manganese dioxide was removed by filtration and washed with acetone. The filtrate and washings were concentrated, made basic with sodium carbonate and extracted three times with ether. The ether extracts were washed with water, dried over magnesium sulfate and evaporated to dryness. The oily residue was taken up in a small volume of boiling methanol. Cooling to room temperature provided 8 mg. (10%) of mesityl phenyl diketone, m.p. 134–135°. A mixture melting point with an authentic sample[12] was not depressed. The methanol filtrate when cooled to 0° yielded 37 mg. (49%) of slightly colored benzoylmesitylene, m.p. 30–33° (lit. 35°).[13]

Acidification of the carbonate wash, extraction with desiccation over magnesium sulfate and evaporation of the solvent gave a residue too small to characterize by ordinary methods. The presence of the diarylglycolic acid, however, was demonstrated by a spot test: a drop of concentrated sulfuric acid caused the residue to turn reddish-purple.[14]

Basic Permanganate Oxidation of 2-Acetoxy-2-mesitylphenylacetaldehyde.—A solution of 99 mg. of the aldehyde and 35 mg. of potassium permanganate in 1 ml. of 10% aqueous sodium hydroxide and 4 ml. of pyridine was allowed to stand at room temperature for 6 hr. The manganese dioxide was removed by filtration and washed with pyridine. The filtrate and washings were concentrated to a small volume, acidified with dilute hydrochloric acid and extracted three times with ether. The extracts were washed with water, extracted twice with aqueous sodium carbonate, washed again with water and dried over magnesium sulfate. Evaporation of the solvent yielded 13 mg. (15%) of mesityl phenyl diketone, m.p. 134–135°; admixture with an authentic sample caused no depression of the melting point.

The basic extracts and the subsequent water wash were acidified with dilute hydrochloric acid, extracted three times with ether, dried over magnesium sulfate and concentrated to a small volume. A milliliter of methanol was added; the resulting solution, when taken to dryness, gave 53 mg. (52%) of the methanolate of mesitylphenylglycolic acid, m.p. 85–88°. This material melted at 87–89° after one crystallization from methanol.[15]

A solution of 84 mg. of mesityl phenyl diketone in 1 ml. of 10% aqueous sodium hydroxide and 4 ml. of pyridine was allowed to stand at room temperature for 6 hr. The solution was concentrated to a small volume, diluted with water and extracted three times with ether. The ether extracts were washed with dilute hydrochloric acid and water, dried over magnesium sulfate and evaporated to dryness. The recovered mesityl phenyl diketone, m.p. 134–135°, weighed 82 mg. (98%).

Mesityl-*p*-tolylacetic Acid.—To a solution of 50 g. of *p*-methylmandelic acid in 200 ml. of mesitylene heated to 70° was added dropwise 53 ml. of fuming stannic chloride. The mixture was heated for 8 hr. and poured into 200 ml. of water. Ether was added and the mixture washed with dilute hydrochloric acid, then extracted with 10% sodium carbonate solution. Acidification of the alkaline extract and recrystallization of the product from ethanol gave 57.4 g. (72%) of the mesityl-*p*-tolylacetic acid, a colorless solid melting at 213–215°. The acid was also prepared in 74% yield by the condensation of 5 g. of mesitylglycolic acid with 50 ml. of toluene by use of 10.2 g. of stannic chloride as catalyst.

Mesityl-*p*-tolylketene.—A solution of 8 g. of mesityl-*p*-tolylacetic acid in 150 ml. of benzene was mixed with 2.2 ml. of thionyl chloride and 0.5 ml. of pyridine and the mixture heated under reflux for 10 hr. The pyridine hydrochloride was removed by filtration and the solvent was evaporated *in vacuo*. The ketene was a yellow oil boiling at 142–145° (4 mm.), yield 6.2 g. (83%).

Mesityl-*p*-tolylvinyl Alcohol.—To the Grignard reagent prepared from 2 g. of magnesium and 9 ml. of *t*-butyl chloride was added 6.2 g. of mesityl-*p*-tolylketene in ether. The solution was heated under reflux for 3 hr. and then poured into a mixture of ice and hydrochloric acid. The ether layer was washed with water, dried and evaporated. The mesityl-*p*-tolylvinyl alcohol was recrystallized from high-boiling petroleum ether to give 2.87 g. (46%) of a colorless solid, m.p. 104–105°.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 86.12; H, 8.08.

The benzoate, prepared by the use of benzoyl chloride and pyridine, was recrystallized from ethanol, m.p. 151–152°.

Anal. Calcd. for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79. Found: C, 84.51; H, 6.84.

The Mixed Anhydride of Acetic and Mesitylphenylacetic Acids.—A slow stream of ketene gas, prepared by pyrolysis of acetone, was bubbled through a solution of 5 g. of mesitylphenylacetic acid in 75 ml. of ether for 1 hr. The solution was washed with water and sodium carbonate solution, then dried. After the solvent had been removed by evaporation, the product slowly became crystalline. It crystallized from high-boiling petroleum ether in colorless rhombic crystals melting at 74–75°.

Anal. Calcd. for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.50; H, 6.91.

A portion of this anhydride was hydrolyzed by treatment with sodium hydroxide to give mesitylphenylacetic acid which was characterized by a mixture melting point determination with an authentic specimen.

Diphenylacetaldehyde was prepared according to the method of Danilov.[16]

(12) A. R. Gray and R. C. Fuson, THIS JOURNAL, **56**, 739 (1934).

(13) K. Elbs, *J. prakt. Chem.*, **35**, 465 (1887).

(14) C. D. Shacklett and H. A. Smith, THIS JOURNAL, **75**, 2654 (1953).

(15) H. H. Weinstock, Jr., and R. C. Fuson, *ibid.*, **58**, 1233 (1936).

(16) S. Danilov, *Ber.*, **60**, 2391 (1927).

URBANA, ILLINOIS

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

The Addition of *t*-Butylmagnesium Chloride to 2,2-Diphenyl-1-acenaphthenone

BY REYNOLD C. FUSON AND GARY W. GRIFFIN[1]

RECEIVED DECEMBER 17, 1956

2,2-Diphenyl-1-acenaphthenone (I) has been found to condense with *t*-butylmagnesium chloride in the 1,6-manner to yield a dihydroaromatic derivative II. As a by-product was isolated a completely aromatized ketone, likewise containing the *t*-butyl group, which is believed to be the 8-*t*-butyl derivative XII. The action of methylmagnesium iodide on the original acenaphthenone was found to convert it to the corresponding olefin XIV. Under forcing conditions the acenaphthenone also was attacked readily in the conjugate manner by phenylmagnesium bromide to give an aromatized phenyl adduct.

2,2-Diphenyl-1-acenaphthenone (I) was selected for study because of its close similarity to β-benzopinacolone, which had been found to react in the conjugate manner with Grignard reagents.[2–4] Although the acenaphthenone had been reported to

(1) Union Carbide and Carbon Company Fellow, 1954–1956.

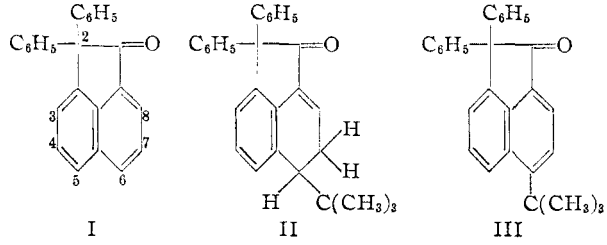
(2) J. Schmidlin and J. Wohl, *Ber.*, **43**, 1145 (1910).

(3) W. A. Mosher and M. L. Huber, THIS JOURNAL, **75**, 4604 (1953).

(4) R. C. Fuson and P. E. Wiegert, *ibid.*, **77**, 1138 (1955).

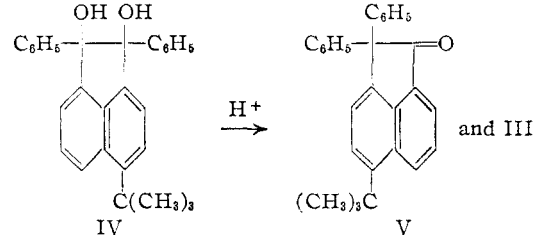
be unreactive toward the phenyl reagent,[5] it seemed possible that more aggressive reagents might bring about addition.

Experiments with *t*-butylmagnesium chloride have borne out this expectation; two ketones were obtained, each having a *t*-butyl radical. The major product (29%) proved to be a dihydroaromatic compound which contained a conjugated carbonyl group and which was eventually shown to have structure II. Treatment with chloranil in *m*-xylene at the reflux temperature converted it to an aromatic *t*-butylated diphenylacenaphthenone (6.1% yield), which was assigned structure III. A by-product in this, as well as other attempted dehydrogenation reactions (sulfur, Pd/C), was 2,2-diphenyl-1-acenaphthenone (I), formed by the loss of the elements of isobutane.



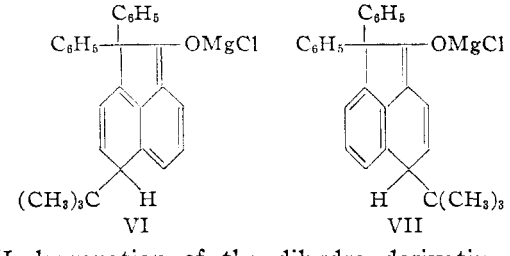
I II III

The aromatized *t*-butyl addition compound III was prepared also by the acid-catalyzed rearrangement of 5-*t*-butyl-1,2-diphenylacenaphthene-1,2-diol (IV); this reaction produced the 5-*t*-butyl isomer simultaneously, of course.



IV V

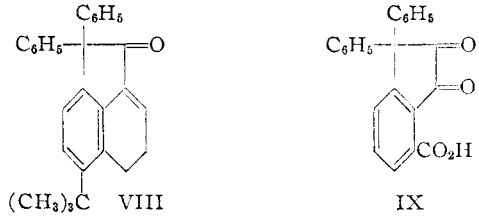
This synthesis established only that the addition compound must have structure III or V. Structure III was heavily favored since the literature offers no precedent for attack of a Grignard reagent in the non-benzoyl ring. Furthermore entry of the *t*-butyl group in position 5 would require disruption of the aromaticity of the entire naphthalene system as indicated in structure VI. Attack at the 6-position, on the other hand, would leave one of the rings intact as in structure VII.



VI VII

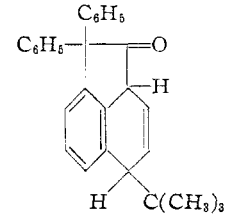
Hydrogenation of the dihydro derivative was accompanied by a shift of the carbonyl infrared absorption band from 1727 to 1747 cm.$^{-1}$, a result which would be expected if the olefinic bond is conjugated with the carbonyl group as represented in structure II. It is worthy of note that this is the only conjugated structure that can be written which does not destroy the aromaticity of the entire naphthalene nucleus. That this system still possesses aromatic character seems evident from the infrared absorption of the compound in the region 810–750 cm.$^{-1}$, which exhibits bands that cannot be attributed to monosubstitution in a benzene ring. Also, the spectrum has no band that can be attributed to *para* substitution, which would rule out structure VIII. This fact, taken together with the observations that the olefinic bond is conjugated with the carbonyl group and that the position of the *t*-butyl group is limited to either the 5- or 6-position, restricts the structure of the hydroaromatic *t*-butyl adduct to II.

Confirmation of structure II was obtained by subjecting the ketone to oxidation with alkaline permanganate, which destroyed the non-aromatic ring and simultaneously *removed the t-butyl group*. All available data support the assignment of structure IX to the oxidation product.



VIII IX

Whether the conjugated dihydroaromatic ketone II is produced directly from the enolate VII or by way of ketone X is problematical.



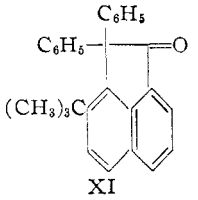
X

The characteristic attack of Grignard reagents on hindered aromatic ketones dictates that the *t*-butyl group select the 3,5,6- or 8-position in structure I. Since the aromatic adduct obtained as a by-product (5.1%) in the condensation of *t*-butylmagnesium chloride with 2,2-diphenylacenaphthenone (I) was shown to be dissimilar to the ketones III and V, it is to be assigned either structure XI or XII. Production of isomer XI would require 1,6-addition with concurrent destruction of the aromaticity of the naphthalene nucleus; compound XII, on the other hand, could be produced by 1,4-addition and preservation of the aromatic character of one of the rings of naphthalene. Moreover, there would appear to be little, if any, steric advantage to favor attack at position 3. Thus, the aromatic *t*-butyl adduct appears to be 2,2-diphenyl-8-*t*-butyl-1-acenaphthenone (XII).

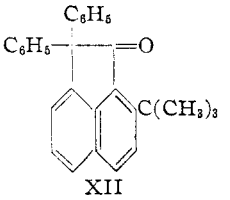
This assignment is extraordinary in that it is the first example of a 1,4-addition reaction of *t*-butylmagnesium chloride embracing an aromatic nucleus having a position in the benzoyl ring open for 1,6-attack.

(5) G. Wittig and H. Petri, *Ber.*, **68B**, 924 (1935).

The methyl reagent, as might be expected, combines with the acenaphthenone in the 1,2-manner. The product, however, is not the carbinol XIII but the hydrocarbon XIV that would be obtained from

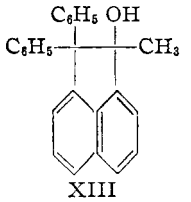


XI

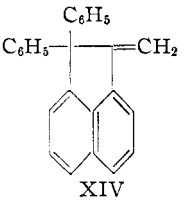


XII

it by dehydration. This behavior is very similar to that observed with certain mesityl ketones.[6] The structure of the olefin XIV was confirmed by permanganate oxidation which reconverted it to the parent ketone I.

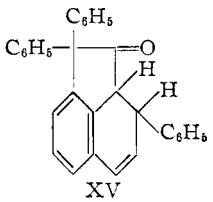


XIII

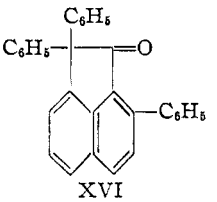


XIV

With phenylmagnesium bromide the acenaphthenone yielded a fully aromatic phenylation product. The infrared spectrum of the crude material, before the solvents were driven off by an air stream, exhibited absorption bands characteristic of a five-membered unconjugated cyclic ketone; thus it seems probable that the dihydro ketone XV was formed first and oxidized by the air to the fully aromatic derivative XVI.



XV



XVI

The assignment of the entering phenyl group to the 8-position is based on analogy; no further study was made of the compound.

Experimental[7]

2,2-Diphenyl-1-acenaphthenone (I).—This ketone was made by rearrangement of the corresponding glycol, formed in turn by the addition of phenylmagnesium bromide to acenaphthenequinone. The conditions employed were essentially those described by Bachmann and Chu.[8]

Condensation of 2,2-Diphenyl-1-acenaphthenone (I) with *t*-Butylmagnesium Chloride.—A solution of 4.0 g. (0.012 mole) of the ketone in 80 ml. of dry benzene was added, over a period of 0.5 hour, to a Grignard reagent prepared from 1.52 g. (0.062 g. atom) of magnesium, 6.67 g. (0.069 mole) of *t*-butyl chloride and 65 ml. of anhydrous ether. When the addition was completed the temperature was slowly raised to 60°, the ether being allowed to escape through the condenser. The apparatus was then sealed by attaching a balloon to the condenser, and the reaction mixture maintained at 60° for 16 hours. The initial brown color of the mixture later acquired a reddish tint. The mixture was allowed to cool, and oxygen was passed into it for 5 minutes; an exothermic reaction occurred, and the brown color returned. The mixture was treated with 200 ml. of water containing 10 ml. of concentrated hydrochloric acid. The organic layer was removed and the aqueous phase extracted three times with 150-ml. portions of ether. The combined organic layers were dried for 1.5 hours over anhydrous sodium sulfate and then concentrated on a steam-bath with an air jet to a volume of 20 ml. Absolute ethanol was added and the solution cooled in an ice-bath; 0.82 g. of colorless crystals, m.p. 185° dec., was deposited. Further concentration of the filtrate and subsequent cooling afforded an additional 0.5 g. of the product, m.p. 184° dec.—a total yield of 29%—as well as 3.80 g. of a red oil. The solid could be purified by recrystallization from a mixture of benzene and ethanol or from a pyridine–water mixture, m.p. 191.5° dec.

Anal.[9] Calcd. for $C_{28}H_{26}O$: C, 88.85; H, 6.92. Found: C, 88.87; H, 6.71.

The infrared spectrum[10] of the compound, measured in chloroform, has bands assignable to a carbonyl group (1727 cm.$^{-1}$) and an olefinic bond (1650 cm.$^{-1}$, very intense). Bands at 1453, 1403 and 1373 cm.$^{-1}$ were attributed to the *t*-butyl group. These data are in agreement with the structure 2,2-diphenyl-6-*t*-butyl-6,7-dihydro-1-acenaphthenone (II).

Chromatographic separation of the red oil permitted the isolation of 0.23 g. (5.1%) of crystalline material. It was purified by recrystallization from ethanol and benzene or from methylcyclohexane, m.p. 177–178°.

Anal. Calcd. for $C_{28}H_{24}O$: C, 89.32; H, 6.43. Found: C, 89.50, 88.92; H, 6.56, 6.54.

The infrared spectrum of this compound, determined in carbon disulfide, exhibits bands assignable to a conjugated ketone (1720 cm.$^{-1}$), a *t*-butyl group (1402 and 1370 cm.$^{-1}$) and *para*-substitution (absorption in the 810–850 cm.$^{-1}$ region). These data are consistent with the structure 8-*t*-butyl-2,2-diphenyl-1-acenaphthenone (XII).

Dehydrogenation of 2,2-Diphenyl-6-*t*-butyl-6,7-dihydro-1-acenaphthenone (II).[11]—A solution of 0.50 g. of the hydroaromatic ketone and 0.33 g. of chloranil in 3 ml. of *m*-xylene was heated under reflux for 4 hours, cooled and filtered. The filtrate was diluted with an equal volume of ether and then extracted with 5-ml. portions of 5% aqueous potassium hydroxide. The organic layer was concentrated on a steam-bath and absolute ethanol was added; 0.32 g. of impure 2,2-diphenyl-1-acenaphthenone was deposited (75.9%). The infrared spectrum was identical with that of an authentic sample of the ketone. When the mother liquor was concentrated, 0.0305 g. of another material was isolated, m.p. 170–189° (6.1%). Recrystallization from ethanol gave ketone III melting at 189–190°.

Anal. Calcd. for $C_{28}H_{24}O$: C, 89.32; H, 6.43. Found: C, 89.20; H, 6.30.

Dealkylation of 2,2-Diphenyl-6-*t*-butyl-6,7-dihydro-1-acenaphthenone (II).—A mixture of 0.34 g. of the ketone, 0.04 g. of 30% palladium-on-charcoal catalyst and 4.5 ml. of mesitylene was heated at the reflux temperature for 0.5 hour, during which time the system was flushed with a continuous stream of nitrogen. After the catalyst had been collected on a filter the filtrate was concentrated under reduced pressure. The oily residue afforded a crystalline solid (m.p. 170–172°) when treated with ethanol. Subsequent recrystallization from ethanol yielded a product which, by a mixed melting point determination with an authentic specimen, proved to be 2,2-diphenyl-1-acenaphthenone. The yield of the diaryl acenaphthenone was 82% of the theoretical amount.

The infrared spectrum of the compound, determined in potassium bromide, exhibits bands assignable to a conjugated carbonyl group (1717 cm.$^{-1}$), *para*-substitution (840 cm.$^{-1}$), and the *t*-butyl group (1398 and 1370 cm.$^{-1}$).

Hydrogenation of 2,2-Diphenyl-6-*t*-butyl-6,7-dihydro-1-acenaphthenone.—A solution of 0.10 g. of the dihydroaro-

(6) R. C. Fuson, M. D. Armstrong, W. E. Wallace and J. W. Kneisley, THIS JOURNAL, **66**, 681 (1944).

(7) All melting points are corrected.

(8) W. E. Bachmann and E. Ju-Hwa Chu, THIS JOURNAL, **58**, 1118 (1936).

(9) The microanalyses were performed by Mr. Joseph Nemeth, Mrs. R. Maria Benassi, Mrs. Lucy Chang, Mrs. Esther Fett, Miss Claire Higham, Mrs. Ruby Ju and Mr. Rollo Nesset.

(10) The infrared spectra were determined and interpreted by Mr. James Brader and Mrs. Louise Griffing.

(11) N. D. Cheronis, "Micro and Semimicro Methods," Vol. VI, Technique of Organic Chemistry, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1954, p. 267.

matic ketone in 40 ml. of benzene was subjected to microhydrogenation in the presence of 0.048 g. of prereduced platinum oxide catalyst. The reaction was discontinued when the hydrogen uptake reached 110 ml. The catalyst was then collected on a filter, and the volatile solvent removed from the filtrate. Absorption at 1745 cm.$^{-1}$ in the infrared spectrum of the crude residue indicated the presence of a five-membered unconjugated cyclic ketone.

Oxidative Degradation of 2,2-Diphenyl-6-*t*-butyl-6,7-dihydro-1-acenaphthenone.—A solution of 0.25 g. of the hydroaromatic *t*-butyl adduct in 10 ml. of pyridine was diluted with hot water until the mixture became cloudy. Two-tenths of a gram of sodium hydroxide and 1.62 g. of finely powdered potassium permanganate were added and the resulting mixture was heated under reflux for 3 hours. A few drops of methanol were then added and heating was continued for an additional 5 minutes in order to reduce the excess permanganate. After the manganese dioxide had been removed from the reaction mixture by filtration, the filtrate was concentrated on a steam-bath with an air jet. The oily residue was then digested during a 15-minute period with 20 ml. of a 1% sodium hydroxide solution, and the resulting mixture filtered to remove the insoluble residue. Acidification of the filtrate with concentrated sulfuric acid afforded 0.022 g. of a white solid. This material IX, after one recrystallization from ethanol and water (m.p. 197.5–202.5°) and two further recrystallizations from benzene and cyclohexane, melted at 203.5–205.5°.

Anal. Calcd. for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12. Found: C, 76.84; H, 4.25.

The infrared spectrum has bands assignable to a five-membered cyclic ketone (1742 cm.$^{-1}$) and an aromatic carboxyl group (2720, 2640, 1697, 1275 and 860 cm.$^{-1}$). A band at 762 cm.$^{-1}$ is indicative of vicinal trisubstitution. Absorption characteristic of aliphatic substituents is not apparent in the spectrum, which was determined in crystalline bromide.

Preparation of 5-*t*-Butyl-1,2-diphenylacenaphthene-1,2-diol.—To the Grignard reagent, prepared from 3.92 g. (0.025 mole) of bromobenzene and 0.61 g. (0.025 g. atom) of powdered magnesium in 30 ml. of anhydrous ether, was added dropwise a solution of 2.75 g. (0.012 mole) of 5-*t*-butylacenaphthenequinone in 30 ml. of dry benzene. The quinone was prepared from 5-*t*-butylacenaphthene by essentially the procedure described by Illingworth and Peters.[12] The reaction mixture was heated under reflux for 4 hours and, after being cooled, was poured into 200 ml. of a 10% aqueous acetic acid solution and allowed to stand overnight. The organic layer was removed and the aqueous phase extracted repeatedly with ether. After the combined organic layers had been dried for 12 hours over anhydrous sodium sulfate, the volatile solvent was removed. The residual oil was heated with enough hot low-boiling petroleum ether to give a homogeneous solution. When the solution was cooled in an ice–salt-bath, 3.60 g. of crystals separated, m.p. 184–187°. After being recrystallized from ethanol and water, the product melted at 197.5–199.5° (42.2%).

Anal. Calcd. for $C_{28}H_{26}O_2$: C, 85.24; H, 6.64. Found: C, 85.09, 85.00; H, 7.03, 6.79.

The infrared spectrum, determined in chloroform, shows bands characteristic of a hydroxyl function (3560 cm.$^{-1}$), *para*-substitution (840 cm.$^{-1}$) and the *t*-butyl group (1398 and 1370 cm.$^{-1}$).

Pinacol Rearrangement of 5-*t*-Butyl-1,2-diphenylacenaphthene-1,2-diol.—To a boiling solution of 1.81 g. of 5-*t*-butyl-1,2-diphenylacenaphthene-1,2-diol in 75 ml. of glacial acetic acid was added several drops of concentrated sulfuric acid. The reaction mixture was maintained at the reflux temperature for 5 minutes and then poured, while still hot, on 300 g. of cracked ice. The resulting solution was allowed to stand for 1.5 hours. The solid was then collected on a filter; after one recrystallization from ethanol and benzene, it melted at 90–140°.

The infrared spectrum has bands assignable to a carbonyl group (1719 cm.$^{-1}$) and shows a *para*-substitution band (840 cm.$^{-1}$).

Fractional crystallization from absolute ethanol proved to be a satisfactory method of effecting the separation of the isomeric *t*-butylated pinacolones while chromatography was found to be unavailing for this purpose. The less soluble isomer, after repeated recrystallization from ethanol, melted at 190–191°.

Anal. Calcd. for $C_{28}H_{24}O$: C, 89.32; H, 6.43. Found: C, 89.02; H, 6.47.

The infrared spectrum of this compound, measured in potassium bromide, was identical to that of the chloranil dehydrogenation product, and a mixed melting point determination showed no depression. A small quantity of another substance, presumably the isomer V, was isolated; after recrystallization from methanol, it melted at 147.5–148°.

Condensation of 2,2-Diphenyl-1-acenaphthenone (I) with Methylmagnesium Iodide.—To a Grignard reagent, prepared from 1.22 g. (0.050 g. atom) of magnesium turnings, 7.81 g. (0.055 mole) of methyl iodide and 50 ml. of ether, was added a solution of 3.18 g. (0.010 mole) of 2,2-diphenyl-1-acenaphthenone in 50 ml. of benzene. Ether was then distilled from reaction mixture until the temperature rose to 60°, and heating was continued under reflux for 22 hours. The reddish reaction mixture was then cooled and treated with 150 ml. of 10% hydrochloric acid. The aqueous layer was extracted repeatedly with ether, and the combined organic phases were concentrated to a volume of 20 ml. Dilution with methanol and subsequent removal of additional solvent by evaporation caused the separation of 2.02 g. of a crystalline hydrocarbon, m.p. 171–175°, which was recrystallized from ethanol and sublimed at 120° (0.10 mm.), m.p. 174–175°.

Anal. Calcd. for $C_{25}H_{18}$: C, 94.30; H, 5.70. Found: C, 94.06; H, 5.68.

The infrared spectrum of the product has bands assignable to a conjugated ethylenic bond (1643 and 891 cm.$^{-1}$) and vicinal trisubstitution (753 cm.$^{-1}$) as well as a mono-substitution (700 and 750 cm.$^{-1}$).

Oxidation of 1,1-Diphenyl-2-methylideneacenaphthene (XIV).—A solution of 0.22 g. of the hydrocarbon in 5 ml. of pyridine was added to a solution of 0.30 g. of finely powdered potassium permanganate in 5 ml. of water. One milliliter of a 10% sodium hydroxide solution was then added and the resulting mixture was heated to 110° where it commenced to boil. It was maintained at this temperature for 4.5 hours, at the end of which time the purple color had been discharged. The mixture was allowed to cool and then was acidified by careful addition of concentrated sulfuric acid. The manganese dioxide was reduced with 9.5 ml. of a 10% sodium meta-bisulfite solution. The resulting mixture afforded 0.07 g. of a yellow solid which was collected on a filter. This solid was dissolved in ethanol and benzene and inorganic salts were removed by filtration. Sublimation of this material at 120° (0.10 mm.) afforded a product (m.p. 173–174°) having an infrared spectrum which is nearly superimposable on that of 2,2-diphenyl-1-acenaphthenone; the melting point of a mixture of the two ketones was not depressed.

Condensation of 2,2-Diphenyl-1-acenaphthenone (I) with Phenylmagnesium Bromide.—To the Grignard reagent prepared from 1.47 g. (0.060 g. atom) of magnesium and 10.4 g. (0.066 mole) of bromobenzene in 55 ml. of ether was added a solution of 3.87 g. (0.012 mole) of 2,2-diphenyl-1-acenaphthenone in 75 ml. of benzene. The addition was carried out as fast as possible. The color of the reaction mixture changed from brown to dark green during the course of the addition while the temperature rose 10°. Ether was then distilled from the reaction mixture until the temperature reached 60°. This temperature was maintained for a total of 16 hours, during which time the mixture was stirred; however, after the first 6 hours had elapsed, an additional 0.025 mole of phenylmagnesium bromide was added to the reaction mixture in the inverse manner and the resulting mixture was again heated to a temperature of 60° by distilling ether from the system. Two hundred milliliters of 10% hydrochloric acid was then added to the green reaction mixture. The aqueous phase was extracted repeatedly with ether, and the resulting solution was concentrated to one-third the original volume. A 1-ml. portion was pipetted from the resulting solution and freed of volatile solvents. The infrared spectrum of the residual oil has two bands of about equal intensity (1716 and 1745 cm.$^{-1}$) which are assignable to conjugated and unconjugated five-membered cyclic ketones, respectively. The remainder of the above solution was treated in turn with 100 ml. of ethanol and

(12) E. Illingworth and A. T. Peters, *J. Chem. Soc.*, 1602 (1951).

methanol and concentrated on a steam-bath under an air jet in an unsuccessful attempt to induce crystallization.

Chromatographic separation of a sample of the oily residue on alumina permitted the isolation of 1.02 g. of crystalline material (m.p. 158–160°). Recrystallization from benzene and ethanol afforded a solid of m.p. 160–161.5°. The yield, extrapolated from a plot of the weight of the eluted material *versus* fraction number, was 90% of the theoretical amount, while the material balance for the chromatograph was 91.5%.

Anal. Calcd. for $C_{30}H_{20}O$: C, 90.88; H, 5.09. Found: C, 91.21, 90.82; H, 5.28, 4.78.

The infrared spectrum of this substance, determined in Nujol mull, has bands assignable to *para*-substitution (848 cm.$^{-1}$), a mono-substituted benzene ring (698 cm.$^{-1}$) and a conjugated five-membered cyclic ketone (1717 cm.$^{-1}$). It is noteworthy that only one major peak was detected in a plot of the weight of the eluted material *versus* fraction number. Similarly the infrared spectrum of a sample of the oil which was subsequently chromatographed indicated the presence of only the conjugated carbonyl group (1726 cm.$^{-1}$, CS_2).

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

The Chemistry of Sultams. II.[1] Chloromethylation and Bromination of Substituted 1,8-Naphthosultam. Reaction of 1,8-Naphthosultam with Organic Halides

BY AHMED MUSTAFA AND MOHAMED IBRAHIM ALI

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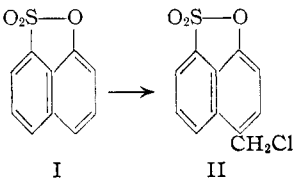
N-Arylsulfonyl derivatives of 1,8-naphthosultam (IIIa,b) undergo chloromethylation to yield the corresponding 4-chloromethyl derivatives (IVa,b), together with V in the case of IIIa. IVa is readily reduced to 4-methyl-N-phenylsulfonyl-1,8-naphthosultam, and both IVa,b condense with *p*-cresol and with 2,4-dimethylphenol to give the products VIIa-d (Table I), respectively. Whereas the bromination of N-methyl-1,8-naphthosultam leads to the formation of the monobromo derivative IXb and to the dibromo derivative (Xb), N-acetyl-1,8-naphthosultam leads mainly to the formation of the monobromo derivative IXc. Similarly, the bromination of the N-aroyl- and N-arylsulfonyl derivatives yields monobromo derivatives, presumably the 4-bromo compounds. The 2,4-dibromo derivatives (Xc,d) now have been prepared by acetylation and by benzoylation of 2,4-dibromo-1,8-naphthosultam. A number of new N-substituted 1,8-naphthosultams (XIa-h, XIIa-f) (Tables II and III) have been synthesized for pharmacological testing. Water-soluble salts of 1,8-naphthosultam with piperidine, benzylamine and cyclohexylamine now have been prepared.

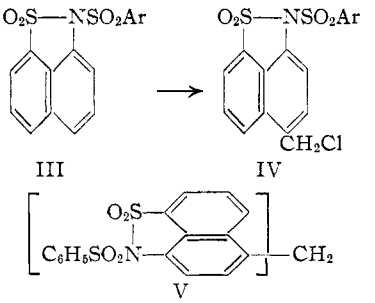
(a) **Chloromethylation.**—Recently, it has been shown[2] that 1,8-naphthosultone (I) condenses with paraformaldehyde and hydrogen chloride in the presence of anhydrous zinc chloride to form 4-chloromethyl-1-naphthol-8-sulfonic acid sultone (II) (*cf.* A).



I II (A)

We now have investigated the behavior of the N-arylsulfonyl derivatives of 1,8-naphthosultam, the nitrogen analog of I, toward chloromethylating agents.[3] Thus, when an acetic acid solution of N-phenylsulfonyl-1,8-naphthosultam (IIIa) is treated with paraformaldehyde, hydrogen chloride and zinc chloride under the same experimental conditions for the chloromethylation of I, 4-chloromethyl-N-phenylsulfonyl-1,8-naphthosultam (IVa), is obtained together with a high melting substance which analyzes correctly for a compound like V.[4] Similarly, 4-chloromethyl-N-(*p*-tolylsulfonyl)-1,8-naphthosultam (IVb) is obtained from N-(*p*-tolylsulfonyl)-1,8-naphthosultam (IIIb).

Although substitution may occur in more than one way, only one product was isolated. Fractional crystallization of the crude reaction product failed to reveal the presence of any other isomer. It seemed probable, by analogy with the behavior



a, Ar = C_6H_5; b, Ar = $C_6H_4CH_3$-*p*

of I and with α-naphthyl ethers,[3,5] that the chloromethyl group in IV occupied the 4-position of the nucleus in preference to the 2-position.[1]

IVa,b are valuable intermediates for the production of 4-substituted derivatives of 1,8-naphthosultam. Thus, when IVa is treated with zinc dust and acetic acid, it is reduced readily to 4-methyl-N-phenylsulfonyl-1,8-naphthosultam (VI). Condensation of IVa and IVb with *p*-cresol and with 2,4-dimethylphenol leads to the formation of VIIa-d, respectively.

(1) Part I, A. Mustafa and M. I. Ali, THIS JOURNAL, **77**, 4593 (1955).

(2) G. Schetty, *Helv. Chim. Acta*, **32**, 24 (1949).

(3) *Cf.* A. Mustafa, *Chem. Revs.*, **54**, 195 (1954).

(4) R. Adams, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 65.

(5) There have been several reports of the reactions of 1,8-naphthosultam and its N-substituted derivatives, which show similarity to α-naphthol and α-naphthyl ethers, *e.g.*, the behavior of 1,8-naphthosultam toward chlorine (T. Zincke and G. Schürmann, *Ann.*, **412**, 718 (1916)), in condensation with isatin, isatin chloride and isatinanilide (P. Friedländer and L. Sander, *Ber.*, **57**, 637 (1924), W. König and E. Wagner, *ibid.*, **57**, 1056 (1924)), and in coupling with diazotized solutions (W. König and J. Keil, *ibid.*, **55**, 2149 (1922), W. König and K. Köhler, *ibid.*, **55**, 2139 (1922)).