* NaOH solution for 2 hrs. and after addition of 30 cc. of water, the reaction mixture was thoroughly extracted with ether. After drying and removal of solvent, the ethereal extract gave crystals which were recrystallized from benzene to afford 0.35 g. of white crystals, m.p. 158~159°. The m.p. was undepressed on admixture with *trans*-hydrindeneglycol. When the blue alkaline solution, after above extraction with ether, was neutralized with H_2SO_4, the color turned dark blue under simultaneous emulsification. This was extracted with ether. After drying of the solution and evaporation of

7) Synthesized by the method of P.H. Hermans: Ber., **57**, 824(1924).
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ether, the extract furnished dark green crystals. Recrystallization from acetone and hexane (2 : 1) gave 83 mg. of azulene-5-carboxylic acid (IV), as dark green needles, m.p. 205~207°. Visible spectrum : $\lambda_{max}^{petr.\ ether}$ mμ (log ε) : 563(325), 586(320), 618(323), 645(270), 680(215). *Anal.* Calcd. for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found : C, 76.50; H, 4.51.

T. N. B complex of (IV) was recrystallized from EtOH to brown villose crystals, m.p. 152~153°. *Anal.* Calcd. for $C_{17}H_{11}O_8N_3$: N, 10.91. Found : N, 11.05.

The parts adsorbed on alumina was eluted out with 0.5*N* Na_2CO_3 solution. The resultant blue fraction was neutralized with H_2SO_4 and extracted with ether. The extract was evaporated to dryness and the residue was recrystallized from petr. ether. The crystals were purified by sublimation in high vacuum yielding 18 mg. of azulene-6-carboxylic acid (V), as beautiful green crystals, m.p. 224~225°(decomp.). Visible spectrum : $\lambda_{max}^{petr.\ ether}$ mμ (log ε) : 600(300), 630(325), 655(295), 693(290), 750(193). *Anal.* Calcd. for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found : C, 76.48; H, 4.62.

T. N. B complex of (V), recrystallized from EtOH, melted at 182~183°. *Anal.* Calcd. for $C_{17}H_{11}O_8N_3$: N, 10.91. Found : N, 10.59.

Saponification and Dehydration of Fraction (3′)—1.2 g. of the orange yellow fraction (3′), the one separated in chromatography of the condensation products (II or IIa and III), was dissolved in 20 cc. of EtOH and added with 1.5 g. of NaOH in 10 cc. of water, the mixture was boiled in N_2 for 2 hrs. After addition of 40 cc. of water to the reaction mixture, EtOH was removed *in vacuo*. The aq. solution was extracted with ether to separate a neutral part from which 0.82 g. of hydrindeneglycol was recovered. The residual alkaline solution was neutralized with H_2SO_4 giving 60 cc. of a light yellow solution, which was divided into two parts (each 30 cc.). The first half, 30 cc. of the neutralized solution, was lyophilized, and gave dusky green crystals contaminated with inorganic salts. The residue was completely extracted with petr. ether. The extract was condensed by evaporation and the separated crystals were recrystallized from the same solvent affording 10 mg. of dark green neeldes, m.p. 205~207°. Admixture of this with azulene-5-carboxylic acid (IV) obtained previously showed no depression of m.p. Evaporation of the mother liquor of recrystallization gave a small amount of greenish crystals, m.p. 215~222°(decomp.). The mixed melting point of the latter with azulene-6-carboxylic acid, m.p. 224~226°(decomp.), melted at 217~225° and no depression was observed. When another half, 30 cc. of the neutralized solution, was concentrated, a small quantity of blue oily material distilled out with water. The distillate was extracted with petr. ether. After drying, the petr. ether extract was poured through an alumina column and eluted with petr. ether. The eluted blue fraction was evaporated to remain 10 mg. of violet thin plates. The crystals, after sublimation, melted at 98~99°. Visible spectrum : $\lambda_{max}^{petr.\ ether}$ mμ (log ε) : 555(210), 580(270), 603 (235), 635(247), 662(120), 700(127). The T. N. B complex melted at 165~167°. Admixture of the azulenic product and its T. N. B complex[14] respectively with authentic azulene prepared from Δ^9-octahydroazulene by dehydrogenation, and its T. N. B complex showed no depression of the melting point.

Summary

From the condensation products of *trans*-hydrindeneglycol diacetate with ethyl diazoacetate, through deacetylation and dehydration without dehydrogenation, azulene-5- and -6-carboxilic acids were obtained.

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