evaporated to constant weight at 5 mm. and diluted with about 5 ml. of cumene. Infrared spectra were obtained for the standards and the unknowns in a single cell especially reserved for this purpose.

A prepared mixture of 0.1206 g. of α-tetralol, 0.0896 g. of 2-phenyl-2-propanol and 0.134 g. of tetralin in 2 ml. of cumene was analyzed by the absorption at 8.52 and 10.00 μ. The analysis indicated the presence of the alcohols in a weight ratio of 1.35 to 1 whereas the solution was prepared to contain the alcohols in the ratio of 1.40 to 1.

The rate of decomposition of *t*-butyl perbenzoate in cumene and tetralin solutions was determined by sealing evacuated samples of a standard solution of *t*-butyl perbenzoate in ampoules. At appropriate times ampoules were removed from an oil-bath, opened and analyzed for peroxide content.[25] The following data were obtained for solutions of *t*-butyl perbenzoate originally 0.02 *M*.

TABLE IV

DECOMPOSITION OF *t*-BUTYL PERBENZOATE IN CUMENE AND TETRALIN SOLUTIONS AT 90°

Time, hr.	% of peroxide decomposed Cumene	Tetralin
6	7.0	7.0
12	13.1	13.2
18	17.3	18.5
24	24.0	25.1
30	29.2	31.0
36	34.0	36.9
42	38.1	42.2
48	41.5	47.0

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE UNIVERSITY]

Reactions of α-Halotetralone and Certain Alkyl Derivatives with Base[1]

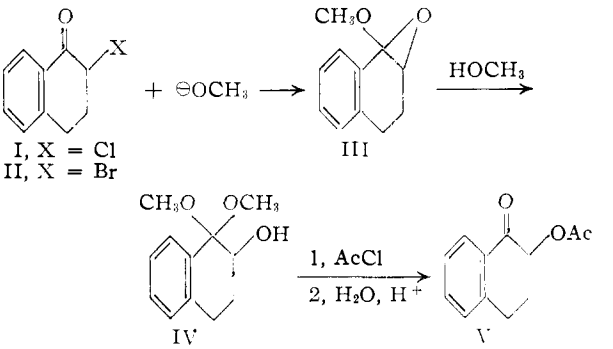
BY CALVIN L. STEVENS, JOHN J. BEEREBOOM, JR., AND KENNETH G. RUTHERFORD[2]

RECEIVED MARCH 9, 1955

α-Bromotetralone (II), when allowed to react with alcoholic sodium methoxide, gave the α-hydroxy ketal IV in 80% yield. The intermediate epoxyether III could not be isolated. The corresponding α-chloroketone gave the α-hydroxy ketal in 33% yield. α,α-Dichlorotetralone (VI), α-chloro-α-methyltetralone (XII) and α-chloro-α-ethyltetralone (XIII), when treated with alcoholic sodium methoxide, were dehydrohalogenated to the corresponding naphthols.

The investigation of the reactions of α-halotetralones with base was undertaken because α-chlorotetralone (I) was one of the few α-haloketones which had been reported to undergo a carbon skeleton rearrangement in the presence of alcoholic sodium methoxide, but which could not form a cyclopropanone intermediate.[3,4] Previously, α-halocyclohexyl phenyl ketone, a haloketone which similarly cannot form a cyclopropane intermediate, had given a high yield of epoxyether when treated with alcoholic sodium methoxide.[5] In the present study, no evidence of carbon skeleton rearrangement could be found. In addition to reactions proceeding *via* epoxyethers, dehydrohalogenation of certain of the α-halotetralone derivatives gave naphthols.

α-Bromotetralone (II) was converted smoothly at room temperature by alcoholic sodium methoxide into the crystalline hydroxy ketal IV in 80% yield. The hydroxy ketal was acetylated with acetyl chloride and the ketal group preferentially hydrolyzed with dilute acid to give the keto acetate V. Although the formation of α-hydroxy ketals from α-haloketones is known to proceed *via* the epoxyethers,[6] the reactive intermediate III could not be isolated from the α-bromotetralone II. In this respect the haloketone II resembled α-chlorocyclohexanone, the epoxyether of which could not be isolated in this Laboratory.[7]



The chlorotetralone I was prepared in 97% yield by direct chlorination of tetralone in methylene chloride at 0°. Since the chlorotetralone II melted sharply at 44–45°, and since Mousseron[3] reported the melting point as 72°, the position of the halogen was determined by conversion of both the bromotetralone and the chlorotetralone to the same crystalline iodoketone, using sodium iodide in acetone solution. Straus[8] has shown that the bromine in II is in the position alpha to the ketone; therefore, the chlorine atom of I must be in the same position. Furthermore, both haloketones I and II gave the same keto acetate V when treated with sodium acetate. The formation of V *via* the hydroxy ketal provides additional support for structure I.

Although the chloroketone I reacted with alcoholic sodium methoxide more slowly than the bromoketone I, the only product isolated was the hy-

(1) Abstracted in part from the M.S. thesis of J. J. Beereboom, Jr., Wayne University, 1952, and the Ph.D. thesis of K. G. Rutherford, Wayne University, 1955.

(2) Supported in part by a Grant-in-aid from the Research Corporation of New York.

(3) M. Mousseron and A. D. Grange, *Bull. soc. chim.*, [5] **10**, 428 (1943); M. Mousseron and Nguyen-Phuoc-Du, *Compt. rend.*, **218**, 281 (1944).

(4) *Cf.* also the discussion of R. B. Loftfield (THIS JOURNAL, **73**, 4707 (1951)), and of C. L. Stevens and E. Farkas (*ibid.*, **74**, 5352 (1952)).

(5) C. L. Stevens and E. Farkas, *ibid.*, **74**, 618 (1952).

(6) C. L. Stevens, W. Malik and R. Pratt, *ibid.*, **72**, 4758 (1950); C. L. Stevens, M. L. Weiner and R. C. Freeman, *ibid.*, **75**, 3977 (1953); C. L. Stevens and J. J. DeYoung, *ibid.*, **76**, 718 (1954); C. L. Stevens, E. Farkas and B. Gillis, *ibid.*, **76**, 2695 (1954).

(7) C. L. Stevens and J. Tazuma, *ibid.*, **76**, 715 (1954).

(8) F. Straus, O. Bernoully and P. Mautner, *Ann.*, **444**, 165 (1925); F. Straus and A. Rohrbacher, *Ber.*, **54B**, 40 (1921).

droxy ketal. No evidence could be found for carbon skeleton rearrangement.

The chlorotetralone I readily underwent further chlorination to give a dichlorotetralone VI in 77% yield, m.p. 74–75°. Examination of the carbonyl region of the infrared spectrum indicated that the second chlorine atom also had entered the position alpha to the carbonyl. Table I lists the positions of the carbonyl absorption bands in the infrared spectra of tetralone, α-methyltetralone and α-ethyltetralone (XI, X and IX, respectively,) along with data for the corresponding α-monochlorinated derivatives. For each pair, the shift in frequency is *ca.* 10 cm.$^{-1}$, a shift comparable in size to that accompanying mono-α-chlorination of cyclopentanone, cyclohexanone or cycloheptanone.[9] The fact that dichlorination of tetralone produced a significantly larger shift (*ca.* 30 cm.$^{-1}$) was interpreted according to the data of Jones[10] and Corey[11] to mean that the second chlorine had entered the alpha position and that the new C–Cl bond was more nearly coplanar with the C=O bond than was the original C–Cl. A less likely interpretation of the large shift would involve chlorination at another point in the molecule, the steric requirements of which could change the conformation and cause the original C–Cl bond to become more nearly coplanar with the C=O bond[12] than it had been.

The structure of the dichlorotetralone was confirmed as the α,α-dichloroketone VI by an independent synthesis from the enol acetate VII.[13] Treatment of the dichlorotetralone VI with alcoholic sodium methoxide gave 2-chloro-1-naphthol[14] (VIII) in 97% yield, m.p. 64–65°.

Since in the reaction of the halotetralones I and II with alcoholic sodium methoxide, formation of the enolate ion by attack of the base upon the active hydrogen alpha to the carbonyl was a complicating factor,[13] the two alkylated chlorotetralones XII and XIII were prepared. Each of these crystalline chloroketones, when treated with alcoholic sodium methoxide, gave the corresponding 2-alkyl-1-naphthol in good yield.

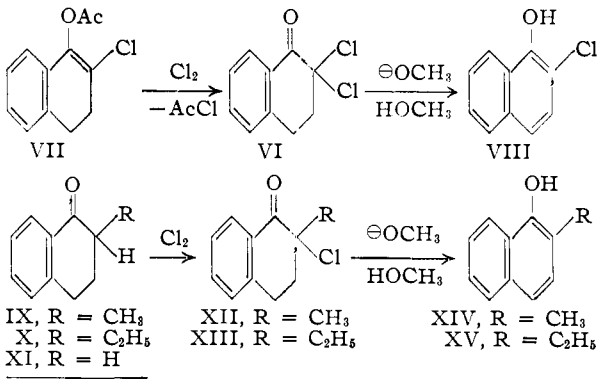


TABLE I[a]

	Position of C=O absorption cm.$^{-1}$	Frequency shift Δ, cm.$^{-1}$
α-Methyltetralone (IX)	1689	
α-Methyl-α-chlorotetralone (XII)	1698	Δ9
α-Ethyltetralone (X)	1686	
α-Ethyl-α-chlorotetralone (XIII)	1698	Δ12
Tetralone (XI)	1687	
α-Chlorotetralone (I)	1697	Δ10
α,α-Dichlorotetralone (VI)	1715	Δ28

[a] The authors wish to acknowledge the assistance of Dr. J. M. Vandenbelt and Mr. R. Bruce Scott, Parke–Davis Research Laboratories, who performed the infrared determinations with a Beckman IR-2 spectrophotometer equipped with a calcium fluoride monochromator. Carbon tetrachloride was used as a solvent.

Experimental

Reaction of α-Bromotetralone (II) with Alcoholic Sodium Methoxide.—The α-bromotetralone (2-bromo-3,4-dihydro-1(2H)-naphthalenone), m.p. 39–40°, was prepared by the method of Wilds[15] in 87% yield. Ten grams (0.045 mole) of II was dissolved in 200 ml. of absolute methanol, and 50 ml. of a methanol solution containing one equivalent of sodium methoxide was added. The reaction mixture was allowed to stand at room temperature for two hours and the solvent was then removed by distillation under vacuum at room temperature. Ether was added and the mixture filtered to remove 4.93 g. of sodium bromide and unreacted sodium methoxide. The ether was evaporated *in vacuo* to give 8.30 g. of a light brown oil. The oil was dissolved in an ether–petroleum ether mixture and after the solution had been cooled, 7.55 g. (81%) of white, crystalline hydroxy ketal (2-hydroxy-3,4-dihydro-1(2H)-naphthalenone dimethyl ketal), m.p. 93–94°, was separated by filtration.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74; OCH_3, 29.80. Found: C, 69.34; H, 7.73; OCH_3, 29.97.

The filtrate was concentrated and the residue treated with semicarbazide reagent to give 0.75 g. (7%) of derivative, m.p. 216–217°. The melting point was not depressed when the sample was mixed with authentic α-tetralone semicarbazone.

Titration of a water solution of the inorganic salts indicated that only 85% of the base was used.

α-Hydroxytetralone Acetate V.—Two grams of the hydroxy ketal IV was refluxed with 1 g. of acetyl chloride for 15 minutes. The reaction mixture was then poured into dilute hydrochloric acid solution and the organic material extracted with benzene. After the solvent was removed the residue was recrystallized from an ether–petroleum ether mixture to give 1.20 g. (61%) of the hydroxytetralone acetate V (2-hydroxy-3,4-dihydro-1(2H)-naphthalenone acetate), m.p. 72–73°.

Preparation of α-Chlorotetralone (I).—Ten grams (0.057 mole) of tetralone XI was dissolved in 200 ml. of methylene chloride and cooled to 0° in an ice-bath. A solution of 6.32 g. of chlorine (1.3 equivalents) dissolved in 100 ml. of methylene chloride was added slowly while the mixture was stirred. After all of the chlorine had been added, the reaction was allowed to warm to room temperature for one hour.

The solution was washed successively with water, 5% sodium bicarbonate and water, and then dried over anhydrous sodium sulfate and the solvent evaporated *in vacuo*. The resulting oil crystallized from an ether–petroleum ether solution in the form of large rhombic crystals. The yield of the chlorotetralone (I) (2-chloro-3,4-dihydro-1(2H)-naphthalenone) was 12.0 g. (97%), m.p. 44–45.5°.

(9) E. J. Corey, THIS JOURNAL, **75**, 2301 (1953).

(10) R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, *ibid.*, **74**, 2828 (1952).

(11) E. J. Corey, *ibid.*, **75**, 3297 (1953).

(12) *Cf.* the position of the carbonyl bands in α-bromocyclohexanone and 2-bromo-4,4-dimethylcyclohexanone, ref. 9.

(13) K. G. Rutherford and C. L. Stevens, THIS JOURNAL, **77**, 3278 (1955).

(14) It is interesting to note that Mousseron (ref. 3) claimed the monochlorotetralone I to melt at 72° and indicated that the reaction of this compound with alcoholic sodium methoxide gave an ester, of which the acid, m.p. 58–59°, was said to be 2,3-dihydro-1-indenecarboxylic acid. However, W. Riebensahm, German Patent 377,587 [P. Friedlaender, *Fortschritte der Teerfarbenfabrikation*, **14**, 464 (1925); *Chem. Zentr.*, **951**, 956 (1924)] claimed the preparation of α-chlorotetralone (I), m.p. 45°, and α,α-dichlorotetralone, m.p. 75–76°, but gave no structure proof.

(15) A. L. Wilds, THIS JOURNAL, **64**, 1421 (1942).

Anal. Calcd. for $C_{10}H_9ClO$: C, 66.49; H, 5.02; Cl, 19.63. Found: C, 66.64; H, 5.17; Cl, 19.18.

Reaction of the α-chloroketone with alcoholic sodium methoxide was carried out as with the bromoketone. Crystalline α-hydroxyketal IV could be isolated that was identical with that synthesized from the bromoketone, but the reaction was much slower and the yield was never over 33%.

Reaction of the Halotetralones I and II with Sodium Iodide.—Ten grams (0.045 mole) of the α-bromoketone II was dissolved in 100 ml. of anhydrous acetone and added to a solution of 7.3 g. (1.1 equivalents) of sodium iodide in 75 ml. of acetone. After standing at room temperature for three hours, 4.5 g. (97%) of sodium bromide was filtered from the reaction. The filtrate was diluted with water and the resulting solid filtered. The light tan crystalline material melted at 67–69° and was recrystallized from acetone to give large needles, m.p. 76–77°. The yield of α-iodotetralone (2-iodo-3,4-dihydro-1(2H)-naphthalenone) was 10.48 g. (87%) and the material was extremely irritating to the skin.

Anal. Calcd. for $C_{10}H_9IO$: C, 44.14; H, 3.33. Found: C, 44.37; H, 3.21.

The same procedure was used for the crystalline α-chlorotetralone (I). However, the yield was never above 35% although the reaction was allowed to stand for several days. The mixture melting point of the α-iodoketone from this reaction and that synthesized from α-bromoketone was not depressed. The iodoketone decomposed within a few days at room temperature.

Preparation of the α-Hydroxytetralone Acetate from the Halotetralones.—The method of F. Straus[8] was used to convert α-bromotetralone (II) to the acetate V in 42% yield. After the product was recrystallized from ether, the m.p. was 60–63°. Recrystallization from methanol raised the melting point to 74–75°. The product was identical with V made from the hydroxyl ketal as shown by mixture melting point determinations.

By the same procedure the chlorotetralone I was converted to the same keto acetate V in 19% yield.

Preparation of the α,α-Dichlorotetralone (VI).—To a stirred solution of 20 g. (0.14 mole) of tetralone XI dissolved in 400 ml. of methylene chloride was added during a period of one hour a solution of 25.3 g. (2.3 equivalents) of chlorine dissolved in 300 ml. of methylene chloride. The reaction mixture was stirred for an additional two hours and then washed with water, sodium bicarbonate and again with water. The solvent was evaporated *in vacuo*, and the remaining light yellow solid had a m.p. 61–64°. Recrystallization from an ether–petroleum ether mixture gave 25.0 g. (85%) of the α,α-dichloroketone VI (2,2-dichloro-3,4-dihydro-1(2H)-naphthalenone), m.p. 74–75°.

Anal. Calcd. for $C_{10}H_8Cl_2O$: C, 55.84; H, 3.74; Cl, 32.97. Found: C, 56.05; H, 4.01; Cl, 33.04.

The same dichloroketone was prepared in 77% yield starting with α-chlorotetralone (I) and 1.3 equivalents of chlorine, using exactly the same procedure.

Preparation of 2-Chloro-1-naphthol.—The α,α-dichloroketone (6.2 g., 0.03 mole) was dissolved in 75 ml. of absolute methyl alcohol and an alcoholic solution of three equivalents of sodium methoxide was added. The reaction was refluxed for three hours, cooled, poured into 300 ml. of water, and the mixture acidified with dilute hydrochloric acid. The resulting solid was filtered and dried to give 4.63 g. (97%) of 2-chloro-1-naphthol,[16] m.p. 64–65°.

4-Bromo-2-chloro-1-naphthol,[17] m.p. 112–113°, was prepared as a derivative.

α-Methyl-α-chlorotetralone (XII).—α-Methyl-α-carbomethoxytetralone was prepared in 85% yield by the reaction of methyl iodide, α-carbomethoxytetralone, and sodium methoxide, according to the method of Bachmann.[18] The alkylated ketoester was hydrolyzed with sodium hydroxide solution and decarboxylated following the procedure of Kloetzel[19] to obtain α-methyltetralone (IX). This latter ketone was purified by fractional distillation.

The chlorination of IX proceeded smoothly when acetic acid was used as the solvent medium. α-Methyltetralone (6.28 g., 0.04 mole) was dissolved in 75 ml. of acetic acid and a small amount of chlorine was bubbled into the reaction mixture. After a short induction period the characteristic yellow color of the dissolved chlorine disappeared. At this point the reaction flask was cooled with an ice-bath and chlorine was bubbled slowly with stirring into the reaction mixture until a yellow color persisted. The reaction mixture was poured with stirring on cracked ice, whereupon XII crystallized. Recrystallization from petroleum ether (b.p. 30–60°) yielded 7.4 g. (97%) of I (2-chloro-2-methyl-3,4-dihydro-1(2H)-naphthalenone), m.p. 38–39°.

Anal. Calcd. for $C_{11}H_{11}ClO$: C, 67.87; H, 5.70; Cl, 18.22. Found: C, 67.43; H, 5.91; Cl, 17.80.

α-Ethyl-α-chlorotetralone (XIII).—α-Ethyl-α-carbomethoxytetralone was prepared in 90% yield from the reaction of ethyl iodide, α-carbomethoxytetralone and sodium methoxide according to the method of Bachmann.[20] This alkylated ketoester was obtained as a solid and was purified by recrystallization from methylcyclohexane, whereupon colorless prisms, m.p. 55.5–57.5°, were obtained.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.21; H, 7.19.

A modification of the method of Kloetzel[19] was used to hydrolyze and decarboxylate α-ethyl-α-carbomethoxytetralone. The ketoester was stirred vigorously for 4 hours at 60° with 200 ml. of 12% sodium hydroxide solution. The reaction was cooled, made slightly acidic with 10% sulfuric acid, and subjected to steam distillation. This distillate was extracted three times with 50-ml. portions of ether. The ether extracts were combined and dried over anhydrous sodium sulfate. The ether was removed *in vacuo* and the remaining oil was subjected to fractional distillation *in vacuo*, whereupon a yield of 70% (12 g.) of α-ethyltetralone X was obtained, b.p. 74–75° (0.2 mm.), $n^{25}D$ 1.5460.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.63; H, 7.89.

α-Ethyltetralone (X) was chlorinated in the manner previously described for the preparation of XII. Thus, from 14.13 g. (0.08 mole) of α-ethyltetralone in 100 ml. of acetic acid, a yield of 85% (15.4 g.) of pure XIII was obtained. Crystallization from petroleum ether (b.p. 30–60°) yielded the 2-chloro-2-ethyl-3,4-dihydro-1(2H)-naphthalenone XIII as colorless prisms, m.p. 47.5–49°.

Anal. Calcd. for $C_{12}H_{13}ClO$: C, 69.06; H, 6.28; Cl, 16.99. Found: C, 68.92; H, 6.19; Cl, 17.20.

Reaction of α-Methyl-α-chlorotetralone (XII) with Sodium Methoxide.—A calculated amount of XII (2.85 g., 0.015 mole) was dissolved in 25 ml. of anhydrous methanol. The solution was heated to reflux temperature in a 125-ml. erlenmeyer flask and 25 ml. of a 2.96 *M* solution of sodium methoxide (0.075 mole) was introduced into the boiling reaction mixture by means of a pipet. The boiling was continued for 5 minutes and the reaction mixture was poured on cracked ice. The organic material was extracted with three 50-ml. portions of ethyl ether. The ether extracts were combined and dried over anhydrous sodium sulfate. After filtration through glass wool, the ether was removed *in vacuo*. The remaining oil was dissolved in 10 ml. of acetic acid and poured on cracked ice, whereupon XII precipitated. Recrystallization from petroleum ether (b.p. 30–60°) yielded 0.3 g. (10%) of starting material XII, m.p. 38–39°.

The water portion of the original reaction mixture was treated with Dry Ice until no further precipitation appeared. The solid was removed by filtration and recrystallized from petroleum ether (b.p. 30–60°). A yield of 64% (1.5 g.) of 2-methyl-1-naphthol (XIV) was obtained, m.p. 64–65° (recorded 63–64°).[21]

A small amount of XIV (0.2 g.) was dissolved in 3 ml. of ethyl ether. The solution was heated to reflux temperature and a saturated solution of picric acid in ethyl ether was added dropwise until the reaction mixture became saturated. After boiling for a short time the reaction mixture turned blood-red in color. At the end of 15 minutes, benzene (5 ml.) was added and the excess ether was removed

(16) R. Lesser and G. Gad, *Ber.*, **56**, 972 (1923).

(17) R. Willstätter and L. Schuler, *ibid.*, **61**, 362 (1928).

(18) W. E. Bachmann and D. G. Thomas, THIS JOURNAL, **63**, 598 (1941).

(19) M. C. Kloetzel, *ibid.*, **62**, 1708 (1940).

(20) W. E. Bachmann and J. C. Sheehan, *ibid.*, **63**, 2598 (1941).

(21) M. Tishler, L. F. Fieser and N. L. Wendler, *ibid.*, **62**, 2866 (1940).

by heating. On cooling, the picrate crystallized in large blood-red needles, m.p. 129–131° (recorded 133–134°).[22]

Reaction of α-Ethyl-α-chlorotetralone (XIII) with Sodium Methoxide.—The α-chloroketone XIII (6.15 g., 0.03 mole was treated with an excess of sodium methoxide solution (0.15 mole) following the procedure previously described for XII. 2-Ethyl-1-naphthol (XV) was obtained in 63% yield (2.95 g.), m.p. 68–69° (recorded 69°).[23] Starting material XIII was isolated in 7% yield (0.45 g.). The picrate of XV was obtained in the same manner previously described for that of XIV and crystallized from benzene in blood-red needles, m.p. 119–120° (recorded 119.5°[23] and 123°[24]).

(22) J. W. Cornforth, R. H. Cornforth and R. Robinson, *J. Chem. Soc.*, 168 (1943).

(23) G. Levy, *Compt. rend.*, **195**, 801 (1932).

(24) M. Akram, R. D. Desai and A. Kamal, *Proc. Indian Acad. Sci.*, **11A**, 139 (1940).

DETROIT, MICHIGAN

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

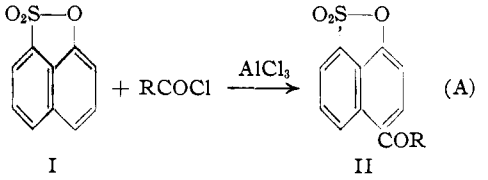
The Chemistry of Sultams. I. Friedel–Crafts Reactions of 1,8-Naphthosultam and its Derivatives. The Rearrangement of N,N-Di-(*p*-toluenesulfonyl)-aniline, N-Acyl- and N-Arylsulfonyl-1,8-naphthosultam Derivatives

BY AHMED MUSTAFA AND MOHAMED IBRAHIM ALI

RECEIVED FEBRUARY 23, 1955

1,8-Naphthosultam (IIIa), the nitrogen analog of 1-naphthol-8-sulfonic acid sultone, and its N-methyl derivative condense with acyl-, aroyl- and arylsulfonyl chlorides in the presence of aluminum chloride to give good yields of 4-acylated products (*cf.* Tables IIa and IIb). N-Acylated 1,8-naphthosultam derivatives (IIIc, d) undergo migration of the acyl group under the influence of aluminum chloride to give the corresponding 4-acyl derivatives (IVa,b). Similar migrations of the arylsulfonyl groups also have been observed with N,N-di-(*p*-toluenesulfonyl)-aniline and N-arylsulfonyl-1,8-naphthosultam derivatives (IIIe,f). N-Phenylsulfonyl-1,8-naphthosultam (IIIe) undergoes thermal migration of the phenylsulfonyl group when refluxed with nitrobenzene or aniline. When IIIe is refluxed with aniline, IIIa and benzenesulfonanilide are isolated besides IVd (scheme B).

Recently, it has been shown that aryl sultones, *e.g.*, 1-naphthol-8-sulfonic acid sultone[1] (I), undergo the Friedel–Crafts reaction to give good yields of 4-acylated 1-naphthol-8-sulfonic acid sultone (II) (*cf.* A) without the cleavage of the sultone ring.

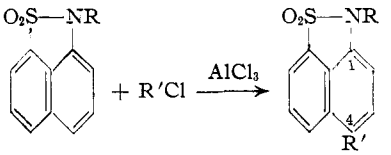


(A)

I II

We now have investigated the behavior of 1,8-naphthosultam (IIIa), the nitrogen analog of I, toward acylating agents in the presence of aluminum chloride. Thus, when IIIa is treated with acetyl, benzoyl, *p*-nitrobenzoyl, benzenesulfonyl and *p*-toluenesulfonyl chlorides under the same experimental conditions described for the acylation of I, the corresponding 4-acyl-, 4-aroyl- and 4-arylsulfonyl derivatives of 1,8-naphthosultam (IVa-e) (*cf.* Table IIa) are obtained in good yields. Similarly, N-methyl-1,8-naphthosultam (IIIb) leads to the formation (Table IIb) of the corresponding 4-acylated products (IVf-l).

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. The structure of the reaction products was not rigorously proved. It seemed probable, by analogy with the behavior of I and α-naphthyl ethers,[2] that the acyl group in IV occupied the 4-position of the nucleus more preferably than the 2-position.



IIIa, R = H; b, R = CH_3
c, R = $COCH_3$; d, R = COC_6H_5
e, R = $SO_2C_6H_5$; f, R = $SO_2C_6H_4CH_3$-*p*
g, R = $COC_6H_4NO_2$-*p*

IVa, R = H, R′ = $COCH_3$
b, R = H, R′ = COC_6H_5
c, R = H, R′ = $COC_6H_4NO_2$-*p*
d, R = H, R′ = $SO_2C_6H_5$
e, R = H, R′ = $SO_2C_6H_4CH_3$-*p*
f, R = CH_3, R′ = $COCH_3$
g, R = CH_3, R′ = COC_6H_5
h, R = CH_3, R′ = $COC_6H_4NO_2$-*p*
i, R = CH_3, R′ = COC_6H_4Cl-*p*
j, R = CH_3, R′ = $SO_2C_6H_5$
k, R = CH_3, R′ = $SO_2C_6H_4CH_3$-*p*
l, R = CH_3, R′ = $COCH_2CH_2COOH$

When N-phenylsulfonyl-1,8-naphthosultam (IIIe) is allowed to undergo the Friedel–Crafts acylation reaction, the phenylsulfonyl group is eliminated and the corresponding 4-acyl derivatives (*cf.* Table IIa) are obtained. The production of 4-acyl derivatives, not contaminated with 4-phenylsulfonyl-1,8-naphthosultam (IVd), is unusual in that IIIe is isomerized into IVd by treatment with aluminum chloride (see below). Thus when IIIe is allowed to react with acetyl, benzoyl and *p*-toluenesulfonyl chlorides, IVa, IVb and IVe are obtained, respectively. The formation of IVd, on treatment of IIIe with benzenesulfonyl chloride in presence of

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

(2) There have been several reports of the reactions of IIIa and its N-substituted derivatives which showed similarity to α-naphthol and α-naphthyl ethers, *e.g.*, the behavior of IIIa toward chlorine (T. Zincke and G. Schürmann, *Ann.*, **412**, 718 (1916)), in condensation with isatin, isatin chloride and isatinanilide (P. Friedlander and L. Sander, *Ber.*, **57**, 637 (1924); W. König and E. Wagner, *ibid.*, **57**, 1056 (1924)) and in the coupling with diazotized solutions (W. König and J. Keil, *Ber.*, **55**, 2149 (1922) and W. König and K. Köhler, *ibid.*, **55**, 2139 (1922); *cf.* also A. Mustafa, *Chem. Revs.*, **54**, 195 (1954)).