g. of impure IV in 48 hr. Finally, after addition of 3 ml. of concd. sulfuric acid in 10 ml. of water, continued refluxing gave 72.3 g. more impure IV in 168 hr.

Stability of cis-2,2,4,4-tetramethyl-3-cyclobutanediol (IIIa). The *cis* isomer of III[1] (77.5 g.) was mixed with 500 ml. of water and 20 ml. of concd. sulfuric acid, and the solution was refluxed for 271 hr. in apparatus equipped with a continuous azeotrope separator. No IV was formed and apparently no change occurred. An additional 50 ml. of concd. sulfuric acid was added; again no IV was formed during 21 hr. of refluxing. The mixture was cooled and 180 ml. of concd. sulfuric acid was added. When heating was resumed, the solid glycol dissolved, the color of the reaction solution rapidly darkened, and tar gradually formed. After 41 hr., heating was stopped and the small amount of organic distillate in the azeotrope separator was examined. It was a complex mixture in which no IV could be found by distillation.

KINGSPORT, TENN.

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

Acenaphthene Chemistry. VII.[1,2] The Synthesis and Properties of an Acenaphthenequinolimide Acetate

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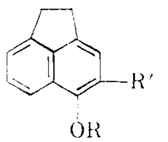
Received March 13, 1961

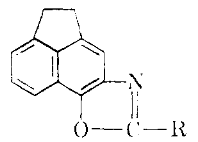
5-Acetoxyacenaphthene undergoes the Fries rearrangement to form 4-acetyl-5-acenaphthenol. The oxime of this ketone in acetic anhydride-acetic acid with hydrogen chloride formed 4,5-acenaphtho[*d*]2-methyloxazole. 4-Amino-5-acenaphthenol hydrochloride formed the same oxazole when treated with acetic anhydride followed by treatment of the product with concentrated hydrochloric acid. 4-Benzenesulfonamido-5-methoxyacenaphthene was oxidized to 4-benzenesulfonamido-5-methoxy-5-acenaphthenequinol acetate by lead tetraacetate. This quinol acetate is converted into 4,4′-dibenzenesulfonamido-5,5′-dimethoxy-2,1′-biacenaphthylidine when a suspension in acetic acid is treated with concentrated hydrochloric acid.

The preparation and characterization of 4,5-acenaphthenequinonedibenzenesulfonimide has been described.[4] In this work attention was directed toward a similar study of an acenaphthene compound with a quinonemonoimide structure. Quinonemonoimides with benzenoid and naphthenoid ring systems have been extensively investigated by R. Adams and his co-workers.[5]

In our work 5-acenaphthenol (I)[6] was treated with acetic anhydride to produce the acetate, II, which was found to undergo the Fries rearrangement on treatment with anhydrous aluminum chloride. The bright yellow product from this rearrangement, III, formed an oxime IV which was expected to produce 4-acetamido-5-acenaphthenol (V) when subjected to Beckmann rearrangement conditions.



I. R = H; R′ = H
II. R = $COCH_3$; R′ = H
III. R = H; R′ = $COCH_3$
IV. R = H; R′ = $\overset{\text{N—OH}}{\overset{\|}{\text{C}}}\text{—CH}_3$
V. R = H; R′ = $NHCOCH_3$
VI. R = H; R′ = $\overset{\text{N—OCOCH}_3}{\overset{\|}{\text{C}}}\text{—CH}_3$



VII. R = CH_3
VIII. R = $CH{=}CHC_6H_5$

Two products were obtained. One separated from the reaction mixture in 26% yield and is believed to be the oxime acetate VI and the other obtained in 62% yield was precipitated as a tan solid m.p. 139–140°, VII, when the filtrate was poured into water. The anticipated acetamide V is reported[6] to melt at 165°. A comparison of the infrared spectra of our substance and that of V obtained from a sample kindly supplied by Professor H. Rapoport showed them to be different. The material melting at 139–140° exhibited strong absorption at 1580 cm.$^{-1}$ indicative of C=N.[7] Chemical analysis indicated $C_{14}H_{11}NO$ which corresponds to 4,5-acenaphtho[*d*]2-methyloxazole (VII). The literature[8–10] discloses the formation of oxazoles from

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[1] Previous paper: H. J. Richter and W. C. Feist, *J. Org. Chem.*, **25**, 356 (1960).

[2] This work was supported by research grant CY-2997 from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service and by a Monsanto Chemical Co. grant-in-aid.

[3] This paper and number VI of this series represent a portion of a thesis submitted by William C. Feist in partial fulfillment of the requirements for the Ph.D. degree at the University of Colorado, 1960. Presented at the 140th National Meeting of the American Chemical Society at Chicago in Sept. 1961.

[4] H. J. Richter and B. C. Weberg, *J. Am. Chem. Soc.*, **80**, 6446 (1958).

[5] R. Adams and W. Reifschneider, *Bull. Soc. Chim. France*, 23 (1958).

[6] H. Rapoport, T. P. King, and J. B. Lavigne, *J. Am. Chem. Soc.*, **73**, 2718 (1951).

[7] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley & Sons, Inc., New York, N. Y., 1958, 2nd ed., (a) page 96, (b) page 179.

[8] J. Meisenheimer, *J. Pr. Chem.*, [11], 119, 315 (1928).

[9] A. H. Blatt, *J. Am. Chem. Soc.*, **60**, 205 (1938).

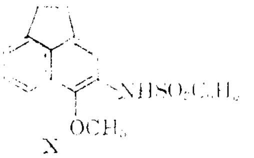
[10] J. Meisenheimer and R. Meis, *Ber.*, **57**, 289 (1924).

o-hydroxyketoximes when subjected to Beckmann rearrangement conditions.

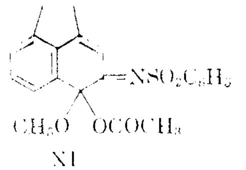
Oxazoles are reported to form hydrochlorides[11] and an unstable hydrochloride, m.p. 204–206° dec., was formed from VII. 2-Methyloxazoles have also been reported to undergo an aldol type condensation with benzaldehyde.[12] Our product VII condensed with benzaldehyde to form 4,5-acenaphtho-[*d*]-2-styryloxazole (VIII). This substance absorbed bromine slowly whereas the oxazole VII appeared inert.

The structure of the oxazole VII was confirmed by synthesis from the known 4-amino-5-acenaphthenol hydrochloride (IX).[6] The hydrochloride was refluxed with acetic anhydride and the product obtained from this mixture, when treated with concentrated hydrochloric acid, produced the same oxazole.

It is reported[13] that the oxidation of *N*-benzenesulfonyl-*p*-anisidine, with lead tetraacetate, in dry chloroform, led to the formation of *p*-quinonemonobenzenesulfonimide. Since the preparation of a benzenesulfonamide from 4-amino-5-acenaphthenol hydrochloride (IX) was unsuccessful and since a quinonemonoimide had been prepared from a methyl ether, our attention was directed toward the preparation of a quinonemonoimide containing the acenaphthene nucleus by the lead tetraacetate oxidation of 4-benzenesulfonamido-5-methoxyacenaphthene (X). This compound was prepared from the known 4-amino-5-methoxyacenaphthene hydrochloride[6] and benzenesulfonyl chloride. The benzenesulfonamide X, suspended in glacial acetic acid or chloroform, was oxidized by lead tetraacetate to produce a yellow solid which showed absorptions at 1545 cm.$^{-1}$ and 1735 cm.$^{-1}$ indicative of C=N and acetate carbonyl,[14] respectively. Chemical analysis indicated $C_{21}H_{19}NO_5S$ and suggested 4-benzenesulfonimido-5-methoxy-5-acenaphthenequinol acetate (XI). The quinolimide acetate is readily reduced to the methoxybenzenesulfonamide X.



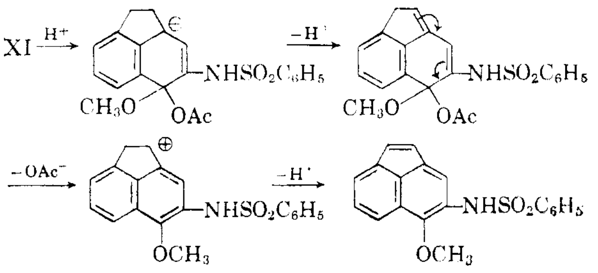
X



XI

In previous work[4] it was shown that 4,5-acenaphthenequinonedibenzenesulfonimide was converted into 4,5-dibenzenesulfonamidoacenaphthylene. This acid-catalyzed prototropic shift was induced by the addition of concentrated hydrochloric acid to an acetic acid suspension of the quinonediimide.

When the yellow imide acetate XI was suspended in glacial acetic acid and concentrated hydrochloric acid added, the suspension slowly changed to a yellow-orange solution and, after forty minutes, a yellow-orange solid XII separated. This product, after crystallization from benzene-chloroform, melted at 265° with darkening. A chloroform solution of the material was red and exhibited a blue fluorescence. It was soluble in warm 5% aqueous sodium hydroxide from which it was recovered unchanged upon acidification. Compound XII was oxidized by bromine in carbon tetrachloride to a brown amorphous solid and did not decolorize a potassium permanganate solution in acetone. This yellow-orange product XII was rapidly oxidized by lead tetraacetate in acetic acid to a red-brown solid which could not be purified but whose infrared spectrum did not show N—H absorption but did show acetate carbonyl group absorption. The material XII did not contain chlorine and gave a deep blue-green color with concentrated sulfuric acid. The chemical analysis indicated $C_{19}H_{15}NSO_3$ which suggests that it is the expected acenaphthylene derivative XIII, which would arise from a prototropic shift and loss of acetic acid as shown:



XIII

The product XII did not absorb hydrogen with either 10% palladium on charcoal or platinum oxide as catalyst, at a hydrogen pressure of 30 p.s.i. The infrared spectrum of XII exhibited an absorption at 3240 cm.$^{-1}$ indicative of N—H[14] but no absorption at 1650–1710 cm.$^{-1}$ characteristic of C=O.[7b] The high melting point of the material suggested that it may be a dimer, a trimer or even a tetramer of an acenaphthylene.[15-18] Preliminary molecular weight determinations were not satisfactory because of the very limited solubility of XII.

It is reported that acenaphthylene, when treated with hydrochloric acid in glacial acetic acid gave

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[11] E. H. Rodd, *Chemistry of Carbon Compounds*, Vol. IV, Part A, Elsevier Publishing Co., Amsterdam, 1957, p. 376.

[12] D. M. Brown and G. A. R. Kon, *J. Chem. Soc.*, 2147 (1948).

[13] R. Adams and K. R. Browe, *J. Am. Chem. Soc.*, **80**, 5800 (1958).

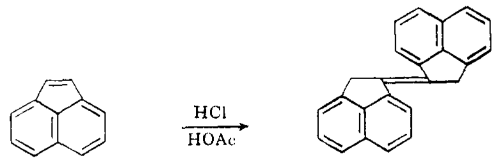
[14] R. Adams and E. L. DeYoung, *J. Am. Chem. Soc.*, **79**, 705 (1957).

[15] P. Rehländer, *Ber.*, **36**, 1583 (1933).

[16] K. Dziewonski and G. Rapolski, *Ber.*, **45**, 2491 (1912).

[17] K. Dziewonski, *Ber.*, **46**, 2156 (1913).

[18] K. Dziewonski and Z. Leyko, *Ber.*, **47**, 1679 (1914).

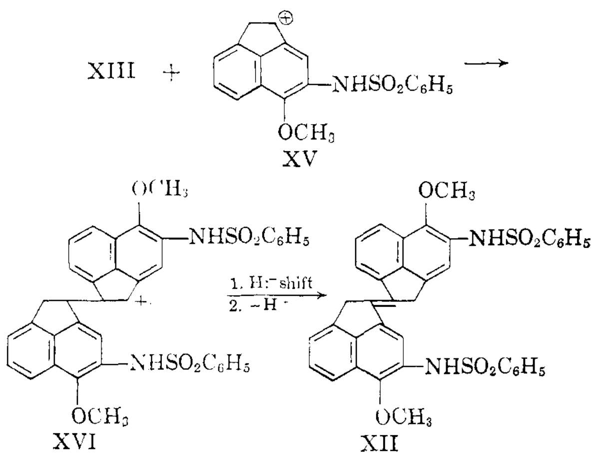


XIV

biacenaphthylidine XIV, isolated as the picrate in 37–40% yield.[19]

When acenaphthylene, dissolved in acetic acid, was treated with concentrated hydrochloric acid and allowed to react for seven hours, a yellow-orange solid was formed. A melting point of 273–275° confirmed that it was the known biacenaphthylidine.[19] This substance, dissolved in benzene, exhibited a blue fluorescence very similar to that shown by XII. An indigo-green color formed when XIV was treated with concentrated sulfuric acid. The dimer XIV failed to absorb hydrogen at low pressure in the presence of 10% palladium on charcoal, and did not decolorize a bromine-chloroform solution nor an acetone solution of potassium permanganate.

Due to the similarities of XII and XIV it is proposed that XII is the dimer *trans*-4,4′-dibenzenesulfonamido-5,5′-dimethoxy - 2,1′ - biacenaphthylidine which could be formed by the route outlined below.



The addition of a proton to the 1- position of the intermediate XIII would give the carbonium ion XV and this ion could in turn add to the 1- position of another acenaphthylene XIII, to give the new carbonium ion XVI. A hydride shift followed by the loss of a proton would give the acenaphthylidine XII and the more stable configuration should be the *trans* configuration due to steric interactions. We were unable to prepare the acenaphthylene intermediate XIII.

The acenaphthylidine XII could not be obtained by the reaction of the quinolimide acetate XI with anhydrous pyridine.[4] The dark material formed resisted attempts at purification and could not be characterized. When XI was treated with refluxing 10% aqueous hydrochloric acid, a dark amorphous material, which could not be characterized, was obtained.

1,2-Diphenylacenaphthylene was recovered unchanged after treatment with concentrated hydrochloric acid in glacial acetic acid at room temperature.

EXPERIMENTAL[20]

5-Acetoxyacenaphthene (II). Fifteen g. of 5-acenaphthenol[6] (0.0885 mole) was dissolved in 50 ml. of water containing 5.4 g. of sodium hydroxide. Crushed ice (100 g.) was added and 10.7 ml. (0.11 mole) of acetic anhydride was introduced into the reaction mixture. An exothermic reaction occurred and a gray precipitate resulted. After filtration and drying, the gray solid weighed 17.8 g. (95%), m.p. 81–90°. Crystallization from dilute ethanol resulted in nearly colorless crystals of II, m.p. 100–101°, in 75% yield.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.22; H, 5.56.

4-Acetyl-5-acenaphthenol (III). 5-Acetoxyacenaphthene (II), (6.9 g., 0.022 mole) dissolved in 90 ml. of dry nitrobenzene was added dropwise to a stirred solution of 4.3 g. (0.024 mole) of anhydrous aluminum chloride in 60 ml. of dry nitrobenzene. The yellow solution turned green in 30 sec. and the temperature rose several degrees. The 5 acetoxyacenaphthene solution was added over a period of 45 min. and the temperature was kept between 25° and 30°. The solution was stirred for 12 hr. and then warmed to 50° for 1 hr. The green complex containing mixture was decomposed by pouring into iced hydrochloric acid with stirring. The resulting two-phase solution was steam distilled until all of the nitrobenzene was removed. Filtration of the aqueous solution remaining gave 6.9 g. of a brown solid. This brown solid was dissolved in dry chloroform leaving a small residue. Chromatography of the brown solution over 100 g. of alumina gave a bright yellow product, 4.8 g. (65.2%) m.p. 168–170°. Crystallization from ethanol-water gave 4.5 g., m.p. 169–170° of 4-acetyl-5-acenaphthenol (III) as yellow needles.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.22;H, 5.70. Found: C, 79.36; H, 5.76.

With anhydrous aluminum bromide, 4-acetyl-5-acenaphthenol (III) was obtained in 55% yield. An attempt to effect the rearrangement of II with carbon disulfide as the solvent resulted in recovery of the 5-acetoxyacenaphthene. Without a solvent and reaction temperature of 110–125° there was obtained a low yield of 5-acenaphthenol.

4-Acetyl-5-acenaphthenol oxime (IV). Four g. (0.0189 mole) of 4-acetyl-5-acenaphthenol (III) and 4 g. of hydroxylamine hydrochloride were refluxed in 20 ml. of absolute ethanol and 20 ml. of dry pyridine for 2 hr. The resulting yellow solution was evaporated *in vacuo* and water added. The resulting yellow precipitate was collected on a filter, washed well with water, and dried, 4.25 g., 99% yield, m.p. 205–208°. Crystallization from ethanol-water (Darco) gave pale yellow needles, 3.85 g. (90%), m.p. 209–210° of 4-acetyl-5-acenaphthenol oxime (IV).

Anal. Calcd. for $C_{14}H_{13}NO_2$: N, 6.16. Found: N, 6.33.

Beckmann rearrangement of 4-acetyl-5-acenaphthenol oxime. A. To a mixture of 56 ml. of glacial acetic acid and 56 ml. of acetic anhydride was added 3.8 g. (0.0167 mole) of 4-acetyl-5-acenaphthenol oxime (IV). Anhydrous hydrogen chloride was passed through this yellow suspension. Within 15 min. heat was evolved and the yellow solid started to dissolve. After 2 hr., a green-brown solution resulted and at the end of 3 hr. a white solid had separated from the reaction mixture. After passing in hydrogen chloride gas for 6 hr., the flask was stoppered and left overnight. The white solid was

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(19) G. Dolinski and K. Dziewonski, *Ber.*, 48, 1917 (1915).

(20) All melting points are uncorrected.

filtered off and washed well with water and after drying weighed 1.0 g., m.p. 190–194°. Several crystallizations from ethanol gave colorless crystals, m.p. 208.5–209.5°.

Anal. Calcd. for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.62. Found: C, 71.56; H, 5.82.

The analysis corresponded to that calculated for 4-acetyl-5-acenaphthenol oxime acetate (VI). An oxime acetate was also obtained by rearranging 3,5-diacetylacenaphthene dioxime under similar conditions.[21]

The filtrate from the above separation was poured into 600 ml. of cold water. A tan solid separated which was removed by filtration and washed well with water. This substance weighed 2.1 g. and melted at 138–140°. Several crystallizations from cyclohexane (Darco) gave metallic gray crystals which were white when ground, m.p. 139–140°. Extraction of the aqueous filtrate with ether and benzene resulted in the recovery of an additional 0.25 g. of tan solid, m.p. 128–135°. The total yield of 4,5-acenaphtho[*d*]2-methyloxazole (VII) was 62%.

Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30, N, 6.69. Found: C, 80.21; H, 5.03; N, 6.77.

This compound was shown to be 4,5-acenaphtho[*d*]2-methyloxazole (VII) by comparison with a sample prepared from the known 4-amino-5-acenaphthenol hydrochloride

The oxazole VII, dissolved in absolute ether, with anhydrous hydrogen chloride gave an immediate precipitate of a white hydrochloride, m.p. 204–208°. Attempts to crystallize this hydrochloride salt from ethanol-benzene resulted only in the recovery of the starting oxazole. The hydrochloride gave a strong odor of hydrogen chloride while standing at room temperature.

B. Two grams (0.0088 mole) of 4-acetyl-5-acenaphthenol oxime was dissolved in absolute ethyl ether and 2.6 g. (0.0146 mole) of phosphorus pentachloride was added in one portion. After several minutes, a yellow precipitate slowly formed. The resulting yellow-green suspension was stirred for 30 min. Evaporation of the ether followed by the addition of 75 ml. of water and subsequent filtration gave a pale yellow solid which was crystallized from dilute ethyl alcohol to give 0.65 g., m.p. 90–115°, of yellow crystals. This material was chromatographed over alumina using chloroform as the eluent. There was obtained 0.41 g. of pale yellow solid, m.p. 128–133°. A mixed melting point of this material and 4,5-acenaphtho[*d*]2-methyloxazole showed no depression and their infrared spectra were superimposable.

4,5-Acenaphtho[*d*]*2-styryloxazole* (VIII). Anhydrous zinc chloride (0.75 g.), freshly fused and ground, was placed in a small glass tube along with 0.5 g. of 4,5-acenaphtho[*d*]2-methyloxazole (VII) and 1 ml. of freshly distilled benzaldehyde. The tube was sealed and heated at 175° for 8 hr. After cooling, the contents of the tube were washed into 400 ml. of water with benzene. The aqueous solution was boiled until the odor of benzaldehyde was absent. The resulting dark solid was extracted with ether and benzene and the combined extracts dried over anhydrous sodium sulfate. Chromatography of this solution resulted in an orange solid in the ether-benzene fractions, m.p. 130–160°. This orange solid was chromatographed again using benzene as the eluent. A pale yellow solid resulted which was crystallized from petroleum ether (b.p. 60–80°) using decolorizing charcoal and yielded pale yellow-green needles, m.p. 183–184°, (0.15 g.) of VIII.

Anal. Calcd. for $C_{21}H_{15}NO$: C, 84.82; H, 5.09. Found: C, 85.15; H, 5.12.

4,5-Acenaphtho[*d*]*2-methyloxazole from 4-amino-5-acenaphthenol.* A suspension of 0.4 g. of freshly prepared 4-amino-5-acenaphthenol hydrochloride,[6] obtained from 4-nitro-5-acenaphthenol,[22] in 20 ml. of acetic anhydride was refluxed for 2 hr. during which time it changed to a brown-orange solution. The solution was cooled and poured into iced hydrochloric acid. The resulting orange suspension was extracted with benzene and the benzene dried over anhydrous sodium sulfate. Evaporation of the solvent gave 0.4 g. of an orange solid which was crystallized from cyclohexane (Darco) to give 0.25 g. of pale yellow crystals, m.p. 123–124°. This product was treated with 18 ml. of concd. hydrochloric acid and the resulting pale green solution was warmed on a steam bath for 15 min. Water (200 ml.) was added and a gummy solid separated which was removed by extraction with benzene. The benzene solution was dried over anhydrous sodium sulfate and evaporated leaving a dark solid. This solid was crystallized from cyclohexane (Darco) yielding pale yellow crystals, m.p. 110–121°. Chromatographic purification over alumina using ethyl ether as eluent, gave a pale yellow substance, m.p. 131–136° which did not depress the melting point of a sample of 4,5-acenaphtho[*d*]2-methyloxazole (VII) obtained from the Beckmann rearrangement of 4-acetyl-5-acenaphthene oxime (IV). The infrared spectra of these two materials were superimposable.

4-Benzenesulfonamido-5-methoxyacenaphthene (X). A solution of 5.5 g. (0.0244 mole) of 4-amino-5-methoxyacenaphthene hydrochloride[6] in 25 ml. of dry pyridine was treated with 7.92 g. (0.0488 mole) of benzenesulfonyl chloride with cooling and shaking. The resulting cherry red solution was allowed to stand for 30 min. with occasional shaking. Iced hydrochloric acid was added to this solution and the tan solid which separated was collected on a filter, washed well with water and dried. The yield of X was 7.6 g. (91.6%), m.p. 213–216° with darkening. Crystallization from benzene-petroleum ether (b.p. 80–100°) gave white crystals, m.p. 219–220° with darkening, in 80% yield.

Anal. Calcd. for $C_{19}H_{17}NSO_3$: C, 67.23; H, 5.05. Found: C, 67.60, 66.64; H, 5.51, 5.24.

4-Benzenesulfonimido-5-methoxy-5-acenaphthenequinol acetate (XI). A suspension of 2.0 g. (0.0059 mole) of 4-benzenesulfonamido-5-methoxyacenaphthene (X) in 60 ml. of glacial acetic acid was stirred with a magnetic stirrer while 2.68 g. (0.006 mole) of lead tetraacetate was added in one portion. The reaction was carried out at room temperature. After 5 min., a yellow color developed in the solution and after 10 min. a yellow solid started to appear. The yellow suspension was stirred for 3 hr. At the end of this period, 5 drops of glycerol was added and the reaction mixture stirred for an additional hour. The yellow product was collected on a filter, and thoroughly washed with a dilute solution of sodium carbonate. The crude yield was 1.93 g., m.p. 173–176° with darkening and sintering. The dried crude product was dissolved in boiling benzene, decolorizing charcoal added, and filtered. A small amount of petroleum ether (b.p. 80–100°) was added to the yellow filtrate and the solution was allowed to cool. Yellow crystals formed in a few minutes. The yellow product was collected on a filter, and dried, m.p. 165–166°. The yield of pure 4-benzenesulfonimido-5-methoxy-5-acenaphthenequinol acetate was 1.41 g. (60.5%). This compound on repeated recrystallizations for analysis exhibited different melting points. The observed melting points for one sample were 165–166°; 177–178°; 184–185°; 165–166°. These differences are attributed to different crystalline forms as the infrared spectra of all the different melting substances (potassium bromide pellets) were superimposable.

Anal. Calcd. for $C_{21}H_{19}NO_5S$: C, 63.46; H, 4.82. Found: C, 63.44, 63.60; H, 5.15, 4.84.

Infrared studies on the quinone monoimide showed absorption at 1545 cm.$^{-1}$ indicative of C=N (lit.[14] C=N, 1544 cm.$^{-1}$), the absence of absorption at *ca.* 3240 cm.$^{-1}$ characteristic of N—H,[14] and absorption at 1735 cm.$^{-1}$ indicative of acetate carbonyl (lit.[7b] acetate C=O 1735–1750 cm.$^{-1}$).

Reduction of 4-benzenesulfonimido-5-methoxy-5-acenaphthenequinol acetate. 4-Benzenesulfonimido-5-methoxy-5-acenaphthenequinol acetate (XI) (0.20 g.) was placed in a Parr hydrogenator with 50 mg. of platinum oxide, and 30 ml. of absolute ethyl alcohol. Hydrogen pressure of 37 p.s.i. was applied and the mixture was shaken for a total of 10 hr. The ethyl alcohol solution was warmed, filtered, and the

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[21] H. J. Richter and F. B. Stocker, *J. Org. Chem.*, **24**, 214 (1959).

[22] F. Sachs and G. Mosebach, *Ber.*, **44**, 2852 (1911).

solvent evaporated in air leaving 0.18 g. of pale yellow solid, m.p. 175–210°. Crystallization from benzene–petroleum ether (b.p. 80–100°) gave 0.16 g. of crystals m.p. 218–220°. This material did not depress the melting point of an authentic sample of 4-benzenesulfonamido-5-methoxyacenaphthene (X). The infrared spectra of these materials were superimposable.

The reaction of 4-benzenesulfonimido-5-methoxy-5-acenaphthenequinol acetate and hydrochloric acid. 4-Benzenesulfonimido-5-methoxy-5-acenaphthenequinol acetate (XI), 1.4 g. (0.00352 mole), was suspended in 75 ml. of glacial acetic acid and 7 ml. of concd. hydrochloric acid was added with stirring. The yellow suspension slowly changed to a deeper yellow solution over a period of 40 min. and then a yellow-orange solid began to separate. The reaction mixture was stirred for a total of 10 hr. and then allowed to stand overnight at room temperature. The yellow-orange solid was collected on a filter and dried yielding 0.85 g. Chromatographic purification using 2% methyl alcohol in chloroform as eluent followed by crystallization from benzene chloroform gave 0.8 g. of 4,4′-dibenzenesulfonamido-5,5′-dimethoxy-2,1′-biacenaphthylidine (XII) as yellow-orange crystals, m.p. 264–265°, with darkening.

Anal. Calcd. for $C_{35}H_{30}N_2S_2O_6$: C, 67.64; H, 4.48. Found: C, 67.54; H, 4.57.

The acetic acid–hydrochloric acid filtrate from the above reaction was diluted with a large volume of water and 0.30 g. of a yellow substance, m.p. 145–155° precipitated. This was not identified.

Biacenaphthylidine (XIV). Six g. (0.0394 mole) of acenaphthylene was dissolved in 300 ml. of glacial acetic acid and 21 ml. of concd. hydrochloric acid was added with stirring. The solution became more orange and after 10 hr. stirring the yellow solid formed was collected on a filter and washed well with water. There was obtained 5.0 g. of XIV, m.p. 230–250°. A small sample was crystallized from benzene giving yellow-orange prisms, m.p. 275–277° (lit.[18] m.p. 277°).

BOULDER, COLO.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, DIAMOND ALKALI CO.]

Novel Polyacetylenic Diols[1] and Polyacetylenic Polyurethanes

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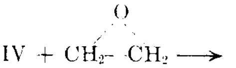
Three novel polyacetylenic-α,ω-diols were prepared by the reaction of formaldehyde, ethylene oxide and trimethylene oxide, respectively, with the α,ω-diGrignard reagent of 1,7,13,19-eicosatetrayne. The diols were converted to the corresponding biscarbanilates and reduced to the known saturated compounds. Reaction of the diols with five different diisocyanates gave a series of polyurethanes. Replacing polypropylene glycol with a polyacetylenic diol in an elastomeric polyurethane formulation gave a polyurethane with a 6.5% greater density and a 20% greater (calories/ml.) heat of combustion.

The preparation of elastomeric polyurethanes by the reaction of polyester glycols or of polyether glycols with diisocyanates is well known.[2] We believed that the use of a long-chain polyacetylenic α,ω-diol, such as could be prepared from 1,7,13,19-eicosatetrayne,[3] should result in a polyurethane having a greater density and energy content than an otherwise similar polyurethane prepared from a polyalkylene ether glycol such as polypropylene glycol (PPG). This paper describes the preparation of several novel polyacetylenic diols, their conversion to polyurethanes and an examination of some mechanical and thermal properties of these polyurethanes.

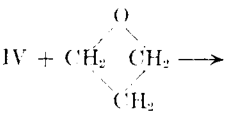
The preparation of 2,8,14,20-docosatetrayne-1,22-diol (I), 3,9,15,21-tetracosatetrayne-1,24-diol (II), and of 4,10,16,22-hexacosatetrayne-1,26-diol (III) was carried out by the reaction of the α,ω-diGrignard reagent of 1,7,13,19-eicosatetrayne with formaldehyde, ethylene oxide, and trimethylene oxide (oxetane) respectively. Treatment of the diols with phenylisocyanate gave the corresponding α,ω-biscarbanilates as derivatives. Catalytic reduction of the polyacetylenic diols gave the corresponding known[4] saturated diols.

$$\text{H}-\text{C}{\equiv}\text{C}[(\text{CH}_2)_4-\text{C}{\equiv}\text{C}]_3\text{H} + \text{C}_2\text{H}_5\text{MgBr} \longrightarrow \text{BrMgC}{\equiv}\text{C}[(\text{CH}_2)_4-\text{C}{\equiv}\text{C}]_3\text{MgBr} \quad (\text{IV})$$

$$\text{IV} + \text{CH}_2\text{O} \longrightarrow \text{HOCH}_2-\text{C}{\equiv}\text{C}[(\text{CH}_2)_4-\text{C}{\equiv}\text{C}]_3\text{CH}_2\text{OH} \quad (\text{I})$$



$$\text{IV} + \text{CH}_2-\text{CH}_2\text{(O)} \longrightarrow \text{HOCH}_2\text{CH}_2\text{C}{\equiv}\text{C}[(\text{CH}_2)_4-\text{C}{\equiv}\text{C}]_3\text{CH}_2\text{CH}_2\text{OH} \quad (\text{II})$$



$$\text{IV} + (\text{CH}_2)_3\text{O} \longrightarrow \text{HOCH}_2\text{CH}_2\text{CH}_2-\text{C}{\equiv}\text{C}[(\text{CH}_2)_4-\text{C}{\equiv}\text{C}]_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \quad (\text{III})$$

Reaction of the diols with tolylene diisocyanate (TDI), diphenylmethane 4,4′-diisocyanate (MDI), hexamethylene diisocyanate (HMDI), 5,11-hexadecadiyne 1,16-diisocyanate ($\text{OCN}[(\text{CH}_2)_4\text{C}{\equiv}\text{C}]_2$-$(\text{CH}_2)_4\text{NCO}$) (HDDI)[5] and hexadecane-1,16 diisocyanate (HDI),[5] without a cross-linking agent, gave the simple polyurethanes whose properties

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[1] Presented in part at the 138th Meeting of the American Chemical Society, New York, September 15, 1960, Abstracts of Papers, p. 74-P.

[2] B. A. Dombrow, *Polyurethanes*, Reinhold, New York, 1957, Chapter 6.

[3] J. H. Wotiz, R. F. Adams, and C. G. Parsons, *J. Am. Chem. Soc.*, 83, 373 (1961).

[4] K. E. Murry and R. Schoenfeld, *Australian J. Chem.*, 8, 432–436 (1955); *Chem. Abstr.*, 49, 16472e (1955).

[5] J. H. Wotiz and F. Huba, unpublished results, and also ref. 1.