hydic material boiling, under nitrogen, at 112–120° at 2.0 mm. A fraction with b. p. 112° at 2.0 mm., n^{28}D 1.4676, was analyzed.

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.34; H, 12.47.

The 2,4-dinitrophenylhydrazone was prepared, and had m. p. 183–184° after recrystallization from alcohol.

Anal. Calcd. for $C_{20}H_{28}N_2O_4$: C, 61.83; H, 7.27. Found: C, 61.65; H, 7.28.

Using undistilled 3,5-di-*s*-butyl-1,2-cyclohexanediol (above), a 63.5% yield of 3,5-di-*s*-butyl-1-cyclopentenealdehyde was obtained, b. p. 120–123° under nitrogen at 3.0 mm., n^{25}D 1.4770.

In contradistinction to the parent glycol, the cyclopentenealdehyde was a limpid liquid with a pale yellow color and an odor reminiscent of acrolein. It was stable under nitrogen at refrigerator temperature.

Oxidation of 3,5-Di-*s*-butyl-1-cyclopentenealdehyde.—The oxidation method was adapted from that used by Kögl, *et al.*, in their work with auxin a.[27] Three g. (0.0135 mole) of the cyclopentenealdehyde was dissolved in 900 ml. of 50% aqueous ethanol. To this was added, with rapid stirring but no external cooling, 2700 ml. of 0.05 *N* potassium permanganate solution containing 15.5 g. of sodium carbonate. The time required for the addition was five hours. The color of the permanganate solution was immediately discharged as each drop engaged the aldehydic solution, and slight warming occurred spontaneously. After the addition was complete, the mixture was stirred an additional four hours, allowed to settle, and then filtered. The filtrate was evaporated on the steam-bath to small bulk, and extracted with ten portions of ether. These were discarded. The aqueous residue was then acidified with dilute hydrochloric acid, and again extracted with ten portions of ether. The ether extracts were dried over sodium sulfate, and evaporated. The residual acidic oil was fractionally distilled through a small Claisen column, under nitrogen, at a pressure of 10^{-4} mm. Three fractions were collected: (1) 0.5 g., b. p. 110–113°; (2) 0.5 g., b. p. 113°; (3) 0.5 g., b. p. 113–127°. All fractions were slightly brownish in color, indicating slight decomposition. It may be noted that the reported b. p.[4] for the analogous product obtained from auxin a (but in which both *s*-butyl groups possess the *d*-configuration), is 100–115° in "hochvacuum." This term very probably indicates a pressure close to that used in our distillation, since the boiling ranges of the two products are very similar. Although the Dutch workers were finally able to obtain their product in solid form (as the dibasic acid), our fractions remained liquid. Fraction (2) was analyzed.

Anal. Calcd. for the dicarboxylic acid, $C_{13}H_{24}O_4$: C, 63.90; H, 9.90. Calcd. for the anhydride, $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 67.28; H, 9.76. That the main portion of our product was preponderantly the anhydride of α,α'-di-*s*-butylglutaric acid was demonstrated by its behavior in neutral equivalent determinations. The compound was insoluble in water, and reacted only slowly with dilute alkali. When a sample was first dissolved in ethanol, and then a titration performed, the neutral equivalent was 274. The calculated neutral equivalent for the mono-ethyl ester of α,α'-di-*s*-butylglutaric acid is 272. On the other hand, when samples were dissolved in water–acetone and treated with excess standard base, the neutral equivalents determined by back titration were 125 and 129. Phenolphthalein indicator was used, and blanks were determined in all cases. The calculated neutral equivalent for α,α'-di-*s*-butylglutaric acid is 122; that for the anhydride is 132.

Summary

The synthesis of 3,5-di-*s*-butyl-1-cyclopentenealdehyde from phenol has been described. The method is of general application.

BALTIMORE 18, MD. RECEIVED MAY 27, 1950

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[27] Kögl, Erxleben and Haagen-Smit, *Z. physiol. Chem.*, **225**, 215 (1934).

[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

The Maleic Anhydride Adduct of N-Phenyl-3,5-diethyl-2-propyl-1,4-dihydropyridine

BY DAVID CRAIG, A. K. KUDER AND JOHN EFROYMSON

The reaction of N-phenyl-3,5-diethyl-2-propyl-1,4-dihydropyridine I with maleic anhydride[1] forms a one to one adduct in spite of the fact that the double bonds in the dihydropyridine ring of I are not conjugated with each other.

The structure of the adduct, an anhydride, m. p. 120°, can be inferred from its behavior toward a variety of reagents. It is exactly dibasic and the careful addition of a strong acid to an aqueous solution of the sodium salt forms the corresponding acid, m. p. 153°, which as previously reported reforms the anhydride by loss of water. Reversion to the adduct also occurs in water. On the other hand, the adduct is soluble in concentrated hydrochloric acid and after standing a hydrochloride, m. p. 187°, crystallizes out. This salt contains two carboxyl groups. Since I contains methylenic hydrogen, reaction by a "substitution" mechanism to form a new dihydropyridine might be expected. However, the adduct is stable toward mild oxidizing agents such as iodine.[1] This and the fact that there is no tendency for the compound to disproportionate or polymerize in the presence of acid indicates that it cannot be a dihydropyridine.

The presence of methylenic hydrogen in I and the mechanism for a related diene synthesis already elucidated by Snyder, Hasbrouck and Richardson[2] suggest that the adduct is III formed by reaction (1).

Adequate support for structure III is found in the alkaline degradation of the adduct which forms aniline and the salts of butyric acid, 3,5-diethylbenzoic acid and an acid believed to be 3,5-diethylphthalic acid. The formation of these salts shows that the dienophile attaches itself to positions three and six of I. Only one crystalline modification of the adduct is formed in the reaction, though theory predicts that III should exist in many stereo forms. Since II, due to the asymmetry of carbon atom 2, must exist, if at all, as a racemic modification it might be predicted that at

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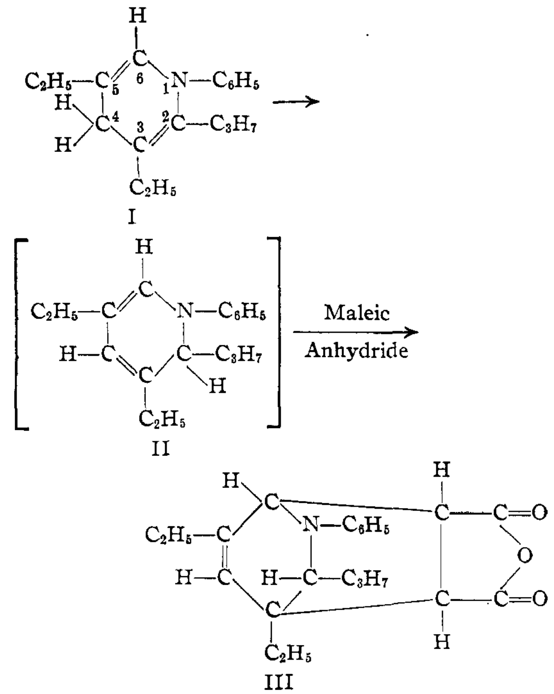
[1] Craig, Schaefgen and Tyler, THIS JOURNAL, **70**, 1624 (1948).

[2] Snyder and others, *ibid.*, **61**, 3558 (1939).

(1)



least two racemic modifications of III would be formed. However, since only one modification is actually formed, it is probable that II has no real existence and that the hydrogen shift from carbon 4 to carbon 2 of I occurs simultaneously with the formation of III. Examination of Stuart type molecular models indicates that the hydrogen shift can occur on the back side of I while the dienophile is adding to the front side. Thus, only one product, so far as the configuration of carbon 2 is concerned, would be expected and this, because of the accumulation of unsaturation in the precursor complex, would have the propyl group on the same side of the molecule as the maleic anhydride moiety.

The ultraviolet absorption[3] of the adduct supports structure III. Thus in neutral or basic aqueous methanol two bands ($E^{0.007\text{ g./l.}}_{261\text{ m}\mu} = 40$ and $E^{0.007\text{ g./l.}}_{296\text{ m}\mu} = 6$) are observed. Since the double bond is not conjugated with the nitrogen atom the absorption expected, in agreement with the observed values, is like that of a dialkylaniline.[1] Also in a solution one- and two-tenths normal with respect to hydrochloric acid the absorption $E^{0.015\text{ g./l.}}_{214\text{ m}\mu} = 25$ is diminished and shifted to shorter wave lengths. Since the compound is a weaker base than a simple dialkylaniline because of the presence of two acidic groups, it is not surprising that the acid solutions absorb somewhat more than acid solutions of unsubstituted dialkylanilinium salts.

Experimental

Titration of III.—A mixture of 3.53 g. (0.01 mole) of III, 60 ml. of water and 21.00 ml. of *N* sodium hydroxide was refluxed for thirty minutes. During this time the adduct dissolved. The solution was cooled and back titrated *N* hydrochloric acid, 1.15 ml. being required, with phenolphthalein as the indicator. In this way the acylation of the indicator by III was avoided. Calcd. for the anhydride of a dibasic acid: neut. equiv., 177. Found: neut. equiv., 178. An oil precipitated when 20.0 ml. (a slight excess) of *N* hydrochloric acid was added. This gradually crystallized during refluxing for 1.5 hours. The solid was separated, dried and found to weigh 3.48 g. (99%). It melted at 113–120° alone or mixed with III. When a similar titration solution was exactly neutralized and the precipitated oil crystallized from alcohol, a yield of 1.7 g. of the acid m. p. 153° resulted.

The Hydrochloride of the Acid of III.—Anhydride III, 3.53 g. (0.01 mole) dissolved completely in 20 ml. of concentrated hydrochloric acid during twenty minutes with vigorous shaking. The solution crystallized during twenty hours of standing. The crystals which formed were large and transparent. They were separated and rinsed with 5 ml. of alcohol; yield 3.60 g. (88%). They melted at 185–187° with dec. A further yield of 0.14 g. (5%) resulted when the aqueous mother liquor was allowed to stand with 5 ml. of concentrated hydrochloric acid. A 0.3530-g. sample was titrated with 0.1 *N* alkali. Calcd. for one HCl and two COOH groups: neut. equiv., 136. Found: neut. equiv., 134. A 0.41-g. (0.01 mole) sample was boiled for ten minutes with 5 ml. of water. The product crystallized when seeded. It was separated, dried and weighed 0.35 g. (99%) and melted at 118–120° alone or mixed with an authentic specimen of III.

The Alkali Fusion of III.—A solution of 20 g. (0.057 mole) of III in a mixture of 20 g. of 85% potassium hydroxide and 40 ml. of water was prepared in a 200-ml. round-bottom flask. The flask had a single 24/40 ₸ neck. A connector led first to a 100-ml. ice-cooled receiver and thence to a Dry Ice cooled trap. The connector was fitted with a glass stirrer mounted with rubber tubing in such a way that it could be manipulated by hand. The flask was heated with a free flame. Only water distilled off during the first thirty minutes. The mixture was then solid. Then with rigorous heating and continuous stirring during the next twenty minutes the mixture became semifluid and finally filled the flask with foam. Heating was stopped when this happened. A nearly colorless oily distillate was collected which amounted to 47.9 g. The condensate in the Dry Ice trap was water and amounted to 0.15 g. The fusion mixture weighed 31.5 g. and uncondensed gases (by difference) 0.45 g. The oily distillate was acidified with 5 ml. of concentrated hydrochloric acid and then was extracted with ether, the extract being discarded. The water layer was made alkaline. This caused the separation of a colorless oil which weighed 5.0 g. (95%), which melted at −8° alone or at −7° when mixed with aniline.

The fusion mixture became yellow on admission of air. It was distilled with a mixture of 25 ml. of water and 25 ml. of concentratd hydrochloric acid until a distillate of 25 ml. was collected. This was titrated with *N* sodium hydroxide, 36.5 ml. being required. This indicates the presence of 3.2 g. (64%) of butyric acid. That butyric acid was present was established by the preparation of the *p*-bromophenylacyl ester,[4] m. p. 63–64°.

After the removal of the butyric acid the fusion mixture was mixed with an additional 5-ml. portion of concentrated hydrochloric acid and extracted with three 150-ml. portions of ether. The ether layers were united, washed with a little water and evaporated so that 5.4 g. of crystals was secured. The remaining mother liquor was evaporated to dryness and distilled. This provided 0.7 g. of (14%) butyric acid as a forerun and 3.3 g. of crude acid, b. p. 145–150° (7 mm.) and m. p. 60–90°. Recrystallization from benzene–hexane mixture and then from methanol gave 0.6 g. (5%) of 3,5-diethylbenzoic acid, m. p.

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[3] Observed and interpreted by Laura Schaefgen.

[4] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 157.

127–129° alone or mixed with an authentic specimen prepared according to Snyder and others.[2,5]

3,5-Diethylphthalic Acid.—The 5.4 g. of crystals obtained during the evaporation of the ether extract of the fusion mixture was crystallized from dilute methanol. The result was 3.4 g. (27%) of nearly pure acid, m. p. 190° with decomp. alone or mixed with a sample prepared from the alkali fusion of the maleic anhydride adduct of 2-ethylhexenal anil.[2] This sample which melted at 194° with decomp. was analyzed.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.83; H, 6.35. Found: C, 65.40; H, 6.51.

The acid lost water when melted and formed the anhydride in the theoretical yield. The anhydride was crystallized from hexane and melted at 55–56°. It was monobasic toward 0.1 *N* sodium methylate.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.55; H, 5.93. Found: C, 70.79; H, 6.10.

The alkali fusion of the 2-ethylhexenal anil adduct was run under conditions similar to the alkali fusion of III. These are somewhat milder than those used by Snyder and others[2] and probably are more favorable to the formation of the 3,5-diethylphthalic acid. The yield of this acid was 10% and that of pure 3,5-diethylbenzoic acid was 14%. The formation of both of these acids is expected from the alkaline fusion of the anil adduct based on the structure elucidated by Snyder and co-workers.[2]

Summary

1. Maleic anhydride has been shown to add to the 3,6-carbon atoms of a 1,4-dihydropyridine.

2. The alkali degradation of the adduct led to butyric, 3,5-diethylbenzoic and 3,5-diethylphthalic acids and to aniline.

3. 3,5-Diethylphthalic acid was also formed as a product of the alkaline degradation of the anil of 2-ethylhexenal.

BRECKSVILLE, OHIO RECEIVED JUNE 12, 1950

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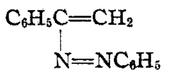
(5) Snyder, THIS JOURNAL, **63**, 3282 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Reaction of Phenylhydrazine with α-Haloacetophenones[1]

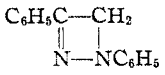
BY DAVID Y. CURTIN AND E. W. TRISTRAM

The reaction of phenylhydrazine with α-iodo, bromo- or chloroacetophenone has been found[2] to give a yellow crystalline product, I, m. p. 137°, which has the empirical formula C_7H_6N. Two possible structures (Ia and Ib) for the compound were suggested by Hess.[2] A dimeric structure, Ic, was later proposed by Culman.[3] More recently Bodforss[4,5] and Van Alphen[6] have accepted structures Ia and Ib, respectively, for I. This paper presents additional chemical and physical data bearing on the structure and proposes a new formulation for I.



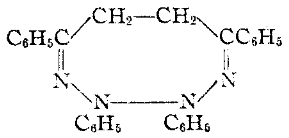
$$\begin{array}{l} C_6H_5C{=}CH_2 \\ \quad | \\ N{=}NC_6H_5 \end{array}$$

Ia



$$\begin{array}{l} C_6H_5C{-}CH_2 \\ \quad \| \quad | \\ \quad N{-}NC_6H_5 \end{array}$$

Ib



Ic

Many molecular weight determinations of I have been made[3,5] in an effort to choose between the monomer, $C_{14}H_{12}N_2$, molecular weight, 208, and the dimer, $C_{28}H_{24}N_4$, molecular weight 416, but most of the values obtained have fallen in the range 300–350.

We have found I to exist in two different crystalline modifications. One crystallizes as yellow needles, m. p. 137–138.5°. The other is obtained as red platelets, m. p. 132–136°. Evidence that the crystals are polymorphic forms of the same compound was obtained by evaporating their benzene solutions and measuring the infrared absorption spectra of the films obtained. The spectra, which are shown in Fig. 1, are identical. All experiments described in this paper except the X-ray analysis described below, were performed with the yellow, higher melting modification of I.

We have redetermined the molecular weight by measuring the freezing point lowering of solutions of I in two different solvents, benzene and diphenylamine. The weighted average of the four determinations in benzene is 387 ± 9; the weighted average of the six determinations in diphenylamine is 393 ± 20. These results are only 7 and 5.5%, respectively, below the dimeric molecular weight.

To obtain further evidence concerning the molecular weight of I a single red crystal was investigated with X-rays. The results of the X-ray study indicate with a high probability that the molecular weight is 416. In view of the cryoscopic determinations which are substantiated by the X-ray data, we feel that the formula of I is established as $C_{28}H_{24}N_4$.

Contributions to the chemistry of I have been made by several investigators. Culman[3] further studied the decomposition of I by acids, first noted by Hess,[2] and from the reaction isolated

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(1) Abstracted from a thesis presented by E. W. Tristram in partial fulfillment of the requirements for the Ph.D. degree at Columbia University. Presented before the Division of Organic Chemistry at the Philadelphia Meeting of the American Chemical Society, April 10, 1950.

(2) Hess, *Ann.*, **232**, 234 (1886).

(3) Culman, *ibid.*, **258**, 235 (1890).

(4) Bodforss, *Ber.*, **52**, 1762 (1919).

(5) Bodforss, *ibid.*, **72**, 468 (1939).

(6) Van Alphen, *Rec. trav. chim.*, **65**, 109 (1946).