a week. Infrared analysis disclosed —NH absorption at 3.01 μ, and the absorption of a hydrogen-bonded carbonyl at 5.83 μ.

Anal. Calcd. for $C_{15}H_{23}SO_3N_2$: C, 60.65; H, 7.81; N, 4.71; S, 10.78. Found: C, 60.4; H, 7.6; N, 4.65; S, 10.7.

N-p-Toluenesulfonyl dimethyl sulfilimine (VII). A. Ten g. (0.058 mole) of I was added slowly to 15 g. (0.19 mole) of dry dimethyl sulfoxide with stirring. Rapid heating occurred, with evolution of gas. The colorless reaction mixture was allowed to stand at room temperature for 5 hr. The product was then isolated by precipitation with water, followed by crystallization from ethanol-water mixture. Yield of pure sulfilimine, m.p. 157–158°, was 11.7 g. (87%).

B. This preparation was adapted from the procedure of Tarbell and Weaver[7] for sulfilimine formation. A solution of 8.6 g. *p*-toluenesulfonamide (0.05 mole) and 3.9 g. (0.05 mole) dimethyl sulfoxide in 25.5 g. acetic anhydride was heated over a steam bath for 1 hr. The solution was then cooled to room temperature and stirred into an ice-cold solution of 20 g. sodium hydroxide in 60 ml. water. The white crystals which separated were collected on a filter and then recrystallized from benzene. Yield was 5.5 g. (47%), m.p. 157–158°. Infrared spectra of samples from A and B were identical.

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(7) D. S. Tarbell and C. Weaver, *J. Am. Chem. Soc.*, **63**, 2939 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Acenaphthene Chemistry. VI.[1,2] Preparation and Reactions of Some Pyracene Glycols

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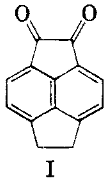
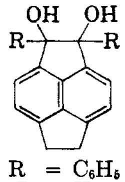
1,2-Diphenylpyracenediol reacts with 47% aqueous hydriodic acid to form the stable orange-colored 1,2-diphenyl-5,6-dihydropyracylene (III). With iodine in glacial acetic acid, the diol is converted to 2,2-diphenylpyracenone-1. The reduction of 1,2-diketopyracene with sodium borohydride produces an equimolar mixture of *cis* and *trans* 1,2-pyracenediols. The rearrangement of these diols affords pyracenone-1.

A number of derivatives of pyracene have been described in the literature.[1,3–5] There are also described some attempts to prepare the conjugated-unsaturated nonalternate hydrocarbon pyracylene.[5b] Anderson and Anderson discuss the calculated resonance energy and the 1,2- and 5,6-bond distances and conclude that such a molecule could exist. With the preparation of 1,2-diketopyracene[1] (I), the introduction of groups into the pyracene molecule has been simplified. This paper describes the preparation and reactions of a number of these derivatives.

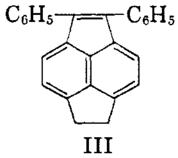
1,2-Diketopyracene (I) was prepared as described by Richter and Stocker[1] and treated with phenylmagnesium bromide to form the *trans* pinacol II. The pinacol II reacted with 47% hydriodic acid to afford 66% of 1,2-diphenyl-5,6-dihydropyracylene (III). This bright orange compound is stable even at its melting point of 226°. The unsubstituted hydrocarbon, 1,2-dihydropyracylene, prepared by Anderson and Anderson[5b] is reported to decompose at room temperature.

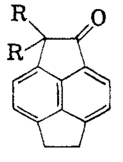

I


II. R = C_6H_5
Va. R = H, *cis*
Vb. R = H, *trans*

A similar elimination with 47% hydriodic acid was observed with 1,2-diphenylacenaphthenediol-1,2 which formed 1,2-diphenylacenaphthylene in good yield. The course of this elimination is uncertain as no iodine color is observed. This does not exclude the formation and decomposition of a 1,2-diiodo compound as iodine dissolves in 47% hydriodic acid to form a colorless solution.[6]

When II was treated with iodine in boiling glacial acetic acid according to Bachmann and Chu,[7] rearrangement of the pinacol led to the formation of 2,2-diphenylpyracenone-1 (IV) in 73.5% yield.


III


IV. R = C_6H_5
VI. R = H

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(1) Previous paper: H. J. Richter and F. B. Stocker, *J. Org. Chem.*, **24**, 366 (1959).

(2) This work was supported by the National Institute of Health, Grant Cy-2997-C3.

(3) M. C. Kloetzel and F. L. Chub, *J. Am. Chem. Soc.*, **72**, 150 (1950).

(4) A. G. Anderson, Jr., and R. H. Wade, *J. Am. Chem. Soc.*, **74**, 2274 (1952).

(5) A. G. Anderson, Jr., and R. G. Anderson, (a) *J. Org. Chem.*, **22**, 1197 (1957). (b) *J. Org. Chem.*, **23**, 517 (1958).

(6) C. A. Jacobsen, *Encyclopedia of Chemical Reactions*, Vol. III, Reinhold Publishing Corp., New York, N. Y., 1949, p. 709.

(7) W. E. Bachmann and E. J. Chu, *J. Am. Chem. Soc.*, **58**, 1118 (1936).

Rearrangement of II in boiling glacial acetic acid with a trace of hydrochloric acid[8] gave considerable decomposition. Chromatographic separation of this latter product afforded a 30% yield of crude ketone IV and a 10% yield of impure diphenyldihydropyracylene III. It is of interest to note that 1,2-diphenylacenaphthenediol-1,2 under similar conditions formed an 85% yield of 2,2-diphenylacenaphthenone-1.

The diketone I is reduced quantitatively by sodium borohydride to form a mixture of *cis* and *trans* diols Va and Vb. A diol melting at 264–265° separated from the reaction mixture in 51.5% yield. This compound formed an isopropylidene derivative with acetone and is thus shown to be the *cis* isomer Va. The *trans* diol Vb m.p. 188–189° was isolated in 48.5% yield from the mother liquor. A reaction time of two hours was required for complete reduction of the pyracene diketone I whereas acenaphthenequinone under similar conditions is reduced almost instantaneously to a mixture of *cis* and *trans* diols.

A mixture of the above diols in glacial acetic acid with iodine as the catalyst rearranged to form pyracenone-1 (VI). This compound was described previously by Anderson and Anderson.[5b] The mixture of *cis* and *trans* acenaphthenediols under similar conditions did not yield any identifiable products.

EXPERIMENTAL

1,2-Diketopyracene (I). This compound was prepared as described by Richter and Stocker.[1] With highly purified oxalyl bromide and technical grade aluminum bromide, the yields were 8–10%.

With naphthalene instead of acenaphthene and identical reaction conditions, the only product obtained was α-naphthoic acid. This was obtained in 75% pure yield. Unchanged naphthalene (25%) was isolated from the carbon disulfide liquor. No acenaphthenequinone was detected.

trans-1,2-Diphenylpyracenediol-1,2 (II). This compound was obtained in 38% yield by Richter and Stocker.[1] A more satisfactory preparation is described. Phenylmagnesium bromide was prepared from 5.4 g. of bromobenzene and 0.85 g. of magnesium turnings in 100 ml. of absolute ether. To this ethereal solution, 1,2-diketopyracene (I) (1.50 g., 0.007 mole) was added in small portions. A vigorous reaction occurred and the light brown Grignard solution turned orange. An additional 100 ml. of absolute ether was added and the solution was refluxed for 2 hr. The mixture was decomposed by pouring into iced acetic acid. The ether layer was separated and the acetic acid solution was extracted twice with additional ether. The combined ether extracts were washed with 10% sodium carbonate solution and with water and dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent *in vacuo* yielded 2.5 g. (98%) of a light yellow solid, m.p. 120–160°. This product was crystallized from ethanol-water with decolorizing charcoal and yielded white needles, 1.85 g. (69%), m.p. 179–181° (lit.[1] 180–181°) of II.

Treatment of II with dry acetone containing 1% anhydrous hydrogen chloride yielded only starting material confirming the formation of *trans*-1,2-diphenylpyracenediol-1,2 (II).

1,2-Diphenyl-5,6-dihydropyracylene (III). 1,2-Diphenylpyracenediol-1,2 (II) (0.5 g.) was treated with 30 ml. of 47% aqueous hydriodic acid at room temperature with stirring. The white suspension of II was warmed on a steam bath for 1 hr. during which time it slowly turned to an orange suspension. Glacial acetic acid (10 ml.) was added and the orange suspension was warmed on a steam bath for 1 hr. It was poured into aqueous sodium bisulfite solution and filtration yielded 0.45 g. of orange III, m.p. 217–220° in quantitative yield. Crystallization from acetone–ethanol–water yielded orange needles, (0.3 g., 66%), m.p. 226–227°.

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.72; H, 5.50.

A solution of III (0.1773 g., 0.0005 mole) in absolute ethanol took up 0.0005 mole of hydrogen over 10% palladium on charcoal catalyst at one atmosphere pressure and room temperature to give 0.180 g. (97%) of 1,2-diphenylpyracene, m.p. 197–198.5°. This product formed white needles from ethanol-water.

Anal. Calcd. for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.44; H, 6.17.

In a similar reaction, 0.5 g. of 1,2-diphenylacenaphthenediol-1,2 was treated with 47% aqueous hydriodic acid and yielded 0.35 g. (81.5%) of 1,2-diphenylacenaphthylene, m.p. 162–163° (lit.[7] m.p. 161.3°). Both 1,2-diphenylacenaphthylene and 1,2-diphenyl-5,6-dihydropyracylene (III) exhibited deep blue colors with concentrated sulfuric acid.

1,2-Diphenylacenaphthylene (0.0064 mole) in absolute ethanol absorbed 0.0067 mole of hydrogen over 10% palladium on charcoal catalyst at one atmosphere pressure and room temperature to give 98% of 1,2-diphenylacenaphthene, m.p. 146–147° which separated as white needles from ethanol-water.

Anal. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 94.30; H, 5.74.

1,2-Diphenyl-5,6-dihydropyracylene (III), like 1,2-diphenylacenaphthylene, was very stable even at its melting point. A sample at room temperature in air showed no decrease in melting point after 6 weeks and the melting point of a once melted sample showed no decrease.

Bachmann and Chu[7] report the formation of 1,2-diphenyl-1,2-dichloroacenaphthene in good yield by passing anhydrous hydrogen chloride through a dry chloroform solution of 1,2-diphenylacenaphthenediol-1,2 at 0°. Under similar conditions, 1,2-diphenylpyracenediol-1,2 (II) produces a mixture of products. These products did not contain chlorine. The mixture was not characterized further.

2,2-Diphenylpyracenone-1 (IV). The pinacol rearrangement of 1,2-diphenylpyracenediol-1,2 (II) was carried out as described by Bachmann and Chu.[7] One-half g. of II was added in one portion to a solution of iodine (2.5 g.) in 250 ml. of glacial acetic acid. This solution was heated at reflux for 30 min. After cooling, the deep purple solution was poured into aqueous sulfur dioxide and the resulting gray precipitate was collected on a filter, 0.45 g., m.p. 160–175°. This product was crystallized from an ethanol-water mixture with decolorizing charcoal to afford light yellow needles, 0.35 g. (73.5%), m.p. 191–192°. The infrared spectrum exhibited absorptions at 1710 cm.$^{-1}$ and 1682 cm.$^{-1}$ 2,2-Diphenylacenaphthenone-1 exhibited only one absorption at 1715 cm.$^{-1}$ This double absorption for the carbonyl group was common to all pyracene compounds containing a carbonyl group.

Anal. Calcd. for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 89.94; H, 5.31.

When the pinacol rearrangement was carried out on II according to Beschke[8] using boiling glacial acetic acid and concentrated hydrochloric acid as catalyst, a black product was formed. Only a low yield of crude IV in addition to some III could be isolated by crystallization from ethanol-water followed by chromatographic separation on alumina.

The rearrangement of 1,2-diphenylacenaphthenediol-1,2 using glacial acetic acid and concentrated hydrochloric acid gave a clean reaction with no decomposition and an 85%

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(8) E. Beschke, *Ann.*, **369**, 184 (1909).

yield of 2,2-diphenylacenaphthenone-1, m.p. 172–173° (lit.[7] 171.3–172.4°). Both the acenaphthene and pyracene diphenyl ketones gave an orange color with concentrated sulfuric acid.

1,2-Pyracenediols. A. cis-1,2-Pyracenediol (Va). To a yellow-orange suspension of 1 g. of 1,2-diketopyracene (I) in 150 ml. of ethanol there was added in one portion 0.5 g. of sodium borohydride. This suspension was stirred for 2 hr. at room temperature during which time the orange solid dissolved to form a nearly colorless solution which showed a blue fluorescence. An additional 0.1 g. of sodium borohydride was added and stirring continued for 20 min. The reaction mixture was then decomposed by the drop-wise addition of excess 10% hydrochloric acid followed by 300 ml. of water. The white precipitate which slowly separated was collected on a filter. There was obtained 0.52 g. of crude Va, m.p. 240–250° dec. This product was crystallized from ethanol to form white needles, (40%), m.p. 264–265° dec.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.18; H, 5.75.

B. trans-1,2-Pyracenediol (Vb). The filtrate from the above preparation of the *cis* diol was saturated with salt and extracted exhaustively with ether. The ethereal solution was dried over anhydrous sodium sulfate and evaporated under reduced pressure leaving 0.5 g. of crude *trans*-1,2-pyracenediol (Vb), m.p. 130–138° which was crystallized from 400 ml. of water to yield white cubes, (35%), m.p. 188–189°.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.19; H, 5.86.

The high melting diol Va (0.2 g.) was suspended in 5 ml. of the acetone–hydrochloric acid solution and anhydrous sodium sulfate (0.1 g.) was added. The white solid slowly dissolved over a period of 14 hr. at room temperature. The solution was filtered and the solvent evaporated. There was obtained 0.2 g. of 1,2-isopropylidenedioxypyracene, m.p. 120–135° dec. Crystallization from petroleum ether (b.p. 40–50°) yielded white needles, m.p. 164–165°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.78; H, 6.55.

The low melting diol Vb (0.2 g.) was subjected to the same reaction conditions as described above but was recovered unchanged.

When acenaphthenequinone was reduced with sodium borohydride as described for 1,2-diketopyracene (I), the reaction was instantaneous and quantitative. A 50–50 mixture of the known *cis* and *trans* acenaphthenediols[9] was obtained although separation proved more difficult.

Pyracenone-1 (VI). A mixture of the *cis* and *trans* 1,2-pyracenediols (Va and Vb) (0.2 g.) was subjected to the conditions of the pinacol rearrangement using glacial acetic acid and iodine.[7] The mixture was poured into aqueous sulfur dioxide. The precipitated gray solid (0.2 g.) melted at 140–165° and then formed a black residue which did not melt above 270°. Approximately one half of this gray product dissolved in hot ethanol. This solution was treated with decolorizing charcoal, filtered, and on cooling very light yellow crystals formed. There was obtained 0.08 g. (40%) of pyracenone-1 (VI), m.p. 180–181° (lit.[5b] m.p. 182–183°). The infrared spectrum showed absorption peaks at 1670 cm.$^{-1}$ and 1715 cm.$^{-1}$ Pyracenone-1 gave an orange-yellow color with concentrated sulfuric acid similar to that obtained with acenaphthenone-1.

A mixture of *cis* and *trans* acenaphthenediols was subjected to the same reaction conditions above but no acenaphthenone-1 was isolable.

BOULDER, COLO.

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[9] R. Criegee, L. Kraft, and B. Rank, *Ann.*, **507**, 159 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, A'IN SHAMS UNIVERSITY]

Studies of Quinoid Structures. IV.[1] Action of Grignard Reagents on Anthraquinone Monoanil

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Grignard reagents add preferentially to the carbonyl group of anthraquinone monoanil under ordinary conditions. The constitution of the products is discussed.

It has been found[1-3] in these laboratories that Grignard reagents add preferentially to the carbonyl group of phenanthrenequinonimine, chrysenequinonimine, phenanthrenequinone monoxime, chrysenequinone monoxime, phenanthrene-quinone and chrysenequinone monosemicarbazones and benzil monosemicarbazone. This study is now extended to *p*-quinoid structures, *e.g.* anthraquinone monoanil (I). Grignard reagents add under normal conditions preferentially to the carbonyl group of I as shown in Scheme A.

The constitution of II is based on: (i) hydrolysis to give a nitrogen free keto compound (III), (ii) infrared spectrum showing the presence of C═N stretching frequency at 1639 cm^{-1}[4,5] and —OH stretching frequency at 3333 cm^{-1},[6] and (iii) elemental analysis. The ketone (III) showed clear carbonyl stretching frequency at 1680 cm^{-1},[7] but it did not show a free —OH stretching fre-

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[1] Studies of Quinoid Structures. III. Action of Grignard reagents on phenanthrenequinone monosemicarbazone, chrysenequinone monosemicarbazone and benzil monosemicarbazone. W. I. Awad, A. R. A. Raouf, and Miss A. M. Kamel (*J. Org. Chem.* in press).

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[4] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Metheun, London, 1957, p. 223.

[5] W. I. Awad, *Egypt. J. Chem.*, **1**, 87 (1958).

[6] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Metheun, London, 1957, p. 84.

[7] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Metheun, London, 1957, p. 176.