[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA]

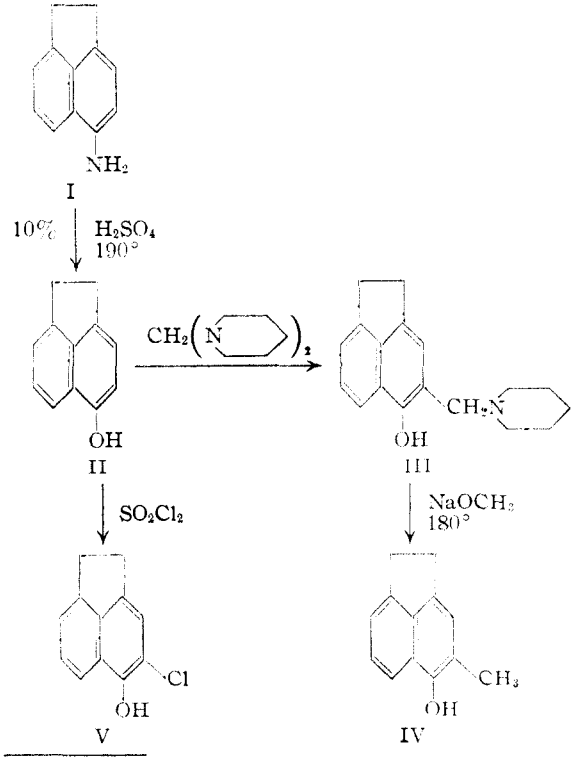
The Preparation of Some Acenaphthoxyacetic Acids

BY HENRY RAPOPORT, TE PIAO KING AND JOE B. LAVIGNE

Oxyacetic acid derivatives of 5-acenaphthenol, 4-methyl-5-acenaphthenol and 4-chloro-5-acenaphthenol have been prepared. Hydrolysis of 5-aminoacenaphthene was used to prepare 5-acenaphthenol which was then converted to the 4-methyl analog through the piperidinomethyl compound. Chlorination of 5-acenaphthenol gave 4-chloro-5-acenaphthenol in which the position of the chlorine was established by an unambiguous synthesis of the methyl ether. Cleavage of this methyl ether (4-chloro-5-methoxyacenaphthene) to the phenol was accompanied by elimination of the chlorine atom.

Recent discovery of the selective herbicidal action of some aryloxyacetic acids[1] has stimulated considerable interest in this type of compound. Our efforts have been directed toward the synthesis of several acenaphthoxyacetic acids since no oxyacetic acid containing the acenaphthene nucleus has heretofore been reported. Such compounds might be of interest as they have the combined structural characteristics of aryloxyacetic acid, used as herbicides, and acenaphthene, used to induce polyploidy. The synthesis of 5-acenaphthoxyacetic acid, 4-methyl-5-acenaphthoxyacetic acid, and 4-chloro-5-acenaphthoxyacetic acid is presented in this report.

5-Acenaphthenol (II) was the key intermediate for the various syntheses and it was readily prepared through the 5-nitro and 5-amino compound. Nitration of acenaphthene gave the well-established 5-nitro compound which was best reduced to 5-aminoacenaphthene by catalytic hydrogenation. Hydrolysis with 10% sulfuric acid at 190°, as suggested by a German patent,[2] converted the amino compound to 5-acenaphthenol.



To prepare the 4-methyl analog, 5-acenaphthenol was first condensed with methylene-bis-piperidine following the general method of Feldman and Wagner[3] and the 4-piperidinomethyl-5-acenaphthol (III) was reduced to 4-methyl-5-acenaphthenol (IV) by heating with sodium methoxide.[4] Since the 4-position is the only ortho–para position available, it was assigned to the entering group, and this structure was confirmed by the lack of coupling between 4-methyl-5-acenaphthenol and diazotized sulfanilic acid.

Chlorination of 5-acenaphthenol with sulfuryl chloride proceeded easily and, since the 4-position is apparently the most receptive to further substitution, 4-chloro-5-acenaphthenol (V) was assigned as the structure of the chlorination product. However, acenaphthene itself is chlorinated under comparable conditions and therefore more definitive evidence was sought for the position taken by the entering chlorine atom.

At first, it was thought that coupling experiments with diazotized *p*-nitroaniline might provide the desired proof of orientation since the analogous reaction with 1-halogeno-2-naphthols apparently proceeds with ejection of the halogen atom.[5] However, later work[6] established that the primary reaction product was a halogen-containing O-azo-compound which, on repeated crystallization, rearranged with displacement of halogen to 1-(*p*-nitrobenzeneazo)-2-naphthol. Also, Joffe[7] has shown that the yield of final halogen-free material may be improved if coupling is carried out in the presence of thiosulfate.

When the chloroacenaphthenol was treated with diazotized *p*-nitroaniline, the product still contained about 30% of the original chlorine, and similar chlorine-containing material was obtained when the reaction took place in the presence of thiosulfate. Although a chlorine-free azo compound conceivably might have resulted after repeated crystallization, the isolation of such a compound in moderate or poor yield would be of doubtful structural significance. A mixture of isomeric chloroacenaphthenols, for example, might lead to such a result through elimination, by repeated crystallization, of the isomer in which the chlorine was at other than the 4-position.

An independent synthesis of 4-chloro-5-acenaphthenol was then attempted from material in which

(1) D. E. H. Frear, "Chemistry of Insecticides, Fungicides, and Herbicides," D. Van Nostrand Company, Inc., New York, N. Y., 1948, p. 315.

(2) German Patent 517,264; *Friedl.*, **17**, 669 (1932).

(3) J. R. Feldman and E. C. Wagner, *J. Org. Chem.*, **7**, 31 (1942).

(4) J. W. Cornforth, R. H. Cornforth and R. Robinson, *J. Chem. Soc.*, 682 (1942).

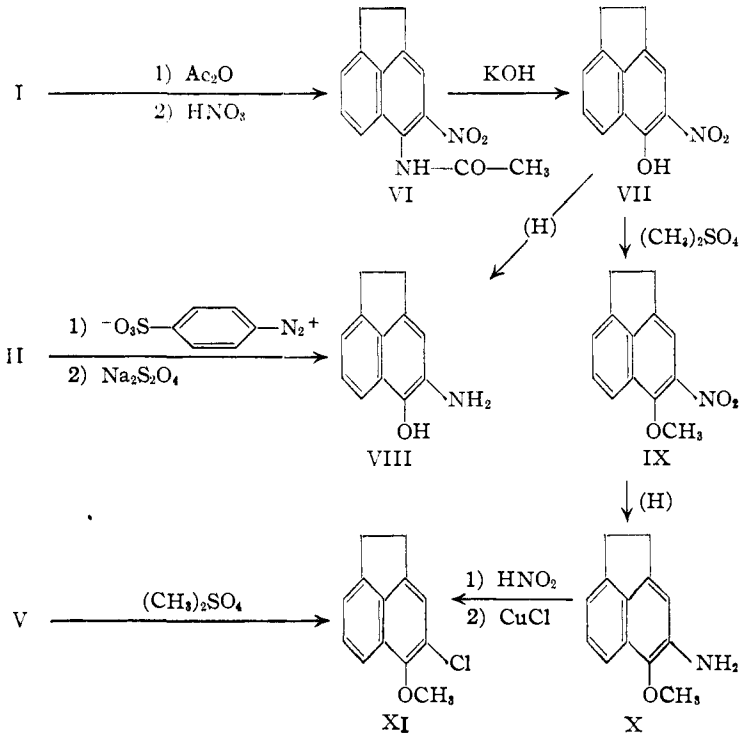
(5) K. H. Saunders, "The Aromatic Diazo Compounds," Longmans, Green and Co., London, 1949, p. 221.

(6) J. Pollak and E. Gebauer-Fülnegg, *Monatsh.*, **50**, 310 (1928).

(7) I. S. Joffe, *J. Gen. Chem. (U. S. S. R.)*, **6**, 1074 (1936); **7**, 2637 (1937).

the 4,5-orientation has been established beyond question. A suitable starting compound was 4-nitro-5-acetaminoacenaphthene (VI) prepared by Sachs and Mosebach[8] from 5-nitroacenaphthene and shown to have the 4,5-orientation by conversion to a diamine which, with phenanthrenequinone, formed a quinoxaline, a reaction given only by *o*-diamines. Confirmation for this structural assignment has been obtained by hydrolysis of VI to 4-nitro-5-acenaphthenol (VII) and reduction of the latter to 4-amino-5-acenaphthenol (VIII), identical with the compound resulting from coupling of 5-acenaphthenol with diazotized sulfanilic acid followed by reduction of the azo compound.

The synthesis of the 4-chloro compound then proceeded from 4-nitro-5-acenaphthenol (VII) to the methyl ether (IX), followed by reduction of IX to 4-amino-5-methoxyacenaphthene (X). Analysis of the extent of diazotization at various temperatures by titration of the diazonium salt solution with titanium trichloride[9] indicated that diazotization should be carried out at 15–16°.



The diazonium salt solution thus prepared was treated with cuprous chloride to form 4-chloro-5-methoxyacenaphthene (XI), identical with the compound obtained by methylation of the chlorination product of 5-acenaphthenol.

Attempts to cleave this ether and make a further comparison through the chlorophenols led to a very unexpected result. With 48% aqueous hydrobromic acid in glacial acetic acid, the only product isolable was 5-acenaphthenol (in 6.5% yield). When pyridine hydrochloride was used as the cleaving agent, 5-acenaphthenol was again the only isolable product (in 30% yield). Since analytically pure 4-chloro-5-methoxyacenaphthene was used as starting material, the reaction must have been accompanied by elimination of the *o*-chlorine atom, a result for which we have no explanation.

The acenaphthoxyacetic acids were prepared from the corresponding acenaphthenols by the various procedures given in the literature. In the cases of the more hindered compounds, 4-methyl and 4-chloro-5-acenaphthenol (IV and V), the more vigorous methods were necessary and the yields were lower.

Experimental[10]

5-Aminoacenaphthene (I).—A 15% solution of 5-nitroacenaphthene[11] in absolute ethanol was hydrogenated using 1% of platinum oxide[12] as catalyst to give a 77% of 5-aminoacenaphthene, m.p. 104–107° (reported m.p. 107°,[13] 108–109[12]).

5-Acenaphthenol (II).—A mixture of 16.9 g. (0.1 mole) of 5-aminoacenaphthene, 100 ml. of water, and 11 g. of concd. sulfuric acid was heated in a sealed tube at 190° for eight hours with shaking. After cooling, the reaction mixture was filtered and the precipitate was warmed with 300 ml. of 1 *N* sodium hydroxide for several minutes. Filter aid was added, the solution was filtered, and the filtrate was acidified. The crude 5-acenaphthenol (12.3 g., 73%) which precipitated was further purified by distillation (b.p. 155–165° (3–4 mm.) and crystallization from a mixture of 20 ml. of glacial acetic acid and 20 ml. of water to give 9.7 g. (57%) of material, m.p. 125–126° (reported[2] m.p. 126°).

Anal. Calcd. for $C_{12}H_{10}O$: C, 84.7; H, 5.9. Found: C, 84.7; H, 5.9.

The **α-naphthylurethan** was prepared following the procedure of French and Wirtel[14] using triethylamine in ether as a catalyst. The material removed by exhaustive extraction of the original precipitate with ligroin (b.p. 90–120°) was crystallized several times from carbon tetrachloride, m.p. 187–188°.

Anal. Calcd. for $C_{23}H_{17}O_2N$: C, 81.4; H, 5.1; N, 4.1. Found: C, 80.7; H, 5.1; N, 4.6.

5-Acenaphthoxyacetic Acid.—The general method of McElvain[15] was used except for the heating period which was extended to sixteen hours. From 8.5 g. (0.05 mole) of 5-acenaphthenol there resulted 7.4 g. (62%) of 5-acenaphthoxyacetic acid which could be further purified by crystallization from ethanol and sublimation at 160° (0.1 mm.). The pure material melted at 190–192°.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3; eq. wt., 228. Found: C, 73.6; H, 5.5; eq. wt., 228.

4-Piperidinomethyl-5-acenaphthenol (III).—To a solution of 23.8 g. (0.14 mole) of 5-acenaphthenol in 140 ml. of absolute ethanol was added 25.8 g. (0.14 mole) of methylene-bis-piperidine[16] and the solution was allowed to stand at room temperature for twenty hours. Cooling in an ice-

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

(9) E. Knecht and E. Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., London, 1925, p. 33.

(10) All melting points are corrected and those above 200° were taken in evacuated capillaries; microanalyses were performed by the Microchemical Laboratory, University of California.

(11) C. Graebe, *Ann.*, **327**, 77 (1903).

(12) Catalytic hydrogenation has previously been used on a 1% alcoholic solution of the nitro compound with platinum black at atmospheric pressure by V. M. Rodionov and A. Mel'nik, *C. A.*, **36**, 1923[9] (1942). The original article, *Nauch. Issledovatel. Trudy Moskov. Tekstil. Inst.*, **8**, No. 1, 90 (1939), was unavailable to us.

(13) F. M. Hamer, *J. Chem. Soc.*, 995 (1930).

(14) H. E. French and A. F. Wirtel, THIS JOURNAL, **48**, 1736 (1926).

(15) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 247.

(16) E. Knoevenagel, *Ber.*, **31**, 2585 (1898).

methanol bath (−20°) followed by filtration gave 35 g. (94%) of the piperidinomethyl compound, m.p. 74–77°. For analysis, a sample was crystallized several times from ethanol and sublimed at 70° (0–1 mm.), m.p. 76–77°.

Anal. Calcd. for $C_{18}H_{21}ON$: C, 80.9; H, 7.9; N, 5.2. Found: C, 81.2; H, 7.6; N, 5.4.

4-Methyl-5-acenaphthenol (IV).—4-Piperidinomethyl-5-acenaphthenol (10 g., 0.038 mole) was heated at 180° for five hours with 24.2 g. (0.45 mole) of sodium methoxide in 120 ml. of methanol. Most of the methanol was then removed under reduced pressure and the residue was diluted with water to 700 ml. and cooled in an ice-bath. The precipitate which formed on acidification was distilled (b.p. 150–160° (2–3 mm.)) to give 3.4 g. (49% yield) of solid distillate. After crystallization from aqueous methanol and sublimation at 80° (0.1 mm.), the 4-methyl-5-acenaphthenol melted at 98–99°.

Anal. Calcd. for $C_{13}H_{12}O$: C, 84.7; H, 6.6. Found: C, 84.3; H, 6.7.

With diazotized sulfanilic acid and a weakly alkaline solution of 4-methyl-5-acenaphthenol, no observable coupling took place.

The **α-naphthylurethan**, prepared as above, was purified by several crystallizations from chloroform, m.p. 208–210°.

Anal. Calcd. for $C_{24}H_{19}O_2N$: C, 81.6; H, 5.4. Found: C, 81.6; H, 5.3.

4-Methyl-5-acenaphthoxyacetic Acid.—Using the procedure of Steinkopf and Höpner,[17] 2 g. (0.011 mole) of 4-methyl-5-acenaphthenol was converted to the acenaphthoxyacetic acid in 27% yield, b.p. 210–215° (1 mm.), m.p. 128–130° after crystallization from ligroin (b.p. 60–90°).

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.4; H, 5.8; eq. wt., 242. Found: C, 73.9; H, 5.9; eq. wt., 240.

4-Chloro-5-acenaphthenol (V).—A solution of sulfuryl chloride (7.94 g., 0.059 mole) in 12 ml. of chloroform was added with stirring to a solution of 5-acenaphthenol (10 g., 0.059 mole) in 40 ml. of chloroform at 0° over a period of twenty minutes. Stirring was continued for twelve hours as the reaction mixture (and bath) reached room temperature, and it was then poured into 250 ml. of chloroform and 100 ml. of water. The chloroform layer was washed with half-saturated sodium bicarbonate solution and then twice with water. Evaporation of the chloroform left a residue which was distilled, b.p. 142–148° (1–2 mm.), and the distillate was crystallized from aqueous acetic acid to give 5.8 g. (48%) of 4-chloro-5-acenaphthenol, m.p. 61–62°.

Anal. Calcd. for $C_{12}H_9ClO$: C, 70.4; H, 4.4; Cl, 17.3. Found: C, 70.6; H, 4.5; Cl, 17.3.

The **α-naphthylurethan** was prepared as described above and purified by crystallization from chloroform, m.p. 202–205° with decomposition.

Anal. Calcd. for $C_{23}H_{16}ClNO_2$: C, 73.9; H, 4.3; Cl, 9.5. Found: C, 74.0; H, 4.5; Cl, 9.4.

4-Chloro-5-acenaphthoxyacetic Acid.—The method of Hansch and Crosby[18] was used to prepare this acenaphthoxyacetic acid in 21% yield except that potassium hydroxide was substituted for sodium hydroxide due to the very slight solubility of the sodium salt. Crystallization from 50% aqueous ethanol gave material melting at 168–170°.

Anal. Calcd. for $C_{14}H_{11}ClO_3$: C, 64.0; H, 4.2; Cl, 13.5; eq. wt., 263. Found: C, 64.0; H, 4.4; Cl, 13.6; eq. wt., 264.

Coupling of Diazotized *p*-Nitroaniline with 4-Chloro-5-acenaphthenol (V).—To a solution of 4-chloro-5-acenaphthenol (0.41 g., 2 millimoles) in 5 ml. of 0.5 *N* sodium hydroxide containing 1 g. of crystalline sodium acetate and just neutralized by the addition of acetic acid was added the diazonium solution prepared from *p*-nitroaniline (0.28 g., 2 millimoles), sulfuric acid, and sodium nitrite. An immediate dark red-brown precipitate formed which was digested thoroughly with water and dried.

Anal. Calcd. for $C_{18}H_{12}ClN_3O_3$: Cl, 10.0. Found: Cl, 3.2.

When the above coupling was carried out in the presence of sodium thiosulfate, similar chlorine-containing material was obtained.

(17) W. Steinkopf and T. Höpner, *J. prakt. Chem.*, **113**, 137 (1926).

(18) C. Hansch and D. G. Crosby, THIS JOURNAL, **71**, 3851 (1949).

4-Amino-5-acenaphthenol (VIII). A. From 5-Acenaphthenol (II).—To a cold solution of 8.5 g. (0.05 mole) of 5-acenapthenol in 40 ml. of 0.25 *N* sodium hydroxide was added with stirring the suspension of diazotized sulfanilic acid prepared from 9.5 g. (0.05 mole) of sulfanilic acid monohydrate. After one hour, 10 g. of sodium chloride was added and after an additional hour at room temperature, the mixture was placed in the cold overnight. The crude sodium salt of the coupling product thus obtained was reduced with sodium hydrosulfite and the product was isolated as the hydrochloride according to the procedure of Fieser.[19] Crystallization from dilute aqueous hydrochloric acid in the presence of sodium hydrosulfite gave 5.5 g. (50%) of 4-amino-5-acenaphthenol hydrochloride, m.p. 275–278°.

Anal. Calcd. for $C_{12}H_{12}ClNO$: C, 65.0; H, 5.5. Found: C, 65.4; H, 5.6.

The **N-acetyl derivative** was prepared by adding 1 ml. of acetic anhydride and 1.5 g. of crystalline sodium acetate (in 20 ml. of water) to a solution of 0.55 g. of the hydrochloride in 40 ml. of water at 0°. The resulting precipitate was crystallized several times from aqueous methanol, m.p. 162–164°.

Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 74.0; H, 5.8; N, 6.2. Found: C, 74.0; H, 6.0; N, 6.0.

B. From 4-Nitro-5-acenaphthenol (VII).—4-Nitro-5-acenaphthenol[8] was hydrogenated to the amino compound as described above for the reduction of 5-nitroacenaphthene except that a hydrogen pressure of 35 p.s.i. was used. After filtration of the catalyst, 1 *N* hydrochloric acid was added, the solution was evaporated to dryness, and the residue was crystallized from dilute hydrochloric acid. The 4-amino-5-acenaphthenol hydrochloride thus obtained melted at the same temperature as the material from 5-acenaphthenol (above) and gave no depression in melting point on mixing.

The **N-acetyl derivative** was prepared exactly as above and proved to be identical (melting point and mixed melting point) with the material from 5-acenaphthenol.

4-Nitro-5-methoxyacenaphthene (IX).—Ullmann's[20] procedure for methylating difficultly etherified phenols was used. A mixture of 44.2 g. (0.175 mole) of the potassium salt of 4-nitro-5-acenaphthenol, 50 ml. (0.53 mole) of dimethyl sulfate, and 360 ml. of toluene was heated under reflux with stirring in a nitrogen atmosphere for two hours. After adding 450 ml. of 3 *N* potassium hydroxide solution, the mixture was filtered and 15.0 g. of unreacted potassium salt was recovered. The organic phase of the filtrate was washed with water and the toluene evaporated to leave a residue which was crystallized from methanol using decolorizing carbon. On the basis of unrecovered potassium salt, the yield was 89%, 23.3 g. After several recrystallizations from methanol, the 4-nitro-5-methoxyacenaphthene melted at 69–70°.

Anal. Calcd. for $C_{13}H_{11}NO_3$: OCH_3, 13.5. Found: OCH_3, 13.9.

4-Amino-5-methoxyacenaphthene (X).—Hydrogenation of 4-nitro-5-methoxyacenaphthene was carried out exactly as in the reduction of the phenol (VII) above, and the 4-amino-5-methoxyacenaphthene was isolated as the hydrochloride in the same manner. The yield was 8 g. (85%) and the melting point was 228–230° (with decomposition) after several recrystallizations from 3 *N* hydrochloric acid.

Anal. Calcd. for $C_{13}H_{14}ClNO$: C, 66.2; H, 6.0; Cl, 15.0. Found: C, 66.1; H, 6.1; Cl, 15.2.

The **acetyl derivative** was prepared by adding acetic anhydride to an aqueous solution of the hydrochloride. The resulting precipitate was crystallized from ethanol, m.p. 164–166°.

Anal. Calcd. for $C_{15}H_{15}NO_2$: C, 74.7; H, 6.3; N, 5.8. Found: C, 74.5; H, 6.3; N, 6.1.

4-Chloro-5-methoxyacenaphthene (XI). A. From 4-Amino-5-methoxyacenaphthene (X).—To a mixture of 30.3 g. (0.13 mole) of 4-amino-5-methoxyacenaphthene hydrochloride, 500 ml. of 1 *N* hydrochloric acid, and 1300 ml. of water maintained at 15–16° was added, with stirring, a solution of 9.03 g. (0.13 mole) of sodium nitrite in 90 ml. of water over a period of twenty minutes. After the addition, the solution was stirred at that temperature for fifteen

(19) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, New York, N. Y., 1941, p. 230.

(20) F. Ullmann, *Ann.*, **327**, 104 (1903).

minutes, and a pinch of urea was added to destroy any excess nitrous acid. This solution of the diazonium salt was added with stirring to a cold solution of 12.8 g. (0.13 mole) of freshly prepared cuprous chloride in 120 ml. of concentrated hydrochloric acid, and the resulting mixture was stirred until it reached room temperature and then warmed on a steam-bath for fifteen minutes. It was extracted with three 500-ml. portions of benzene, and the benzene extracts were washed with water, with several portions of 0.25 *N* sodium hydroxide solution, and again with water. The benzene was evaporated and the residue distilled (b.p. 130–150° (1–2 mm.)) to give 14.2 g. (50% yield) of crude 4-chloro-5-methoxyacenaphthene. After several crystallizations from methanol, material melting at 84–86° was obtained.

Anal. Calcd. for $C_{13}H_{11}ClO$: OCH_3, 14.2; Cl, 16.2. Found: OCH_3, 14.0; Cl, 16.1.

B. **From 4-Chloro-5-acenaphthenol (V).**—A solution of 2.05 g. (0.01 mole) of 4-chloro-5-acenaphthenol and 0.6 g. of sodium hydroxide in 25 ml. of water was treated with dimethyl sulfate at 80° in an atmosphere of nitrogen. A total of 2.86 g. (0.0227 mole) of dimethyl sulfate was added in 1.52, 0.67, and 0.67 g. portions at ten-minute intervals, interspersed with the addition of three 2-ml. portions of 2.5 *N* sodium hydroxide. After an additional twenty minutes at 80°, the reaction mixture was extracted with benzene, and the benzene was washed with water and evaporated. Distillation of the residue gave 1.2 g. (55%) of solid material that melted at 84–86° after crystallization from methanol. A mixed melting point determination with authentic 4-chloro-5-methoxyacenaphthene prepared above showed no depression.

Ether Cleavage of 4-Chloro-5-methoxyacenaphthene (XI).—A mixture of 1 g. of XI, 8 ml. of glacial acetic acid, and 4 ml. of 48% hydrobromic acid was heated under reflux in a nitrogen atmosphere for four hours. It was then poured into 25 ml. of water and extracted with three 25-ml. portions of chloroform. The chloroform extracts were washed with three 25-ml. portions of 0.5 *N* sodium hydroxide and, after acidification, the combined aqueous extracts were re-extracted with three 25-ml. portions of chloroform. After washing with sodium bicarbonate solution and drying, the chloroform was evaporated and the residue sublimed at 80° (0.05 mm.). The sublimate was 5-acenaphthenol (50 mg., 6.5% yield), m.p. 125–126°, no depression on admixture with an authentic sample.

When 1 g. of 4-chloro-5-methoxyacenaphthene was heated with 3 g. of pyridine hydrochloride according to the procedure by Prey,[21] the reaction product, isolated as above, consisted of 230 mg. (30%) of 5-acenaphthenol, m.p. 125–126°.

(21) V. Prey, *Ber.*, **74**, 1219 (1941).

BERKELEY, CALIFORNIA RECEIVED NOVEMBER 4, 1950

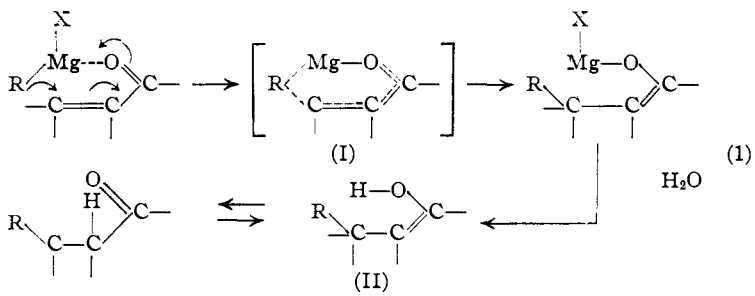
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Studies on the Mechanism of Conjugate Addition. I. The Addition of Grignard Reagents to 2-Cyclohexenone and Some Open Chain Analogs

BY ELLIOT R. ALEXANDER[1] AND GEORGE R. CORAOR

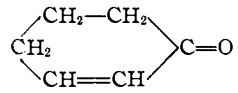
A comparison has been made of the conjugate addition of ethyl, isopropyl and *t*-butyl Grignard reagents to 2-cyclohexenone and its open chain analogs, 3-penten-2-one, 3-hexen-2-one, 3-hepten-2-one and 4-hexen-3-one. Except for the addition of ethylmagnesium bromide, the amount of conjugate addition to 2-cyclohexenone is comparable to the amount of conjugate addition to its open chain analogs. These results suggest that a possible path of reaction involving a cyclic intramolecular transition state is relatively unimportant.

One of the most attractive mechanisms which has been proposed for the conjugate addition of Grignard reagents to α,β-unsaturated ketones[2] involves an intramolecular cyclic transition state (I). It can account for the initial formation of an enol (II) which has been observed in some instances[3] and since lithium alkyls probably do not coördinate



(I) (1) H_2O (II)

as readily as Grignard reagents, it provides an explanation for the fact that organolithium reagents give more 1,2-addition than Grignard reagents.[4] It is clear, however, that the cyclic, intramolecular process cannot be the only route leading to conjugate addition, for it has been reported that 2-cyclohexenone (III) undergoes conjugate addition



(III)

with Grignard reagents[5] yet the distance between the carbonyl oxygen and the β-carbon atom of this compound appears to be too great to permit the formation of a complex such as I. Accordingly it seemed desirable to compare under conditions as nearly standardized as possible, the addition of Grignard reagents to cyclohexenone and its open chain analogs in order to get a measure of the possible importance of an intramolecular cyclic mechanism in conjugate addition. This paper describes the addition of ethyl, isopropyl and *t*-butyl Grignard reagents to 2-cyclohexenone (III), 3-penten-2-one (IV), 3-hexen-2-one (V), 3-hepten-2-one (VI) and 4-hexen-3-one (VII).

Experimental[6]

2-Cyclohexenone.—This compound was prepared by the thermal dehydration of 2-hydroxycyclohexanone.[7] In a representative run 180 g. (1.6 moles) of 2-hydroxycyclo-

(1) Deceased October 23, 1950.
(2) R. E. Lutz and W. G. Reveley, THIS JOURNAL, **63**, 3184 (1941).
(3) E. P. Kohler, *Am. Chem. J.*, **38**, 181 (1906).
(4) H. Gilman and R. H. Kirby, THIS JOURNAL, **63**, 2946 (1941).
(5) F. C. Whitmore and G. W. Pedlow, *ibid.*, **63**, 758 (1941).
(6) All boiling points and melting points are uncorrected.
(7) P. D. Bartlett and G. F. Woods, THIS JOURNAL, **62**, 2933 (1940).