SOME ACENAPHTHENE COMPOUNDS[1]

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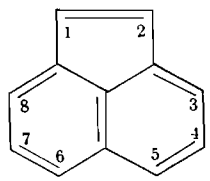
ABSTRACT

A new geometric isomer of 1,2-dichloroacenaphthene has been isolated among the reaction products of acenaphthylene and hypochlorous acid. Some new derivatives of acenaphthenone and acenaphthenol are reported.

INTRODUCTION

A number of students have worked at times in these laboratories in attempts to make the chlorohydrin and epoxide of acenaphthylene (I). This work has not met with success, but a number of compounds containing the acenaphthene nucleus have been prepared, which have been thought worthy of record. In attempts to make the chlorohydrin by treatment of acenaphthylene with hypochlorous acid by the method of Detoeuf (2), a new dichloroacenaphthene, m.p. 64° C., has been isolated. This is undoubtedly a geometric isomer of the 1,2-dichloroacenaphthene of melting point 115° C. prepared by Campbell (1) by the direct chlorination of acenaphthylene in carbon tetrachloride.

The presence of the chlorine in the 1,2-positions of the 64° melting compound has been established by oxidation with dichromate to naphthalic anhydride. Attempts to establish the configuration of these two isomeric 1,2-dichloroacenaphthenes (II and III) have been unsuccessful. Both the isomers on hydrolysis gave a mixture of the two corresponding glycols. Although the configuration of the glycols has been established by Jack and Rule (8), we have not been able to prepare either of the chlorides from the glycols with the usual agents such as zinc chloride – hydrochloric acid, phosphorus trichloride, or thionyl chloride. Both the dichloroacenaphthenes on treatment with potassium acetate and acetic acid were converted to the monoacetate of the *cis*-glycol.



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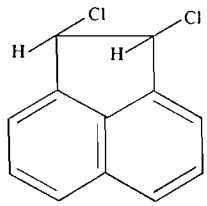

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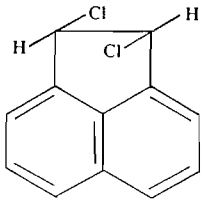

III

A study of the methylene group in acenaphthenone (IV) has been undertaken by a series of condensations with aromatic aldehydes under alkaline (Claisen-Schmidt) and acid conditions. This reaction has been studied previously by two groups of workers, de Fazi (3) in Italy and Sircar and Gopalan (10, 11, 12) in India. In several cases, as shown in Table I, there is disagreement between these authors on the melting point of the isolated product. This suggested that geometric isomers (V and VI) may have been isolated.

In attempts to clarify the situation, we have always isolated, with one exception, one of the described forms only, no matter whose directions we followed. When *o*-nitrobenzaldehyde was employed, both the described condensation products were isolated,

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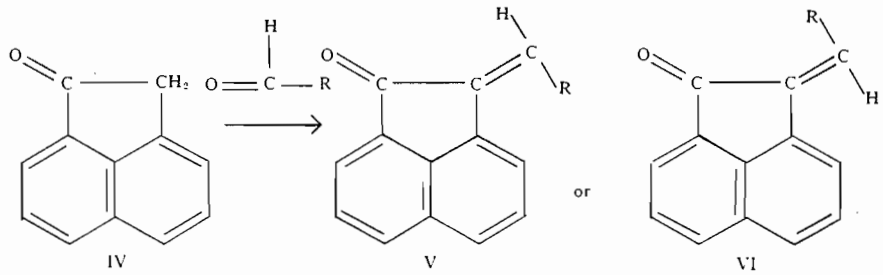
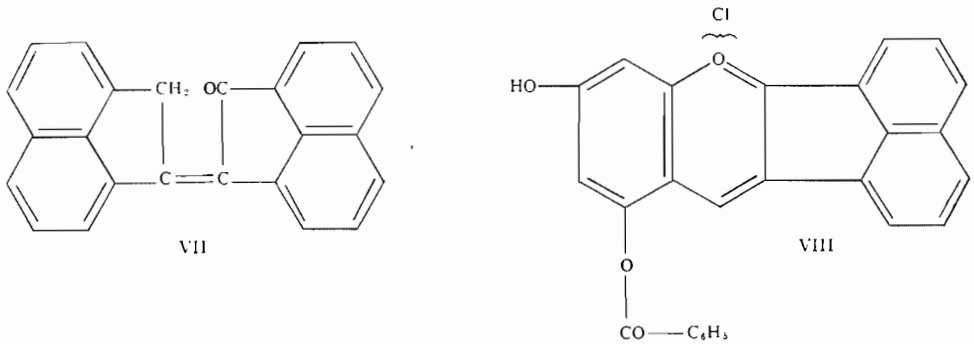


IV V or VI



VII VIII

TABLE I

$C_{10}H_{16}$$C{=}CH.R$ COMPOUNDS FROM ACENAPHTHENONE AND R.CHO

R—C(H)=	Melting point	
	Literature	This investigation
p-Nitrobenzal	202–203° (3) 239–240° (12)	— 241°
o-Nitrobenzal	241–243° decomp. (3) 157° (11)	242–244° 163–165°
p-Methoxybenzal (anisal)	95–98° (1) 126–127° (12)	95–96° —
o-Hydroxybenzal (salicylal)	168° (1) 186–187° (10)	— 185–186°
Cinnamal	167–168° (12) 214–215° (1)	163–165° —
o-Methoxybenzal	Not listed	192–192.5°
5-Nitrosalicylal	Not listed	242–243° decomp.
p-Hydroxybenzal	Not listed	215–216°

the higher melting under alkaline conditions and the lower melting under acid conditions. That the two products were geometric isomers and not polymorphic forms was shown by the difference in the ultraviolet absorption curves. The characteristic peak at 281–282 mμ of the 164° melting compound was missing in the 245° melting compound.

The expected condensation products have been obtained from the three new aldehydes listed in Table I. Naphthalic acid or its anhydride, or biacenone (VII), was the only isolated product, when condensations were carried out with *p*-methylbenzaldehyde, *m*-methylbenzaldehyde, and *m*-methoxybenzaldehyde. Biacenone also resulted when aliphatic aldehydes were employed. This is quite in agreement with the work of Graebe and Gfeller (6), who reported the formation of naphthalic acid by boiling acenaphthenone with sodium hydroxide solution, and of Graebe and Jequier (7), who reported the formation of biacenone from self-condensation of acenaphthenone in alcoholic sodium hydroxide even at room temperature. Phloroglucinaldehyde does not react with acenaphthenone under the normal conditions, but condenses with itself. However, using 2-O-benzoylphloroglucinaldehyde, the pyrylium salt (VIII) was produced.

The semicarbazone of acenaphthenone, which does not seem to have been previously reported, was prepared in the usual manner. A number of characterization derivatives of acenaphthenol, the 3,5-dinitrobenzoate, the *p*-nitrobenzoate, and the α-naphthylurethan, have been prepared.

EXPERIMENTAL

Acenaphthenol acetate, acenaphthenol, and acenaphthenone were prepared as described by Fieser and Cason (4). Acenaphthene (Reilly Tar and Chemical Corporation) was oxidized with lead tetracetate. Alkaline hydrolysis of the resulting acetate gave acenaphthenol, which on oxidation with chromic oxide and acetic acid yielded crude acenaphthenone. It was purified by steam distillation and finally by crystallization from ethanol, as colorless needles which melted at 121° C.*

Acenaphthylene

This substance was prepared essentially as described by Flowers and Miller (5) by passing acenaphthenol acetate vapors and nitrogen through a quartz tube heated to 520° by a nichrome heating element. The crude reddish solid pyrolysis product was washed well with water to remove acetic acid and crystallized several times from ethanol (charcoal). It was thus obtained as lemon yellow plates, m.p. 92° C. in 80% yield. The purification of the crude product could also be somewhat simplified by distillation *in vacuo*, using hydroquinone as a polymerization inhibitor and collecting the fraction boiling at 135–140° (15 mm.). The yields are somewhat lower owing to partial polymerization of the acenaphthylene.

The optimum rate of flow of the acetate through the pyrolysis tube appeared to be when the issuing vapors were thin and pale orange in color. If the vapors were heavy and bright yellow in color, it indicated that unpyrolyzed acetate was passing through the tube. On the average about 2 hours were required to put each 100 g. of the acetate through the tube. The efficiency of the tube was reduced somewhat by carbonaceous material and for best results it should be cleaned after every run of 200 g. To prevent oxidation and photochemical polymerization, the acenaphthylene was stored in amber glass stoppered bottles and kept in the dark.

1,2-Dichloroacenaphthene (m.p. 64°) (II or III)

A variety of unsuccessful attempts were made to obtain acenaphthylene chlorohydrin by the action of hypochlorous acid on acenaphthylene under a variety of conditions.

**Melting points have been determined by the capillary tube method and are uncorrected.*

In several cases the above compound of melting point 64° was isolated. A description follows of the method that seemed to give the largest amount of this substance.

Acenaphthylene (25 g.), monochlorourea solution (250 ml., 9.9% in hypochlorous acid, prepared by the method of Detoeuf (2)), and glacial acetic acid (15 ml.) were placed in a flask (500 ml.) and stirred mechanically. The reaction proceeded very slowly; after 24 hours a gummy solid had collected on the walls of the flask and the loss in hypochlorous acid was about 10% greater than the spontaneous decomposition of the acid. After 5 days the hypochlorous acid concentration was nil. The contents of the flask were then extracted with ether and washed with water and a 5% solution of sodium bicarbonate. The brown oil left after drying and removal of the ether was distilled *in vacuo*. A light yellow oil (14.7 g.) was collected at 170–180° (15 mm.). After the oil had been left for several days in the ice chest, a crop of light yellow crystals (4.8 g.) was obtained. On recrystallization from ethanol these were obtained as fine white needles which melted sharply at 64° C. Found: Cl, 31.83%. Calculated for $C_{12}H_8Cl_2$: Cl, 31.79%. It would seem that this substance is a geometric isomer of the 1,2-dichloroacenaphthene, melting point 115° C., prepared by Campbell (1) by the chlorination of acenaphthylene in carbon tetrachloride solution.

The residue oil, from which the 64° melting crystals were obtained, was distilled *in vacuo*. The yellow oil, b.p. 165–170° (14 mm.), did not crystallize. Found: Cl, 19.93%. Calculated for $C_{12}H_7Cl$: Cl, 19.02%. It would seem that this oil was probably identical with 1-monochloroacenaphthylene, which Campbell (1) prepared by treatment of the 115° melting dichloride with an alcoholic solution of sodium ethylate. With a saturated solution of picric acid in ethanol, the oil gave an orange picrate, m.p. 152–153°. A mixed melting point of this picrate and a sample of the picrate, m.p. 151–152°, prepared from a sample of Campbell's oil gave no depression.

Oxidation of the Dichloroacenaphthene

The 64° melting dichloroacenaphthene (2.0 g.) and sodium dichromate (10 g.) were dissolved in glacial acetic acid, 30 ml., and refluxed for 4 hours. The mixture was diluted with water (150 ml.) and the resulting precipitate filtered off. It was triturated with sodium bicarbonate solution and filtered. The filtrate was decolorized with charcoal and acidified with hydrochloric acid. The resulting precipitate was further purified by a repetition of the process and finally crystallized from ethanol. There was thus obtained a white, halogen-free, crystalline solid which melted at 268–270° and which gave a blue fluorescence in concentrated sulphuric acid. This substance proved to be naphthalic acid and its isolation can be accepted as proof that the halogens in the dichloro compound are in the 1,2-positions. The 115° melting isomer also produced naphthalic acid on oxidation.

Acenaphthylene Glycols

Authentic samples of the two glycols, the *cis*, m.p. 206–208°, and the *trans*, m.p. 155–156°, were prepared by the hydrolysis of the 115° melting 1,2-dichloroacenaphthene according to the directions of Jack and Rule (8). Some of the *cis*-glycol was also prepared by the oxidation of acenaphthene with selenium dioxide following the method of Monti (9).

Hydrolysis of the 64° melting dichloroacenaphthene gave both the *cis*- and *trans*-glycols.

The 64° melting dichloro compound (1.0 g.) was added to a solution of potassium acetate (2 g.) in glacial acetic acid (4 ml.). After the mixture was refluxed for 1 hour it was diluted with water. The resulting solid was crystallized three times from ethanol (charcoal) and gave fine white needles, m.p. 123° C. These were identical with the monoacetate of the *cis*-glycol. The 115° melting dichloro compound on being subjected to similar treatment yielded the same monoacetate of the *cis*-glycol.

Attempted Reactions of Glycols with Halogenating Agents

Various attempts to form the corresponding halogen compounds from the known glycols with agents such as concentrated hydrochloric acid and zinc chloride, phosphorus trichloride, and thionyl chloride (with and without pyridine) failed to yield the halogen compounds or any other identifiable material.

Derivatives of Acenaphthenol and Acenaphthenone

3,5-Dinitrobenzoate

This was prepared by treatment of acenaphthenol in pyridine with 3,5-dinitrobenzoyl chloride in the usual manner. On crystallization from acetone (charcoal) the product was obtained as small pale yellow needles which melted at 166° C. Found: C, 62.4; H, 3.30%. Calculated for $C_{19}H_{12}O_6N_2$: C, 62.6; H, 3.32%.

p-Nitrobenzoate

This ester was prepared in the same manner and crystallized from ethanol (charcoal) in fine pale yellow needles, m.p. 117–118° C. Found: C, 71.5; H, 4.13%. Calculated for $C_{19}H_{13}O_4N$: C, 71.4; H, 4.10%.

α-Naphthylurethan

α-Naphthyl isocyanate was allowed to react with acenaphthenol dissolved in dry pyridine. On crystallization from pyridine, the urethan was obtained as long colorless prisms which melted at 206° with decomposition. Found: C, 81.2; H, 5.06%. Calculated for $C_{23}H_{17}O_2N$: C, 81.4; H, 5.05%.

Acenaphthenone Semicarbazone

Acenaphthenone was allowed to react in the usual manner in hot alcoholic solution with semicarbazide hydrochloride and sodium acetate. The crude yellow semicarbazone which separated was recrystallized twice from ethanol (charcoal) and was obtained as a white fluffy solid, m.p. 241–243°, with decomposition. Found: N, 18.6%. Calculated for $C_{13}H_{11}ON_3$: N, 18.7%.

o-Methoxybenzalacenaphthenone

Acenaphthenone (1 g.) and *o*-methoxybenzaldehyde (0.81 g.) were dissolved in ethanol (50 ml.) and a solution of sodium hydroxide (5 g. in 5 ml. of water) was added slowly over a period of 2 hours. A yellow precipitate started to form during the addition of the alkali. After 24 hours at room temperature, the precipitate was filtered off, washed with ethanol, and crystallized from a mixture of chloroform and ethanol. It separated in yellow prisms (1.2 g.) which melted at 192–193° C. Found: C, 83.8; H, 4.96%. Calculated for $C_{20}H_{14}O_2$: C, 83.9; H, 4.93%.

5-Nitrosalicylalacenaphthenone

This was prepared according to the above directions. The crude dark red solid was crystallized from acetic acid (charcoal) and gave fluffy orange crystals, m.p. 242–243°

with decomposition. Found: C, 71.6. H, 3.53%. Calculated for $C_{19}H_{11}O_4N$: C, 71.9; H, 3.50%.

p-Nitrobenzalacenaphthenone

(1) When this was prepared as described above, which is the method of de Fazi (3), it was obtained as fine yellow needles, m.p. 242° C. This was the melting point of the product made by Sircar and Gopalan. The product of melting point 202–203° described by de Fazi was not obtained.

(2) If prepared according to the directions of Sircar and Gopalan (10, 11, 12) using 10% alcoholic potassium hydroxide as condensing agent, the product again melted at 241° C. Even with variation in temperature of condensation from −20 to +80° C. this product was always obtained under alkaline conditions.

(3) Acenaphthenone (1 g.) and *p*-nitrobenzaldehyde (0.95 g.) were dissolved in glacial acetic acid (10 ml.) and dry hydrogen chloride gas was passed through the mixture at room temperature over a period of 1 hour. The yellow condensation product started to precipitate immediately on the addition of the gas. At the end of the reaction it was filtered off, washed with dilute acetic acid, and crystallized from glacial acetic acid. It again melted at 241° C.

o-Nitrobenzalacenaphthenones

When produced by either of the alkaline condensation conditions described above, it was obtained as very fine yellow needles, m.p. 242–244°. When they were cooled and remelted there was no change in the melting point.

When formed by condensation with hydrogen chloride, yellow needles, m.p. 163–165°, resulted, which, after being cooled, remelted without change. That the two substances were geometric isomers and not polymorphic forms was indicated by the ultraviolet absorption curves. The peak at 281–282 mμ exhibited by the lower melting compound was not present in the higher melting. Both had the same sort of peak at 231–232 mμ.

Attempts to convert the lower melting isomer to the higher by use of ultraviolet light, iodine, heat, or palladized charcoal resulted in recovery of the starting material in the first two cases, and a dark uncrystallizable oil in the latter two. The low melting form if allowed to stand with alcoholic potash yielded, after acidification, naphthalic anhydride.

p-Hydroxybenzalacenaphthenone

This product resulted from both alkaline and acid condensations. It was recrystallized from acetic acid and melted at 215–216° C. Found: C, 83.7; H, 4.16%. Calculated for $C_{19}H_{12}O_2$: C, 83.8; H, 4.43%.

Salicylalacenaphthenone

Alkaline condensations gave the product melting at 185–186° C.

p-Anisalacenaphthenone

The product of melting point 95° was isolated by either of the alkaline methods of condensation. Nothing was isolated under the acid conditions.

Attempted Condensations

Normal condensations failed to occur with acenaphthenone under alkaline conditions and the following substituted benzaldehydes, *m*-methoxy-, *m*-methyl-, and *p*-methyl-.

In the first two cases either naphthalic acid or its anhydride was isolated and in the latter case self-condensation of the acenaphthenone gave yellow crystals of biacenone, m.p. 260° C. Found: C, 90.3; H, 4.43%. Calculated for $C_{24}H_{14}O$: C, 90.5; H, 4.43%. Biacenone was the only isolated product when acenaphthenone was treated with aliphatic aldehydes (propionic and butyric).

Acenaphthyleno-1′,2′;2,3,5-benzoyloxy-7-hydroxybenzopyrilium Chloride

Acenaphthenone (1 g.) and 2-O-benzoylphloroglucinaldehyde (1.5 g.) were dissolved in anhydrous ethyl acetate (5 ml.) and a few drops of glacial acetic acid (to effect complete solution of the aldehyde). Dry hydrogen chloride gas was passed into the mixture for an hour. The solution, which assumed a deep red coloration, was placed in an ice box for 4 or 5 days. A red powdery material separated which melted at 140–141°. To recrystallize this material, it was dissolved in a little absolute ethanol and the solution was again saturated with hydrogen chloride gas. Found: C, 68.3; H, 4.00; Cl, 7.29; loss at 110° *in vacuo* over phosphoric anhydride 6.45%. Calculated for $C_{26}H_{15}O_4Cl.1.5H_2O$: C, 68.9; H, 3.98; Cl, 7.84; H_2O, 5.97%.

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