stabilized acetylene bubbled into the well-stirred solution for 16 hours. A trace of hydroquinone was added and the product was distilled to obtain 74.0 g. (70%) of the vinyl ester (see Table III).

Polyvinyl 2,2,3,3-Tetrafluoropropionate.—A mixture of 6 g. of the vinyl ester and 0.01 g. of benzoyl peroxide in a sealed tube was heated at 80° for 12 hours. The solid plug of polymer was dissolved in acetone and reprecipitated by pouring into low-boiling petroleum ether. The polymer had an inherent viscosity of 1.09 (0.1% in dioxane at 25°) and could be pressed at 125° into a clear, colorless, cold-drawable film.

Anal. Calcd. for $(C_5H_4F_4O_2)_n$: C, 34.9; H, 2.3; F, 44.2. Found: C, 34.3; H, 2.6; F, 44.3.

Phosphorus Derivatives (Table IV).—The preparation of these compounds is illustrated by the conversion of 2,2,3,3-tetrafluoropropionamide to a phosphoramidic ester, *via* the intermediate phosphine imide and phosphoramidic dichloride.

To a suspension of 25.5 g. of phosphorus pentachloride in 50 ml. of benzene was added, in small portions, 17.8 g. of tetrafluoropropionamide. An endothermic reaction occurred at each addition with vigorous evolution of hydrogen chloride. The benzene was evaporated under a stream of nitrogen and the residue was distilled at reduced pressure to afford 24.5 g. of the moisture-sensitive N-(tetrafluoropropionyl)-trichlorophosphine imide.

A benzene solution of the phosphine imide was prepared as described above from 28 g. of tetrafluoropropionamide and 40 g. of phosphorus pentachloride. To this solution was added, dropwise with stirring, 9 g. of formic acid. Vigorous gas evolution occurred. The benzene was removed under reduced pressure and the solid residue was crystallized from cyclohexane to obtain N-(tetrafluoropropionyl)-phosphoramidic dichloride.

Sodium *p*-chlorophenoxide was prepared by azeotropic distillation (three hours) of water from a mixture of 0.067 mole each of sodium hydroxide and *p*-chlorophenol in benzene. To this mixture was added 9.0 g. of the phosphoramidic dichloride dissolved in 50 ml. of tetrahydrofuran. The mixture was stirred at room temperature for three hours, distilled to half-volume, treated with 100 ml. of low-boiling petroleum ether and filtered. The filtrate was concentrated to a sirupy consistency and was allowed to stand for two days during which time the mass crystallized. It was recrystallized once from a benzene–petroleum ether mixture and twice from cyclohexane to obtain the pure *p*-chlorophenyl ester.

WILMINGTON, DELAWARE

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

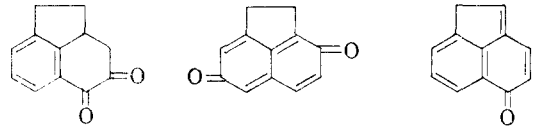
Acenaphthene Chemistry. III.[1] The Preparation and Reactions of 4,5-Acenaphthenequinonedibenzenesulfonimide[2]

BY HENRY J. RICHTER AND BERTON C. WEBERG

RECEIVED MAY 26, 1958

An acenaphthene derivative with a true quinoid structure has been prepared and characterized. Dark red 4,5-acenaphthenequinonedibenzenesulfonimide was prepared by the lead tetraacetate oxidation of 4,5-dibenzenesulfonamidoacenaphthene. Treatment of the quinone diimide with hydrochloric acid or hot pyridine caused isomerization to form the yellow 4,5-dibenzenesulfonamidoacenaphthylene. 4-Amino-5-benzenesulfonamidoacenaphthene when treated with nitrous acid gave 4,5-triazoloacenaphthene.

The literature on acenaphthenequinone, 1,2-diketoacenaphthene is quite extensive. However, acenaphthene derivatives in which the aromatic portion of the molecule is a part of the quinoid structure are unknown. The structural analogy to naphthalene would indicate acenaphthenequinone structures corresponding to



Two of these possibilities were considered by Sachs and Mosebach in 1911,[3] but no such derivative was described.

In 1920 Rowe and Davies[4] reported what they believed to be 4,5-acenaphthenequinone dioxime which they prepared by the oxidation of 4-nitro-5-aminoacenaphthene (I) with sodium hypochlorite followed by reduction with hydroxylamine. The dioxime of the quinone was described as a brown, amorphous, infusible powder. Although an analysis was reported which agrees with the calculated value, no characterization confirming this structure was described. The principal objective of the present work was the synthesis and characterization of an acenaphthene compound with a quinone structure.

4-Nitro-5-aminoacenaphthene (I), first described by Sachs and Mosebach,[3] was the derivative selected for the initial study. The amino nitro compound was reduced to 4,5-diaminoacenaphthene which proved to be too unstable for use in the proposed work. Adams[5–8] and his co-workers have shown that the sulfonimides of benzo- and napthoquinones are characterized by greatly enhanced stability, and efforts were, therefore, directed to the synthesis of an appropriate acenaphthene disulfonamide for oxidation to a diimide possessing a quinoid structure. Treatment of I with benzenesulfonyl chloride afforded only a very low yield of 4-nitro-5-benzenesulfonamidoacenaphthene (II). With a large excess of benzenesulfonyl chloride, an N,N-disubstituted derivative was obtained. A more satisfactory approach to II was realized by nitrating 5-benzenesulfonamidoacenaphthene (III), which gave an 87% yield of II. Compound

(1) Preceding papers: H. J. Richter, THIS JOURNAL, **75**, 2774 (1953), and H. J. Richter, *J. Org. Chem.*, **21**, 619 (1956).

(2) This work was supported by the National Institute of Health, Grant Cy-2997-Cy and by an Ohio Oil Co. Fellowship. It represents a portion of a thesis submitted by Berton C. Weberg in partial fulfillment of the requirements for the Ph.D. degree at the University of Colorado, 1958. Presented at the 134th National Meeting of the American Chemical Society at Chicago in September, 1958.

(3) F. Sachs and G. Mosebach, *Ber.*, **44**, 2852 (1911).

(4) F. M. Rowe and J. S. H. Davies, *J. Chem. Soc.*, 117, 1344 (1920).

(5) R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601 (1950).

(6) R. Adams and J. L. Anderson, *ibid.*, **72**, 5154 (1950).

(7) R. Adams and R. A. Wankel, *ibid.*, **73**, 131 (1951).

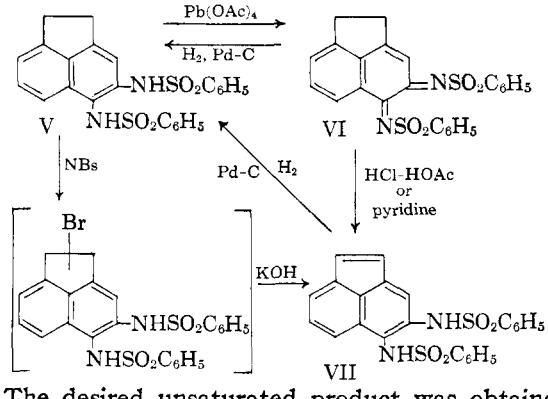
(8) R. Adams and J. H. Looker, *ibid.*, **73**, 1145 (1951).

II was reduced to 4-amino-5-benzenesulfonamidoacenaphthene (IV). The disulfonamide V was obtained in 65% yield by reaction of IV with benzenesulfonyl chloride.

4,5-Dibenzenesulfonamidoacenaphthene (V) was oxidized with lead tetraacetate as described by Adams.[6] The product VI was a stable deep red compound, obtained in 63% yield, and melted at 153–154°. The infrared spectrum showed no absorption at 3240 cm.$^{-1}$ indicating no N–H, but absorbed at 1534 cm.$^{-1}$ characteristic of the C=N group.[9] Reduction of VI reformed the original 4,5-dibenzenesulfonamide V.

In order to characterize further this new derivative of acenaphthene as a true quinoid structure, an attempt was made to effect the addition of hydrogen chloride as has been reported for numerous quinone imides.[5–8, 10–12] When the diimide VI was suspended in glacial acetic acid and treated with hydrochloric acid, the red color was destroyed. An analysis of the yellow product VII obtained from this showed little change from the original diimide VI, and no chlorine was present. The infrared spectrum did not include an absorption band at 1534 cm.$^{-1}$ indicative of the C=N group.[9] The yellow color is characteristic of acenaphthylene and the compound VII was hydrogenated to 4,5-dibenzenesulfonamidoacenaphthene (V).

Further proof for the structure VII was obtained by its synthesis from V. The preparation of the intermediate 1,2-dibromo-4,5-dibenzenesulfonamidoacenaphthene was first attempted by dibromination of V with N-bromosuccinimide in boiling carbon tetrachloride. The corresponding dibromo derivative of the unsubstituted acenaphthene is known to be rather unstable.[13] In this reaction, as the bromination proceeded, hydrogen bromide was liberated, giving a mixture of a monobrominated product and starting material. When this mixture was catalytically hydrogenated, the bromine was removed leaving only V.



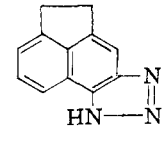
The desired unsaturated product was obtained by the use of a stoichiometric amount of N-bromosuccinimide with chlorobenzene as the solvent. The 1(2)-bromo-4,5-dibenzenesulfonamidoacenaphthene was not isolated. The resulting solution was treated with potassium hydroxide and chromatographic separation afforded a very small yield of the acenaphthylene derivative. A melting point of a mixture of this compound and the rearranged quinone diimide showed no depression, and the infrared spectra were superimposable. The rearranged product is thus shown to be 4,5-dibenzenesulfonamidoacenaphthylene (VII).

It also was observed that 4,5-acenaphthenequinonedibenzenesulfonimide (VI) rearranged in good yields to the acenaphthylene derivative VII merely by warming a pyridine solution of VI on the steam-bath. The transformation of the diimide VI to the disulfonamide VII is an interesting example of a prototropic shift.[14]

Benzoylation of 5-aminoacenaphthene formed 5-benzamidoacenaphthene (VIII) which was mononitrated to yield 4-nitro-5-benzamidoacenaphthene (IX). Benzoylation of 4-nitro-5-aminoacenaphthene (I) to form 4-nitro-5-benzamidoacenaphthene (IX) was more successful than the corresponding reaction with benzenesulfonyl chloride.

Catalytic hydrogenation of IX formed 4-amino-5-benzamidoacenaphthene (X). Treatment of this product with benzoyl chloride formed 4,5-dibenzamidoacenaphthene (XI). Attempts to oxidize this compound with lead tetraacetate at room temperature in anhydrous ether, and also in the same solvent at reflux temperature, were not successful.

4 - Amino - 5 - benzenesulfonamidoacenaphthene (IV) was diazotized in an attempt to prepare 4-hydroxy - 5 - benzenesulfonamidoacenaphthene for subsequent oxidation to a quinone monoimide. The diazotized amine was decomposed and the crystalline compound which resulted was found to be not the expected hydroxy compound, but one which contained only carbon, hydrogen and nitrogen. Analysis indicated $C_{12}H_9N_3$ as the empirical formula which corresponds to a triazole.



XII

XIII

In an effort to establish the formation of a triazole, 4-amino-5-benzamidoacenaphthene (X) was treated with nitrous acid in an identical manner. The product was found to satisfy the analysis for a benzoyltriazoloacenaphthene XIII. The infrared spectrum of this compound contained a strong absorption peak at 1710 cm.$^{-1}$, which can be assigned to the carbonyl function.[15a]

Acid hydrolysis of XIII converted it into the identical compound obtained from the diazotization and decomposition of 4-amino-5-benzenesulfonamidoacenaphthene. This was shown by the melting point of a mixture of the two products, which showed no depression, and by superimposable infrared spectra.

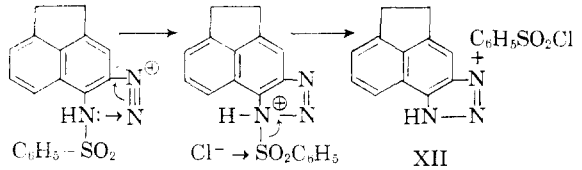
Catalytic hydrogenation of 4-nitro-5-aminoacenaphthene (I), and treatment of the resulting 4,5-

(9) R. Adams and E. L. DeYoung, THIS JOURNAL, 79, 705 (1957).
(10) R. Adams and R. A. Wankel, *ibid.*, 73, 2219 (1951).
(11) R. Adams and C. N. Winnick, *ibid.*, 73, 5687 (1951).
(12) R. Adams and J. M. Stewart, *ibid.*, 74, 5876 (1952).
(13) S. J. Cristol, F. R. Stermitz and P. S. Ramey, *ibid.*, 78, 4939 (1956).
(14) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 543–553.
(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956; (a) p. 183, (b) p. 85.

diaminoacenaphthene (XIV) with nitrous acid[16] again formed XII. A melting point of a mixture of the compound formed by treating the aminosulfonamide IV with nitrous acid, with subsequent decomposition, and the compound formed by treating 4,5-diaminoacenaphthene (XIV) with nitrous acid showed no depression.

4,5-Triazoloacenaphthene (XII) is soluble in base and can be recovered on acidification. Benzoylation of the triazole XII to form XIII was not successful.

A possible mechanism for the triazole formation involves reaction between the diazo group and the nitrogen atom of the sulfonamide. Subsequent attack by chloride ion effects removal of the benzenesulfonyl group.



XII

When a hydrochloric acid diazotizing mixture containing 4-amino-5-benzenesulfonamidoacenaphthene (IV) was decomposed, lachrymatory vapors resembling benzenesulfonyl chloride were detected. When the vapor was passed into a mixture of aniline and pyridine, benzenesulfonanilide was formed.

This result appears significant in view of the fact that the benzenesulfonamides were found to be resistant to acid and base hydrolysis, and that the benzoyl group is not displaced in the similar reaction involving 4-amino-5-benzamidoacenaphthene (X). Since the carbon atom is reported to be more electro-negative than sulfur,[17] the benzenesulfonyl group would be a better leaving group than the benzoyl group.

Experimental

4-Nitro-5-benzenesulfonamidoacenaphthene (II).—Thirteen grams (0.06 mole) of 4-nitro-5-aminoacenaphthene[3] (I) was dissolved in 100 ml. of dry pyridine, and 12.0 g. (0.0680 mole) of benzenesulfonyl chloride was added. The mixture was heated at reflux for 3 hours, after which the reaction mixture was poured into cold water. A heavy dark tar resulted, which was dissolved in acetone, filtered, and the solvent was allowed to evaporate. The dry black cake was powdered. Crystallization from xylene gave a yellow solid in poor yield. This product was heated in concentrated hydrochloric acid to dissolve unreacted amine and the residue was crystallized from glacial acetic acid, m.p. 212° dec.

Anal. Calcd. for $C_{18}H_{14}N_2O_4S$: N, 7.91. Found: N, 8.15.

4-Nitro-5-(N,N-dibenzenesulfonyl)-aminoacenaphthene.—Two grams (0.0093 mole) of I was dissolved in 40 ml. of dry pyridine. Benzenesulfonyl chloride (9.6 g., 0.055 mole) was added, and the mixture was heated at reflux for 2 hours. After cooling to room temperature, the solution was poured into a slurry of ice and concentrated hydrochloric acid. A brown tarry solid resulted, which was boiled in glacial acetic acid and filtered. There was obtained 2.4 g. (72%) of crude product which after three crystallizations from this solvent gave yellow crystals, m.p. 209–210°. A mixed melting point with 4-nitro-5-benzenesulfonamidoacenaphthene (II) showed a depression. Infrared analysis showed the absence of the N–H group.

Anal. Calcd. for $C_{24}H_{18}N_2O_6S_2$: N, 5.66. Found: N, 5.60.

5-Benzenesulfonamidoacenaphthene (III).—Dry pyridine (20 ml.) was used to dissolve 4.5 g. (0.027 mole) of 5-aminoacenaphthene and 5 ml. of benzenesulfonyl chloride was added slowly with stirring and cooling. The mixture was allowed to stand for 15 minutes, and then was poured into a slurry of ice and concentrated hydrochloric acid. A brown solid was formed which was collected and dried. Crystallization from glacial acetic acid resulted in a light tan product (6.37 g., 81%), m.p. 197–198° (lit.[18] 198–199°).

4-Nitro-5-benzenesulfonamidoacenaphthene (II) was best prepared by the nitration of 5-benzenesulfamidonaphthene (III). Two grams of III (0.0065 mole) was suspended in 30 ml. of glacial acetic acid. The mixture was cooled to 10°, and 1 ml. of nitric acid (d. 1.42) in 4 ml. of glacial acetic acid was added slowly with stirring. Stirring was continued for 15 minutes. The yellow product was collected and washed first with a solution of potassium carbonate and then with water (2 g., 87%). Crystallization from glacial acetic acid with decolorizing carbon gave bright yellow crystals, m.p. 213°.

Anal. Calcd. for $C_{18}H_{14}N_2O_4S$: N, 7.91. Found: N, 7.80.

A mixed melting point with the compound prepared from I and benzenesulfonyl chloride showed no depression, and the infrared spectra of the compounds prepared by the two methods were identical.

4-Amino-5-benzenesulfonamidoacenaphthene (IV).—Five grams (0.014 mole) of 4-nitro-5-benzenesulfonamidoacenaphthene (II) which had been recrystallized from methyl Cellosolve was placed in a Parr hydrogenator with 30 ml. of ethanol and 200 mg. of 10% palladium-on-charcoal. Hydrogen pressure of 3 atm. was applied for 2 hours with shaking. The color changed from bright yellow to gray. The mixture was poured into water, and the precipitated amine was collected and dried. Crystallization from 1-butanol yielded 3.2 g. (70%) of the amine, m.p. 187° dec. with darkening at 170°. In the crystallization from 1-butanol it is best to avoid a temperature above 60°. Ethanol or methyl Cellosolve may be used.

Anal. Calcd. for $C_{18}H_{16}N_2O_2S$: C, 66.64; H, 4.97. Found: C, 66.59; H, 5.10.

4,5-Dibenzenesulfonamidoacenaphthene (V). Method A.—Five grams (0.023 mole) of 4-nitro-5-aminoacenaphthene (I) purified by crystallization from thiophene-free benzene, was placed in a Parr hydrogenerator with 200 mg. of 10% palladium-on-charcoal and 25 ml. of thiophene-free benzene. This mixture was shaken with 3 atm. hydrogen pressure for 36 hours and then poured directly into a mixture of 15 ml. of benzenesulfonyl chloride and 15 ml. of dry pyridine. After standing for one hour, a brown solid separated. The crude yield was 6.0 g. (56%). Repeated crystallization from benzene yielded a light tan solid, m.p. 210–210.5° with sintering and darkening from 185°.

Anal. Calcd. for $C_{24}H_{20}N_2O_4S_2$: N, 6.03. Found: N, 5.76.

Method B.—Three grams (0.0093 mole) of 4-amino-5-benzenesulfonamidoacenaphthene (IV) was dissolved in 10 ml. of dry pyridine. Two grams (0.011 mole) of benzenesulfonyl chloride was added slowly with cooling. After 15 minutes, the mixture was poured into a slurry of ice and concentrated hydrochloric acid. A brown solid separated which was collected and dried. Crystallization from methyl Cellosolve gave a tan product, m.p. 210°, in 65% yield. A mixed melting point with the compound prepared by method A showed no depression. The infrared spectra of the compounds are identical. Method B was the preferred preparation.

4,5-Acenaphthenequinonedibenzenesulfonimide (VI).—A suspension of 5.9 g. (0.013 mole) of 4,5-dibenzenesulfonamidoacenaphthene (V) in 100 ml. of anhydrous ether was stirred while 7.5 g. (0.017 mole) of lead tetraacetate[19] was added.[5] The reaction was carried out at room temperature. After 5 minutes, the color had progressed through yellow, orange, and finally dark red. After 30 minutes 5 ml. of ethylene glycol was added, and stirring was continued for 10 minutes. The red product was collected and thoroughly washed with a dilute solution of sodium carbonate. The

(16) R. O. Roblin, Jr., J. O. Lampen, J. P. English, Q. P. Cole and J. R. Vaughan, Jr., THIS JOURNAL, **67**, 290 (1952).

(17) H. P. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1945).

(18) K. Fleischer and K. Schranz, *Ber.*, **55**, 3253 (1922).

(19) Courtesy of Arapahoe Chemicals, Inc., Boulder, Colo.

dried, crude product was dissolved in boiling benzene with decolorizing charcoal and filtered. A small amount of cyclohexane was added to the filtrate and the solution was allowed to stand. Very fine, dark red needles formed in a few minutes, which were collected and dried, m.p. 153–154°. The yield of pure product was 3.7 g. (63%).

Anal. Calcd. for $C_{24}H_{18}N_2O_4S_2$: N, 6.06. Found: N, 6.12.

The infrared spectrum of the quinone disulfonimide showed absorption at about 1534 cm.$^{-1}$, indicative of C=N (lit.[9] C=N, 1544 cm.$^{-1}$), and the absence of absorption at *ca.* 3240 cm.$^{-1}$ characteristic of N—H.[9]

Hydrogenation of 4,5-Acenaphthenequinonedibenzenesulfonimide.—A mixture comprising 0.5 g. (11 mmoles) of 4,5-acenaphthenequinonedibenzenesulfonimide (VI), 100 mg. of 10% palladium-on-charcoal and 20 ml. of thiophene-free benzene was placed in a Parr hydrogenator and pressured to 3 atm. with hydrogen. In 10 minutes the red color of the quinone diimide had disappeared. The benzene solution was filtered, and petroleum ether, b.p. 60–70°, was added, which caused a tan solid to separate. Crystallization from methyl Cellosolve yielded 4,5-dibenzenesulfonamidoacenaphthene, which did not depress the melting point of the dibenzenesulfonamide V.

4,5-Dibenzenesulfamidoacenaphthylene (VII). Method A.—One gram (0.002 mole) of 4,5-acenaphthenequinonedibenzenesulfonimide (VI) was suspended in 10 ml. of glacial acetic acid, and 3 ml. of concentrated hydrochloric acid was added. The red color of the suspended quinone disulfonimide was destroyed almost immediately, and a yellow solution resulted. The solution was diluted with water, and the precipitated solid was collected on a filter. This solid was dissolved in a minimum amount of dry pyridine with decolorizing charcoal and, after filtration, a few drops of water was added to the hot solution. Bright yellow crystals melting at 194–194.5° were obtained in 84% yield after three recrystallizations.

The yellow product absorbed bromine and gave a positive Baeyer test. The bromine adduct was collected and dried. However, any attempts to dissolve it, particularly on warming, resulted in tar formation. The compound showed absorption at 3260 cm.$^{-1}$ characteristic of N—H, and no absorption at 1544 cm.$^{-1}$ characteristic of C=N.[9]

Anal. Calcd. for $C_{24}H_{18}N_2O_4S_2$: C, 62.32; H, 3.92. Found: C, 62.22; H, 4.36.

Method B.—One-half gram (0.0011 mole) of VI was dissolved in 10 ml. of dry pyridine and the red solution warmed on a steam-bath for 30 minutes. The red color faded. Water was added to the warm solution to incipient cloudiness. The light orange solution, on standing, deposited yellow crystals which after one recrystallization from a pyridine–water mixture melted at 188–189° (0.42 g.). The melting point of a mixture of this product with that obtained on attempting to add hydrogen chloride to the diimide (m.p. 194–194.5°) was 191–192°. The infrared spectra of the two compounds were identical.

Hydrogenation of 4,5-Dibenzenesulfamidoacenaphthylene.—A Parr hydrogenator was charged with 0.25 g. of VII, 50 mg. of 10% palladium-on-charcoal and 20 ml. of ethanol. Hydrogen pressure of 3 atm. was applied for one hour. The yellow color disappeared, leaving a colorless ethanol solution which was filtered, and the solvent was allowed to evaporate. The tan solid which remained was crystallized from 1-butanol, m.p. 208°. A mixed melting point with 4,5-dibenzenesulfonamidoacenaphthene (V), m.p. 210°, was found to be 208–209°. The infrared spectra of V and the hydrogenated VII were identical.

Preparation of 4,5-Dibenzenesulfonamidoacenaphthylene (VII) from 4,5-Dibenzenesulfonamidoacenaphthene (V).—A few crystals of benzoyl peroxide was added to a mixture of 0.76 g. (0.0016 mole) of V and 0.29 g. (0.0016 mole) of N-bromosuccinimide[19] in 25 ml. of chlorobenzene. A red color developed almost immediately, and the mixture was shaken at room temperature for one hour. The solution was washed with warm water, and 1.0 g. of solid potassium hydroxide was added, with warming on the steam-bath for one hour. The excess potassium hydroxide was filtered off and petroleum ether, b.p. 60–70°, was added to the chlorobenzene solution. A yellow-brown precipitate formed which was collected and dried. It was chromatographed on alumina using a 50–50 mixture of petroleum ether and anhydrous ether as elution solvent. A yellow band separated on the column, and was removed mechanically and boiled in dry pyridine. The pyridine solution was filtered, a small amount of water added, and the solution was placed in a refrigerator at −15° for 4 hours. The small amount of yellow solid was collected on a filter, m.p. 191–192°. A mixture of this compound, and compound VII, m.p. 194–194.5°, melted at 192–193°. The infrared spectrum of this compound was identical to that of the compound prepared from 4,5-acenaphthenequinonedibenzenesulfonimide by the action of pyridine.

4-Nitro-5-benzamidoacenaphthene (IX). Method A.—A suspension of 1.3 g. (0.026 mole) of 5-benzamidoacenaphthene[20] (VIII) in 20 ml. of glacial acetic acid was cooled to 10°. Concentrated nitric acid (2 ml., d. 1.42) was added slowly with stirring. A gold colored solid soon separated, which was collected on a filter, and thoroughly washed with water and with a solution of potassium carbonate. Crystallization from glacial acetic acid gave a bright yellow product in 73% yield, m.p. 232.5–233.5° (lit.[20] 233°).

Method B.—One gram (0.0047 mole) of 4-nitro-5-aminoacenaphthene (I) in 10 ml. of dry pyridine was added slowly with stirring to a solution of 1.0 ml. of benzoyl chloride in 10 ml. of dry pyridine at room temperature. The mixture was refluxed for 2 hours, cooled, and the solution was poured into a slurry of ice and concentrated hydrochloric acid. A yellow solid precipitated which was collected and dried. Crystallization yielded 0.45 g. (51%) of yellow product, m.p. 233.5–234°. The melting point of a mixture of this compound and that prepared by method A showed no depression.

4-Amino-5-benzamidoacenaphthene (X).—Twenty grams (0.063 mole) of 4-nitro-5-benzamidoacenaphthene (IX), which had been purified by crystallization from methyl Cellosolve, was placed in a Parr hydrogenator with 300 mg. of 10% palladium-on-charcoal and 75 ml. of ethanol. Hydrogen pressure of 3 atm. was applied, and the mixture was shaken for 4 hours. The yellow color of the nitro compound faded, and a gray solid separated. The alcohol suspension was diluted with water, and the separated amine was collected on a filter and dried. The crude yield was quantitative. Crystallization from methyl Cellosolve gave yellow needles, m.p. 270–272°.

Anal. Calcd. for $C_{19}H_{16}N_2O$: C, 79.14; H, 5.59. Found: C, 79.04; H, 5.26.

4,5-Dibenzamidoacenaphthene (XI).—Benzoyl chloride (10 ml.) was added slowly with stirring to a suspension of 5.13 g. (0.018 mole) of 4-amino-5-benzamidoacenaphthene (X) in 80 ml. of 10% sodium hydroxide solution. An additional 5 ml. of benzoyl chloride was put in during the 0.5-hour reaction time. The mixture was cooled, diluted with water and ice, and the brown solid which separated was collected and dried. Crystallization from a pyridine–water mixture gave 5.0 g. (71%) of light tan crystals, m.p. 283–285° (block).

Anal. Calcd. for $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.14; N, 7.14. Found: C, 79.86; H, 5.65; N, 7.25.

4,5-Triazoloacenaphthene (XII).—A mixture of 2.44 g. (0.0075 mole) of 4-amino-5-benzenesulfonamidoacenaphthene (IV) in 25 ml. of warm concentrated hydrochloric acid was cooled in an ice–salt-bath to 0°, and 0.6 g. (0.0087 mole) of sodium nitrite in 15 ml. of cold water was added slowly with stirring. After 15 minutes the excess nitrous acid was destroyed by the addition of 0.5 g. of urea with stirring for 5 minutes. The mixture then was decomposed by passing the solution through a steam line where the color changed from yellow to dark brown. The collected suspension was warmed on the steam-bath for 20 minutes and, after cooling, the solid was collected on a filter and dried. Repeated crystallization from glacial acetic acid with decolorizing charcoal yielded 1.1 g. (75%) of a tan solid which melted at 285–287° (block), with sublimation.

Anal. Calcd. for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.53. Found: C, 74.09; H, 4.56; N, 21.58.

In a subsequent run, the vapors from the decomposition were passed through a solution of 1 g. of aniline hydrochloride in 10 ml. of dry pyridine. The pyridine solution was treated with 10 ml. of concentrated hydrochloric acid, and diluted to 100 ml. with water. On standing overnight, a gray powdery solid formed which was crystallized from cyclohexane, m.p. 109°. A mixed melting point with an authentic sample of benzenesulfonanilide (m.p. 109–109.5°) showed no depression.

(20) F. Quincke, *Ber.*, **21**, 1454 (1888).

4,5-Triazoloacenaphthene (XII) from 4,5-Diaminoacenaphthene.—4-Nitro-5-aminoacenaphthene (I) (1.1 g., 0.005 mole) purified by crystallization from methyl Cellosolve was reduced in a Parr hydrogenator with the aid of 300 mg. of platinum oxide in 20 ml. of ethanol. The ethanol solution was filtered and diluted with water. Fine tan needles of 4,5-diaminoacenaphthene were formed. This diamine, because of its instability, was collected on a filter and quickly dissolved in glacial acetic acid, and 5 g. of sodium nitrite was added all at once. The mixture, which became green in color, was warmed to 80° on the steam-bath and then diluted with water. A brown solid separated which was collected and dried. Crystallization from glacial acetic acid with the aid of decolorizing charcoal gave a tan product which when mixed with the product of the decomposition of the diazonium salt of 4-amino-5-benzenesulfonamidoacenaphthene (IV), gave no depression of the melting point. The infrared spectra were identical.

4,5-(1-Benzoyltriazolo)-acenaphthene (XIII).—Two grams (0.007 mole) of 4-amino-5-benzamidoacenaphthene (X) was suspended in 25 ml. of concentrated hydrochloric acid and warmed. The amine hydrochloride was only partially soluble in concentrated hydrochloric acid. The mixture was cooled to 0°, and 1.0 g. (0.015 mole) of sodium nitrite was added, with subsequent stirring for 30 minutes. The excess nitrous acid was destroyed by the addition of 2 g. of urea with stirring for 10 minutes. The mixture was decomposed by passing the solution through a steam line. A brown solid 1.2 g. (58%) was collected and crystallized from ethanol, m.p. 159.5–160.5°. The infrared spectrum showed no hydroxy absorption at 3500–3700 cm.$^{-1}$,[15b] but did show carbonyl absorption at 1710 cm.$^{-1}$.[15a] This compound was insoluble in 10% sodium hydroxide solution.

Anal. Calcd. for $C_{19}H_{13}N_3O$: N, 14.04. Found: N, 13.85.

Hydrolysis of 4,5-(1-Benzoyltriazolo)-acenaphthene (XIII).—One-half gram (0.0017 mole) of the benzoyltriazole XIII was suspended in a mixture of 10 ml. of ethanol and 10 ml. of 50% sulfuric acid. The mixture was maintained at reflux temperature for 14 hours. During the first part of the reaction a strong odor of ethyl benzoate was noted, and later the odor of diethyl ether was detected. The reaction mixture was cooled to room temperature and the solvent removed under vacuum. The odor of ethyl benzoate was again noted. The residue was treated with 20 ml. of 10% sodium hydroxide solution and warmed for 0.5 hour on the steam-bath, cooled, and acidified with dilute hydrochloric acid. A white solid separated, m.p. 280° (block). Crystallization from glacial acetic acid gave a tan product which when mixed with 4,5-triazoloacenaphthene (XII) showed no depression in melting point. The infrared spectra of the two compounds were identical.

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[CONTRIBUTION FROM THE WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides. VIII. The Mechanism of the Reaction of Tetrachloroethylene with *p*-Toluenethiolate Reagent[1]

BY WILLIAM E. TRUCE AND RUDOLPH KASSINGER

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Sodium *p*-toluenethiolate reacts with tetrachloroethylene (I) in refluxing ethanol to give *cis*-1,2-dichloro-1,2-di-(*p*-tolylmercapto)-ethene (V); the intermediate 1-(*p*-tolylmercapto)-1,2,2-trichloroethane may be isolated. Under forcing conditions, tetra-(*p*-tolylmercapto)-ethene is obtained. Mechanistic interpretations, based on concepts developed with di- and trichloroethylenes, are discussed.

The mechanisms of the reactions of thiolate reagents with 1,2-dichloroethylenes,[2] vinylidene chloride[3] and trichloroethylene[4a] were reported in recent papers.[4b] These studies have now been extended to the last compound in this series, tetrachloroethylene.

Although the reaction of tetrachloroethylene with thiolates has been known for some time,[5] its stereochemical and mechanistic course was unknown. It was observed in this Laboratory that tetrachloroethylene undergoes a stereospecific reaction with sodium *p*-toluenethiolate, the product being *cis*-1,2-dichloro-1,2-di-(*p*-tolylmercapto)-ethene. Previously we had demonstrated that the reaction of vinylidine chloride with sodium *p*-toluenethiolate proceeded by an initial addition,[3] whereas with *cis*-dichloroethylene[2] and trichloroethylene,[4a] initial dehydrohalogenation occurred.[6] Since tetrachloroethylene is incapable of dehydrohalogenation, the initial step in the reaction with thiolate reagent must be nucleophilic "addition" forming either an incipient carbanion (IIa) or a saturated intermediate (IIb), which produces 1-(*p*-tolylmercapto)-1,2,2-trichloroethene (III) by loss of Cl^- or HCl, respectively. By a repetition of this sequence of steps, further treatment with alcoholic sodium *p*-toluenethiolate produces the product, *cis*-1,2-dichloro-1,2-di-(*p*-tolylmercapto)-ethene (V) as outlined.

$$\underset{\text{I}}{ArSNa} + Cl_2C{=}CCl_2 \longrightarrow \underset{\text{IIa}}{[ArSCCl_2\overset{\ominus}{C}Cl_2]} \text{ or}$$

$$\underset{\text{IIb}}{ArSCCl_2CHCl_2} \xrightarrow[\text{or } -HCl]{-Cl^-} \underset{\text{III}}{ArSCCl{=}CCl_2} \xrightarrow{ArSNa}$$

$$\underset{\text{IVa}}{[ArSCClCCl_2SAr\ominus]} \text{ or } \underset{\text{IVb}}{ArSCHClCCl_2SAr} \xrightarrow[\text{or } -HCl]{-Cl^-}$$

$$\textit{cis}\text{-}ArSCCl{=}CClSAr \xrightarrow[ArSNa]{\text{sealed tube}} \underset{\text{V}}{(ArS)_2C{=}C(SAr)_2}$$

(1) For preceding paper see ref. 4a. Taken from Mr. Kassinger's Ph.D. thesis.

(2) W. E. Truce, M. M. Boudakian, R. F. Heine and R. J. McManimie, THIS JOURNAL, **78**, 2743 (1956).

(3) W. E. Truce and M. M. Boudakian, *ibid.*, **78**, 2748 (1956).

(4) (a) W. E. Truce and R. Kassinger, *ibid.*, **80**, 1916 (1958). (b) Furthermore, in the formation of vinyl *p*-tolyl sulfide from vinyl chloride and sodium *p*-toluenethiolate [Truce, Hill and Boudakian, *ibid.*, **78**, 2760 (1956)], an elimination-addition mechanism is suggested for at least part of the reaction product by the facts that (1) the strong base, sodium ethoxide, has an accelerating influence, (2) the presence of acetylene in the reaction mixture was noted and (3) acetylene is known to react with thiolate reagent under similar conditions to form the vinyl sulfide.

(5) N. W. Cusa and H. McCombie, *J. Chem. Soc.*, 767 (1937).

(6) For a further discussion of some of the factors determining whether initial elimination or nucleophilic "addition" occurs in such over-all displacements see paper VII of this series (ref. 4).