

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

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

(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).

(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]

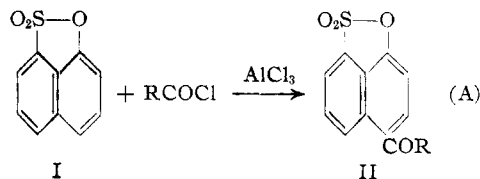
The Chemistry of Sultams. I. Friedel-Crafts Reactions of 1,8-Naphthosultam and its Derivatives. The Rearrangement of N,N-Di-(*p*-toluenesulfonyl)-aniline, N-Acyl- and N-Arylsulfonyl-1,8-naphthosultam Derivatives

By AHMED MUSTAFA AND MOHAMED IBRAHIM ALI

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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 sultone¹ (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.



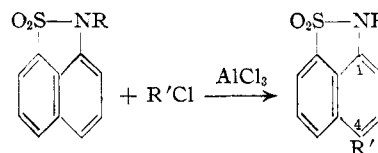
We now have investigated the behavior of 1,8-naphthosultam (IIIa), the nitrogen analog of I, toward acylating agents in the presence of aluminum chloride. Thus, when IIIa is treated with acetyl, benzoyl, *p*-nitrobenzoyl, benzenesulfonyl and *p*-toluenesulfonyl chlorides under the same experimental conditions described for the acylation of I, the corresponding 4-acyl-, 4-aroyle- 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

(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. Friedländer and L. Sander, *Ber.*, **57**, 637 (1924); W. König and E. Wagner, *ibid.*, **57**, 1056 (1924)) and in the

the acyl group in IV occupied the 4-position of the nucleus more preferably than the 2-position.



- IIIa, R = H; b, R = CH₃
 c, R = COCH₃; d, R = COC₆H₅
 e, R = SO₂C₆H₅; f, R = SO₂C₆H₄CH₃-*p*
 g, R = COC₆H₄NO₂-*p*
 IVa, R = H, R' = COCH₃
 b, R = H, R' = COC₆H₅
 c, R = H, R' = COC₆H₄NO₂-*p*
 d, R = H, R' = SO₂C₆H₅
 e, R = H, R' = SO₂C₆H₄CH₃-*p*
 f, R = CH₃, R' = COCH₃
 g, R = CH₃, R' = COC₆H₅
 h, R = CH₃, R' = COC₆H₄NO₂-*p*
 i, R = CH₃, R' = COC₆H₄Cl-*p*
 j, R = CH₃, R' = SO₂C₆H₅
 k, R = CH₃, R' = SO₂C₆H₄CH₃-*p*
 l, R = CH₃, R' = COCH₂CH₂COOH

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

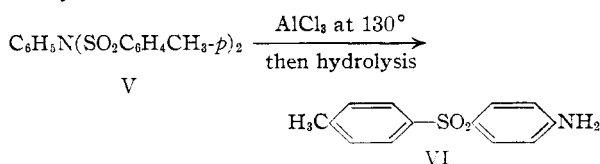
coupling with diazotized solutions (W. König and J. Keil, *Ber.*, **55**, 2149 (1922) and W. König and K. Köhler, *ibid.*, **55**, 2139 (1922); cf. also A. Mustafa, *Chem. Revs.*, **54**, 195 (1954)).

aluminum chloride, also may be attributed to the isomerization of the phenylsulfonyl group.

Rearrangement of N,N-Di-(*p*-toluenesulfonyl)-aniline and N-Acyl- and N-Arylsulfonyl-1,8-naphthosultam Derivatives by the Action of Aluminum Chloride.—The literature contains scattered references to the migration of acyl groups from nitrogen in the side chain to carbon of the aromatic nucleus, *i.e.*, Fries-like rearrangements. The rearrangement of diacetyl- and dibenzoylaniline to *p*-aminoketones under the influence of fused zinc chloride, and the isomeric rearrangement of monoacylanilines under the influence of aluminum chloride to *p*-aminoketones, *via* the initial formation of acetyl chloride, which then attacks the nucleus with the aid of the condensing agent, has been studied recently by Dippy and his co-workers,³ who favor an intermolecular mechanism. Similar isomeric rearrangements also occur when 1-acetylindoles and 9-acetylcarbazoles are heated with aluminum chloride.⁴

We now have investigated the migration of the acyl group in N-acylated 1,8-naphthosultam derivatives and in these experiments aluminum chloride was used as a catalyst and nitrobenzene as a solvent. Thus, when N-acetyl-, N-benzoyl-, N-*p*-nitrobenzoyl-1,8-naphthosultam are heated with aluminum chloride the corresponding 4-acyl derivatives (*cf.* Table IIa) are obtained.

The migration of arylsulfonyl groups in N-arylsulfonated compounds, similar to the Fries rearrangement,⁵ seems not to have been investigated. We now have found that when N,N-di-(*p*-toluenesulfonyl)-aniline (V) is heated with aluminum chloride at 130° for one hour, *p*-aminophenyl *p*-tolyl sulfone (VI) is obtained after the hydrolysis of the reaction product with 70% sulfuric acid. Treatment of V with sulfuric acid under the same experimental conditions does not lead to any rearrangement and aniline is isolated in an almost quantitative yield.



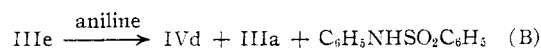
Similar migrations now have been observed when IIIe and IIIf are heated with aluminum chloride for four hours at 100° in nitrobenzene or for one hour at 130–140° with or without the solvent, yielding IVd and IVe, respectively. IIIe is stable when its nitrobenzene solution is heated alone for the same period at 100 or at 130° (see below).

Favorable results were obtained only when a high molecular proportion (2.5 moles) of aluminum chloride was used. This is consistent with the mechanism proposed by Dippy and Wood,³ and it is be-

lieved that similar lines to those proposed by the same authors for the rearrangement of N,N-diacylanilines could be applied here.

Rearrangement of N-Phenylsulfonyl-1,8-naphthosultam by the Action of Heat Alone.—Meyer and Hofmann⁶ have shown that the production of traces of *o*- and *p*-aminoacetophenone could take place by strongly heating acetanilide alone. We now have found that, whereas IIIId and V are recovered almost unchanged when their solutions in nitrobenzene are refluxed for ten hours, IIIe undergoes migration of the phenylsulfonyl group giving rise to IVd in a small yield under the same experimental conditions.

The thermal migration of the phenylsulfonyl group also has been observed when IIIe is refluxed with freshly distilled aniline for eight hours, yielding, beside the rearranged product IVd, benzenesulfonanilide and 1,8-naphthosultam (IIIa). The formation of the latter two products may be attributed to the cleavage of the N–S bond by aniline, accompanied by the formation of IIIa (*cf.* scheme B). IIIe is stable toward the action of aniline when heated at 100° for 15 hours.



Experimental

General Friedel-Crafts Procedure.—In all experiments described in Tables IIa and IIb, 0.01 mole of the naphthosultam and 0.025 mole of aluminum chloride in the case of IIIa and 0.015 mole in the case of IIIb were used, respectively. A solution of the naphthosultam in 25 ml. of freshly distilled nitrobenzene and 0.02 mole of the acyl chloride was treated with aluminum chloride in portions as rapidly as it dissolved. The reactants were maintained at 60–70° for one hour, then at 100° for four hours, followed by hydrolysis with about 150 ml. of ice-water containing 25 ml. of concentrated hydrochloric acid. The aqueous layer was separated from the organic layer; the latter was washed twice with water and the solvent was removed by steam distillation. With naphthosultam, the dark brown residual mass was extracted several times with cold aqueous sodium hydroxide solution (200 ml., 5%). The alkaline extract was acidified with cold dilute hydrochloric acid, and the resulting solid was crystallized from the solvent specified in Table IIa. The products from N-methylnaphthosultam were worked up in the usual way (Table IIb). Fractional crystallization of the reaction products did not raise the melting point.

IVa–e dissolve in aqueous sodium hydroxide with greenish-yellow coloration (orange color with IVc).

The presence of the "imino group" in the reaction products of naphthosultam has been detected by the ready methylation of IVa and IVe to form IVf and IVk, respectively (see below).

Methylation of IVa and IVe.—When 1-g. quantities of IVa and IVe were treated with 2 ml. of dimethyl sulfate in the presence of 20 ml. of aqueous sodium hydroxide (10%) in the usual manner, colorless substances separated. IVf was filtered off, washed thoroughly with water and crystallized from acetic acid (*ca.* 0.62 g.), m.p. 145°. It does not depress a sample of IVf prepared as above. IVk, m.p. 230° (m.p. and mixed m.p.), was obtained in about 75% yield.

Preparation of N-Acyl-, N-Aroyl- and N-Arylsulfonyl-1,8-naphthosultam Derivatives (IIIc–g).—A solution of 5 g. of IIIa (0.025 mole) in 30 ml. of freshly distilled pyridine was treated with 0.03 mole of the acyl chloride: namely, acetyl-, benzoyl-, *p*-nitrobenzoyl-, benzenesulfonyl- and *p*-toluenesulfonyl chloride, respectively. The reaction mixture was heated for one hour (steam-bath), cooled and then poured into 100 ml. of ice-cold water. The solid (IIIc–g) that separated was filtered off and crystallized from the solvent specified in Table I.

(6) H. Meyer and A. Hofmann, *Monatsh.*, **36**, 707 (1915).

(3) J. F. Dippy and J. H. Wood, *J. Chem. Soc.*, 2719 (1949); J. F. Dippy and V. Moss, *ibid.*, 2205 (1952).

(4) W. J. Gaudion, W. H. Hook and S. G. P. Plant, *ibid.*, 1631 (1947); S. G. P. Plant, K. M. Rogers and B. S. C. Williams, *ibid.*, 741 (1935).

(5) J. H. Amin, R. D. Desai, K. Parekh and K. Venkataraman (*J. Scientific Ind. Res.*, **13B**, 181 (1954)) have shown that aryl *p*-toluenesulfonates of phenols undergo the Fries migration smoothly at 130–140° and that most of the migrations take place in the para position to the hydroxyl group.

TABLE I
 N-ACYL-1,8-NAPHTHOSULTAM DERIVATIVES (III)

Naphthosultam derivative ^a	M.p., °C.	Yield, %	Solvent for cryst.	Color with H ₂ SO ₄	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
IIIc ^b	188-189	78	Acetic acid	C ₁₂ H ₉ NO ₃ S	58.3	58.1	3.6	3.5	5.7	5.5	12.9	12.8
IIId	155-156	83	Acetic acid	Green	C ₁₇ H ₁₁ NO ₃ S	66.0	66.1	3.6	3.6	4.5	4.5	10.4	10.2
IIIe ^c	196	89	Chloroform	No color	C ₁₆ H ₁₁ NO ₄ S ₂	55.7	55.6	3.2	3.1	4.0	3.8	18.6	18.5
IIIf	208-209	87	Chloroform	No color	C ₁₇ H ₁₃ NO ₄ S ₂	56.8	56.4	3.6	3.5	3.9	3.8	17.8	17.7
IIIg	203	83	Chloroform	Yellow	C ₁₇ H ₁₀ N ₂ O ₃ S	57.6	57.3	2.8	2.5	7.9	7.6	9.0	8.9

^a The naphthosultam derivatives are insoluble in cold aqueous sodium hydroxide solution (8%); a yellowish color appears on boiling. ^b Cf. T. Zincke and C. Jülicher, *Ann.*, **411**, 195 (1916). ^c Cf. A. Mustafa and O. H. Hishmat, *THIS JOURNAL*, **75**, 4649 (1953).

 TABLE IIa
 FRIEDEL-CRAFTS REACTION WITH 1,8-NAPHTHOSULTAM (IIIa)^f

Reacn. prod. IV	M.p., °C.	Yield, %	Color with H ₂ SO ₄	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
IVa ^a	Above 300	62	Ill defined	C ₁₂ H ₉ NO ₃ S	58.3	58.5	3.6	3.6	5.7	5.7	12.9	12.7
IVb ^b	228-230	72	Yellow	C ₁₇ H ₁₁ NO ₃ S	66.0	66.1	3.6	3.7	4.5	4.2	10.4	10.1
IVc ^a	268-269	57	Orange	C ₁₇ H ₁₃ N ₂ O ₃ S	57.6	57.3	2.8	2.8	7.9	7.7	9.0	8.7
IVd ^a	259-260	59	No color	C ₁₆ H ₁₁ NO ₄ S ₂	55.7	55.8	3.2	3.2	4.0	4.0	18.6	18.5
IVe ^a	277-279	55	No color	C ₁₇ H ₁₃ NO ₄ S ₂	56.8	56.8	3.6	3.3	3.9	3.5	17.8	17.8

 TABLE IIb
 FRIEDEL-CRAFTS REACTION WITH N-METHYL-1,8-NAPHTHOSULTAM (IIIb)^{d,e}

Reacn. prod. IV	M.p., °C.	Yield, %	Color with H ₂ SO ₄	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
IVf ^b	145-146	63	Green	C ₁₈ H ₁₁ NO ₃ S	59.8	59.7	4.2	4.1	5.4	5.4	12.3	12.3
IVg ^b	193-194	75	Yellow	C ₁₈ H ₁₃ NO ₃ S	66.9	66.5	4.0	4.0	4.3	4.1	9.9	9.8
IVh ^b	223-225	78	Orange	C ₁₈ H ₁₂ N ₂ O ₃ S	58.7	58.4	3.3	3.4	7.6	7.4	8.7	8.5
IVi ^b	185-186	82	Orange	C ₁₈ H ₁₂ ClNO ₃ S ^c	60.4	60.4	3.4	3.4	3.9	3.6	8.9	8.6
IVj ^b	209-210	67	No color	C ₁₇ H ₁₃ NO ₄ S ₂	56.8	56.5	3.6	3.5	3.9	3.7	17.8	17.8
IVk ^a	232-234	63	No color	C ₁₈ H ₁₃ NO ₄ S ₂	57.9	57.8	4.0	4.1	3.7	3.6	17.2	17.0
IVl ^a	213-214	58	Brownish-green	C ₁₈ H ₁₃ NO ₆ S	56.4	56.1	4.1	4.1	4.4	4.3	10.0	9.9

^a Nitrobenzene. ^b Acetic acid. ^c Calcd.: Cl, 9.9. Found: Cl, 10.0. ^d The reaction products are insoluble in aqueous sodium hydroxide. ^e For preparation cf. W. König and K. Köhler, *Ber.*, **55**, 2139 (1922). ^f Cf. F. Dannerth, *THIS JOURNAL*, **29**, 1323 (1907).

With IIIc, the addition of acetyl chloride was carried out at 0°, and the reaction mixture was kept at room temperature for three hours.

Rearrangement with Aluminum Chloride of: (a) N,N-Di-(*p*-toluenesulfonyl)-aniline (V).—When a mixture of 2 g. of V and 1.8 g. of aluminum chloride was heated in an oil-bath, the evolution of hydrogen chloride fumes started at about 100°. The temperature was raised slowly to 130°, and the reaction maintained at that temperature for one hour. The dark colored reaction mixture was cooled; then it was decomposed with 100 ml. of ice-water containing 5 ml. of concentrated hydrochloric acid. The solid, so obtained, was collected and refluxed with 30 ml. of 70% sulfuric acid for six hours³ when it went into solution almost completely. The reaction mixture was cooled, diluted with water and filtered from the carbonaceous matter. The filtrate was rendered alkaline, extracted with ether, dried and evaporated. The resulting solid was crystallized from a mixture of benzene and light petroleum (b.p. 40-60°), as colorless crystals (*ca.* 0.5 g.), m.p. 181°, which was identified as *p*-aminophenyl *p*-tolyl sulfone (VI) by m.p. and mixed m.p. determination.⁷

Two grams of V was treated with sulfuric acid as described above. The clear reaction mixture was cooled, rendered alkaline with aqueous sodium hydroxide solution, extracted with ether, dried and evaporated. The oily residue was identified as aniline *via* the formation of benzanilide by the action of benzoyl chloride in the presence of sodium hydroxide solution (Schotten-Baumann) in an almost quantitative yield based on the theoretical yield of aniline formed.

(b) N-Acyl-, N-Aroyl- and N-Arylsulfonyl-1,8-naphthosultam Derivatives.—The rearrangement of IIIc, IIId and IIIe was carried out by heating a solution of 0.01 mole of

each in 15 ml. of nitrobenzene and 0.025 mole of aluminum chloride for four hours (steam-bath). The reaction products (IVa, IVb, IVd) were worked up as described above and were obtained in 52, 58 and 56% yield, respectively.

The experiment was repeated using the same quantity of IIIe, IIIf and IIIf, but the reaction mixture was heated in an oil-bath at 130° for one hour. On working up the reaction mixtures, IVd, IVe and IVc were obtained in 71, 68 and 75% yield, respectively.

Two grams of IIIe was heated with 2 g. of aluminum chloride at 130° for one hour, but without the use of nitrobenzene. The dark brown mass, so obtained, was worked up in the usual manner and IVd (*ca.* 43%) was obtained.

Action of Heat on IIId, V and IIIe.—A solution of 1.5 g. of each of IIId, V and IIIe in 20 ml. of freshly distilled nitrobenzene was refluxed for 10 hours. The solvent was removed by steam distillation and the reaction products were worked up in the usual manner. IIId and V were recovered almost unchanged, whereas IIIe underwent rearrangement to give IVd in *ca.* 30% yield.

Action of Aniline on IIIe.—A mixture of 4 g. of IIIe and 15 ml. of freshly distilled aniline was heated for 15 hours (steam-bath). The reaction mixture was cooled, poured into 100 ml. of ice-cold water containing 20 ml. of concentrated hydrochloric acid, and the solid, so obtained, was crystallized from a mixture of chloroform and light petroleum (b.p. 40-60°) as colorless crystals (*ca.* 3.8 g.), m.p. 195°; identified as unchanged IIIe (m.p. and mixed m.p. determination).

The experiment was repeated with the same quantities of IIIe and aniline, but the reaction mixture was refluxed for eight hours. It was worked up as described above and the solid, so obtained, was extracted with hot light petroleum (b.p. 40-60°, *ca.* 100 ml.), then with petroleum ether (b.p. 80-100°, *ca.* 100 ml.) and the insoluble part was crystallized from benzene as colorless crystals (*ca.* 0.93 g.),

(7) E. Knüsli, *Gazz. chim. ital.*, **79**, 621 (1949); *C. A.*, **44**, 4438 (1950).

m.p. 258–260°, identified as IVd (m.p. and mixed m.p. determination).

The light petroleum extract, on slow evaporation, gave colorless crystals (ca. 1.3 g.), m.p. 110°, identified as benzenesulfonanilide (m.p. and mixed m.p.).

The petroleum ether extract gave, on concentration, colorless crystals (ca. 1.5 g.), m.p. 177°, which were identified as IIIa (m.p. and mixed m.p.).

CAIRO, EGYPT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

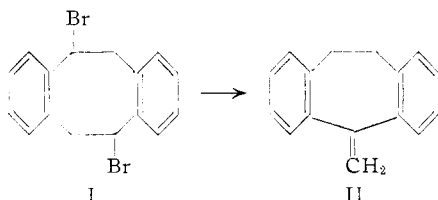
Cyclic Polyolefins. XXXVII. Ring Contraction in Dehydrobromination of 7-Bromo-1,2,5,6-dibenz-1,3,5-cyclooctatriene

By ARTHUR C. COPE AND RONALD DEAN SMITH

RECEIVED MARCH 12, 1955

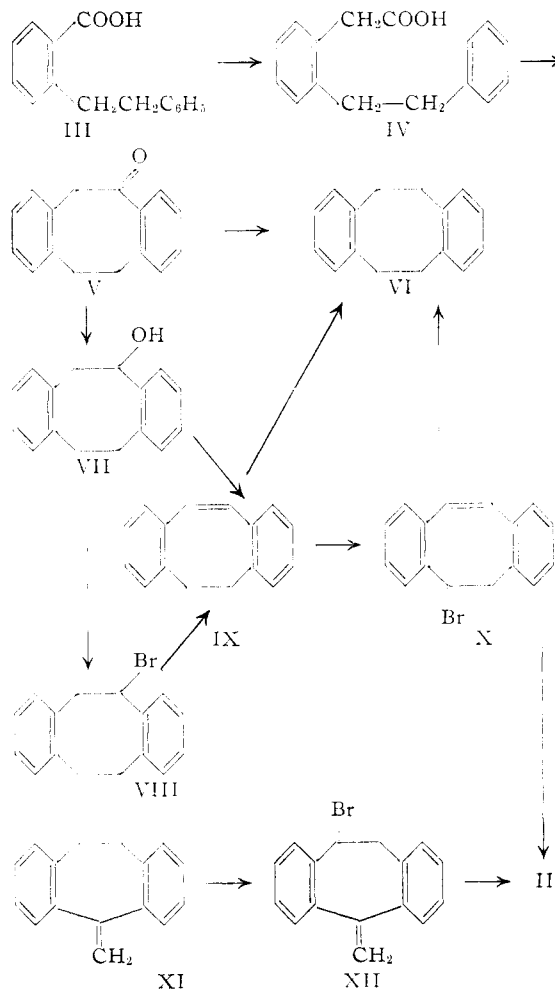
The dehydrobromination of 3-bromo-1,2,5,6-dibenz-1,5-cyclooctadiene (VIII) by α -picoline proceeds without rearrangement, forming 1,2,5,6-dibenz-1,3,5-cyclooctatriene (IX), while dehydrobromination of 7-bromo-1,2,5,6-dibenz-1,3,5-cyclooctatriene (X) occurs with molecular rearrangement to give 1-methylene-2,3,6,7-dibenzcycloheptatriene (II). 4-Bromo-1-methylene-2,3,6,7-dibenz-2,6-cycloheptadiene (XII) also gives II on dehydrobromination.

The rearrangement of 3,7-dibromo-1,2,5,6-dibenz-1,5-cyclooctadiene (I) to 1-methylene-2,3,6,7-dibenzcycloheptatriene (II) on dehydrobromination by amines was described in a previous communication.¹ This paper reports a study of the dehydrobromination of compounds related to I and II designed to determine the step at which molecular rearrangement occurs. 3-Bromo-1,2,5,6-dibenz-1,5-cyclooctadiene (VIII), 7-bromo-1,2,5,6-dibenz-1,3,5-cyclooctatriene (X), and 4-bromo-1-methylene-2,3,6,7-dibenz-2,6-cycloheptadiene (XII) were synthesized, and the structures of their dehydrobromination products were determined.



It has been shown that the reaction of 1,2,5,6-dibenz-1,5-cyclooctadiene (VI) with one molar equivalent of N-bromosuccinimide gives none of the monobromide VIII. Instead, a mixture of the dibromide I and unchanged VI is obtained.² Therefore, for the preparation of VIII, *o*-(β -phenylethyl)-benzoic acid (III) was converted to *o*-(β -phenylethyl)-phenylacetic acid (IV) by the Newman-Beal modification of the Arndt-Eistert sequence³ in an overall yield of 53%. Cyclization of the acid IV to 1,2,5,6-dibenz-1,5-cyclooctadiene-3-one (V) was effected in 90–93% yield by polyphosphoric acid. To our knowledge this is the only reported case of a ring closure in good yield to an eight-membered cyclic ketone by polyphosphoric acid. The effect of the *ortho* substituted benzene ring in the acid IV on the ease of ring closure is remarkable, for the treatment of ϵ -phenylcaproic acid with polyphosphoric acid gives only small amounts of 1,2-benzcyclooct-1-ene-3-one.⁴ The structure of the ketone V was established by its hydrogenation in the presence of a palladium catalyst to the known hydrocar-

bon VI.^{2,5,6} Wolff-Kishner reduction of V also gave VI. Reduction of V with sodium borohydride afforded 1,2,5,6-dibenz-1,5-cyclooctadiene-3-ol (VII) in 97% yield. The bromide VIII was obtained in 91% yield on treatment of VII with anhydrous hydrogen bromide in benzene at 0°.



(1) A. C. Cope and S. W. Fenton, *THIS JOURNAL*, **73**, 1673 (1951).

(2) A. C. Cope and S. W. Fenton, *ibid.*, **73**, 1668 (1951).

(3) M. S. Newman and P. F. Beal, *ibid.*, **72**, 5163 (1950).

(4) Unpublished observations of R. D. Smith and W. R. Moore.

(5) W. Baker, R. Banks, D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, 27 (1945).

(6) L. F. Fieser and M. M. Pechet, *THIS JOURNAL*, **68**, 2577 (1946).