[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE VIRGINIA POLYTECHNIC INSTITUTE]

An Unusual Elbs-type Reaction Observed during a Study of the Cyclization of Ketones[1,2]

BY FRANK A. VINGIELLO, ALEXEJ BOŘKOVEC AND WALTER ZAJAC, JR.

RECEIVED OCTOBER 24, 1957

Using previously described methods, the synthesis of three new ketimine hydrochlorides, six new ketones and six new hydrocarbons has been accomplished. It has been observed that certain ketones undergo both an Elbs-type reaction and a Bradsher aromatic cyclodehydration reaction under the same experimental conditions.

In an attempt to broaden Bradsher's aromatic cyclodehydration reaction[3] we undertook to study the cyclization of two 2-benzylphenyl naphthyl ketones and four 2-(naphthylmethyl)-phenyl naphthyl ketones. The first ketone studied was 2-benzylphenyl 1-naphthyl ketone (I). The cyclization required drastic conditions and the results were quite surprising. High temperature acid-catalyzed cyclization[4] gave 9-(1-naphthyl)-anthracene (II) and 10-phenyl-1,2-benzanthracene (III) in approximately equal quantities. Cyclization of the same ketone using the recently developed alumina method[5] gave mainly 10-phenyl-1,2-benzanthracene (III) and only a small amount of 9-(1-naphthyl)-anthracene (II). Compound II was expected as the normal product of the acid-catalyzed cyclization of ketone I according to all previous work[6]; however, the presence of compound III was surprising, indeed, and the cyclization seems to have followed a path similar to an Elbs reaction.[7] Such reactions were thought to occur only at higher temperatures and with no solvent or catalyst present.

The acid-catalyzed cyclization of the isomeric ketone IV gave exclusively 9-(2-naphthyl)-anthracene (V) in excellent yield. The alumina cyclization on the other hand yielded not only the expected hydrocarbon V but also a considerable amount of the Elbs-type product 9-phenyl-1,2-benzanthracene (VI).

The acid and alumina cyclizations of 2-(1-naphthylmethyl)-benzophenone and 2-(2-naphthylmethyl)-benzophenone (isomers of ketones I and II) have been reported previously[4-6] and in every case only the product resulting from aromatic cyclodehydration was obtained and in excellent yield. On the basis of the study of Vingiello, Van Oot and Hannabass[8] on the mechanism of aromatic cyclodehydration, cyclization should proceed more readily into a naphthyl ring than into a phenyl ring. Elbs reactions are also thought to proceed more readily into a naphthyl ring than into a phenyl ring.[9]

The acid and alumina cyclizations of ketones VII and IX proceeded smoothly and in good yield to give VIII and X, respectively. Examination of the structures of these two ketones reveals that the naphthyl groups in each ketone are identical. Consequently cyclization by a Bradsher-type aromatic cyclodehydration or by an Elbs-type ring closure would result in the same product and the product isolated does not reveal the reaction path.

Cyclization of ketone XI by either acid or alumina gave a good yield of the aromatic cyclodehydration product XII.

The acid cyclization of ketone XIII gave surprising results. The reaction required vigorous conditions and yielded only 10-(2-naphthyl)-1,2-benzanthracene resulting apparently from an Elbs-type ring closure. None of the expected 9-(1-naphthyl)-1,2-benzanthracene could be isolated. On the other hand, alumina cyclization of XIII gave only the product of aromatic cyclodehydration (XIV).

Considering the acid cyclizations of the four isomeric 2-(naphthylmethyl)-phenyl naphthyl ketones, we find that as the carbonyl group becomes increasingly sterically hindered the yield of aromatic cyclodehydration product decreases (see Table I). Finally, the most hindered ketone (XIII) fails to give any aromatic cyclodehydration product and only Elbs-type product is obtained. If electronic effects were paramount, ketone IX should undergo aromatic cyclodehydration the easiest and ketone VII should be the most difficult to cyclize. Since this is not the case, it appears that the steric factor is most important in governing the path of cyclization of these four isomeric ketones.

TABLE I

Ketone	Yield of product, % Aromatic cyclodehydration	Elbs-type
XI	95	..
VII	68	..
IX	61	..
XIII	..	48

Acknowledgment.—This work was sponsored by the Office of Ordnance Research, U. S. Army, and by the Research Corporation of New York.

Experimental[10,11]

2-(2-Naphthylmethyl)-phenyl 1-Naphthyl Ketone (XIII).—A Grignard reagent was prepared from 3.8 g. (0.15 mole)

---

(1) Presented in part before the Division of Organic Chemistry at the 129th Meeting of the American Chemical Society, Dallas, Texas, April, 1956, and in part before the Division of Organic Chemistry at the XVIth International Congress of Pure and Applied Chemistry, Paris, July, 1957.

(2) This paper has been abstracted from the Doctorate thesis of Mr. Alexej Bořkovec and the Masters thesis of Mr. Walter Zajac, Jr., presented to the Virginia Polytechnic Institute in 1955 and 1956, respectively.

(3) C. K. Bradsher, THIS JOURNAL, **62**, 486 (1940).

(4) F. A. Vingiello, A. Bořkovec and J. Shulman, *ibid.*, **77**, 2320 (1955).

(5) F. A. Vingiello and A. Bořkovec, *ibid.*, **78**, 3205 (1956).

(6) F. A. Vingiello and A. Bořkovec, *ibid.*, **77**, 4823 (1955), and references listed there.

(7) L. F. Fieser, The Elbs Reaction, in "Organic Reactions," Vol. I, R. Adams (editor), John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 129–155.

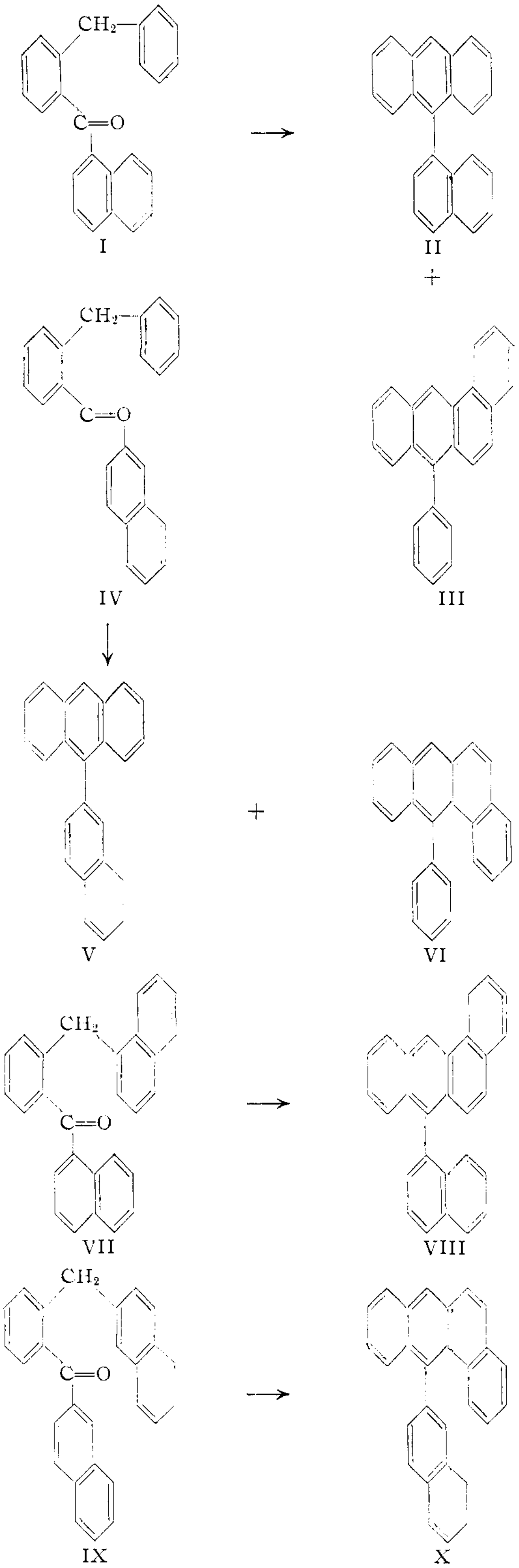
(8) F. A. Vingiello, J. G. Van Oot and H. H. Hannabass, THIS JOURNAL, **74**, 4546 (1952).

(9) W. E. Bachmann, *J. Org. Chem.*, **1**, 347 (1937).

(10) All melting points are corrected.

(11) All the analyses were carried out by the Micro-Tech Laboratories, Skokie, Ill.

of magnesium and 32.7 g. (0.16 mole) of 1-bromonaphthalene in 150 ml. of dry ether. After all the magnesium had reacted the ether was replaced with 150 ml. of dry toluene and a solution of 25 g. (0.10 mole) of 2-(2-naphthylmethyl)-benzonitrile[6] in 75 ml. of dry toluene was added slowly. The mixture was then heated under reflux overnight, cooled and decomposed with a 20% ammonium chloride solution.[12] The toluene layer, which possessed a strongly yellow-green fluorescence, was decanted from the hard residue, washed with water and concentrated. The residual oil and 85 ml. of 40% sulfuric acid was sealed in a Carius tube and heated in a Carius furnace for six hours at 180°. The tube was cooled and the brown oil which separated was dissolved in benzene. This solution was washed with water, a 10% sodium bicarbonate solution, again with water and finally concentrated. The residue was fractionated giving a very viscous oil, b.p. 285–289° (1 mm.), yield 21 g. (55%). An analytical sample was prepared by redistilling the oil and collecting a sample after half the material had distilled, b.p. 291° (1 mm.).



I

II

\+

III

IV

V

\+

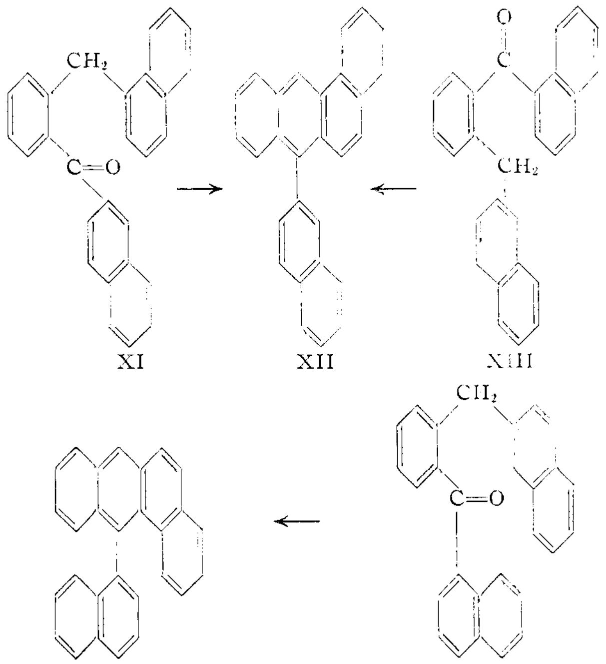
VI

VII

VIII

IX

X



XI

XII

XIII

XIV

Anal. Calcd. for $C_{28}H_{20}O$: C, 90.30; H, 5.41. Found: C, 90.59; H, 5.42.

On standing the ketone solidified and could be recrystallized from ethanol as colorless rods, m.p. 98–98.5°. The other ketones were prepared in a similar way.[12]

9-(2-Naphthyl)-anthracene (V).—A mixture of 1.5 g. of 2-benzylphenyl 2-naphthyl ketone (IV) and 25 g. of alumina[13] was heated at 260–270° for two hours under a reduced pressure (1.5 mm.) and then chromatographed.[14] The first fraction, eluted with 30–60° petroleum ether, yielded 0.63 g. (45%) of 9-(2-naphthyl)-anthracene (V), m.p. 199–200° (see Table IV for analytical data). The second fraction, eluted with a mixture of benzene and petroleum ether (1:4), yielded 0.15 g. (11%) of 9-phenyl-1,2-benzanthracene (VI), m.p. 154° (lit.,[15] m.p. 154–155°). The third fraction, eluted with benzene, yielded *ca.* 0.10 g. of an unidentified yellow oil.

---

(12) In the three cases given below the ketimine hydrochlorides were prepared and isolated; however, it was found that this resulted in a lower yield of ketone. 2-Benzylphenyl 1-naphthylketimine hydrochloride, m.p. 169° dec. from chloroform–ether (1:4), 98%. Calcd. for $C_{24}H_{20}NCl$: N, 3.92. Found: N, 4.35. 2-Benzylphenyl 2-naphthylketimine hydrochloride, m.p. 197° dec. from alcohol–ether (1:5), 80%. Calcd. for $C_{24}H_{20}NCl$: C, 80.54; H, 5.66. Found: C, 80.07; H, 5.38. 2-(1-Naphthylmethyl)-phenyl 1-naphthylketimine hydrochloride, m.p. 186° dec. from alcohol–ether (1:3), 70%. Calcd. for $C_{28}H_{22}NCl$: C, 82.44; H, 5.44. Found: C, 82.42; H, 5.46.

(13) The alumina used in all cyclization experiments was obtained from the Fisher Scientific Co. It was 80–200 mesh and was dried at 300° at 1 mm. for three hours prior to use.

(14) Throughout this work a column (15 mm. × 400 mm.) packed with 80-200 mesh alumina was used.

(15) E. Clar and D. Stewart, *J. Chem. Soc.*, 687 (1951).

TABLE II

NEW KETONES

Ketone	Yield, %	M.p., °C.	B.p., °C.	Mm.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
I	76		215–217	0.8	89.41	89.35	5.63	5.45
IV	85	83	233–234	1.5	89.41	89.30	5.63	5.66
VII	78		285–287	1.5	90.30	90.15	5.41	5.43
IX	57	120.5–121.5	251–252	0.1	90.30	90.55	5.41	5.33
XI	97	99–100	277–279	1,0	90.30	89.98	5.41	5.17
XIII	55	98–98.5	285–289	1.0	90.30	90.59	5.41	5.42

The other alumina cyclizations were carried out using essentially the same procedure and the results are summarized in Table III,

TABLE III

Ketone	Yield of product, % Aromatic cyclodehydration	Yield of product, % Elbs-type	Temp., °C.	Time, hr.
I	4 (II)	49 (III)	240–270	2.5
IV	45 (V)	11 (VI)	260–270	2.0
VII	57 (VIII)	.....	260–280	1.5
IX	47 (X)	.....	260–270	1.5
XI	52 (XII)	.....	280–290	2.0
XIII	34 (XIV)	.....	290–300	2.5

TABLE IV

NEW HYDROCARBONS[a] [b]

Hydrocarbon	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
II	160–161	94.70	94.27	5.30	5.68
V	200	94.70	94.26	5.30	5.43
VIII	190	94.87	94.80	5.13	5.24
X	153	94.87	94.72	5.13	5.27
XII	174–175	94.87	94.67	5.13	5.23
XIV	210–211	94.87	94.33	5.13	5.48

[a] Hydrocarbon VI was first prepared by E. Clar and D, Stewart, *J, Chem. Soc.*, 687 (1951), Hydrocarbon III was first prepared by F, A, Vingiello, A. Bořkovec and J, Shulman, ref. 4. [b] The ultraviolet spectra of all new hydrocarbons were taken with a Beckman spectrophotometer (model DU, 1-cm. silica cell) using 95% ethanol as the solvent, The wave length maxima (λ, mμ) for the hydrocarbons are: II and V (concn. 5 mg./l. from 210–300 mμ and 10 mg./l. from 300–390); II, 223, 250, 256, 285, 330, 347, 365, 385; V, 226, 254, 332, 348, 356, 387, All the other spectra were taken at a concn. of 10 mg./l.: VIII, 224, 260, 272, 281, 292, 319, 337, 390; X, 224, 228, 258, 271, 280, 290, 324, 335, 352, 363, 390; XII, 224, 228, 258, 272, 282, 293, 318, 337, 353, 369, 392; XIV, 224, 260, 270, 281, 292, 320, 337, 371, 390,

10-(1-Naphthyl)-1,2-benzanthracene (VIII),—A mixture of 2.0 g. of 2-(naphthylmethyl)-phenyl 1-naphthyl ketone (VII), 30 ml, of glacial acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated in a Carius furnace for eight hours at 180°. The black solid which formed was separated, dissolved in benzene and washed with water, The solution was concentrated and poured into a column[14] packed with alumina and eluted with a mixture of benzene–petroleum ether (1:5), The percolate was concentrated and the hydrocarbon crystallized; yield 1,3 g, (68%), m.p. 186°, Four recrystallizations from benzene–ethanol (1:3) raised the m.p, to 190° (see Table IV for analytical data),

The other acid cyclizations were carried out using essentially the same procedure and the results are summarized in Table V,

TABLE V

Ketone	Yield of product, % Aromatic cyclodehydration	Yield of product, % Elbs-type
I	45 (II)	36 (III)
IV	89 (V)	....
VII	68 (VIII)	....
IX	61 (X)	....
XI	95 (XII)	....
XIII	......	48 (XIII)

BLACKSBURG, VIRGINIA

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

The Replacement of Bromine by Chlorine in Aromatic Compounds

BY WILLIAM B. HARDY AND ROBERT B. FORTENBAUGH

RECEIVED SEPTEMBER 26, 1957

The reaction of cuprous chloride with 2-acetylamino-3-bromoanthraquinone to give the corresponding chloro compound is reported. A side reaction resulting in elimination of halogen is discussed and means of preventing it are demonstrated. The halogen exchange reaction is shown to be applicable to aromatic compounds.

2-Acetylamino-3-chloroanthraquinone is an intermediate for an important solubilized vat dye.[1] Since the established process[2] for this intermediate involves five steps from 4′-chloro-*o*-benzoylbenzoic acid some alternate methods of synthesis were considered. In contrast to chlorination the bromination of 2-aminoanthraquinone results in a high yield of 2-amino-3-bromoanthraquinone which can be acetylated without isolation.[3] Accordingly, we considered it of interest to examine procedures for the conversion of the bromo derivative to the corresponding chloro compound.

Little work has been reported on the replacement of bromine by chlorine in aromatic compounds[4–7] and in no case has such a reaction been carried out in the anthraquinone series. The drastic conditions employed and the low yields ob-

---

(1) The product referred to is the tetrasulfuric ester of leuco dichloroindanthrene. See K. Venkataraman, "Chemistry of Synthetic Dyes," Vol. II, Academic Press, Inc., New York, N. Y., 1952, p. 1049.

(2) P. B. Report L 25624, Frames 908–915, "Bibliography of Scientific and Industrial Reports," 8 (No. 4): 288, 290 (January 23, 1948).

(3) P. B. Report L 70341, Frame 14178, "Bibliography of Scientific and Industrial Reports," 9 (No. 3): 197 (April 16, 1948).

(4) A. Seyewetz and P. Trowitz, *Compt. rend.*, **136**, 242 (1903).

(5) J. Schmidt and G. Ladner, *Ber.*, **37**, 4402 (1904).

(6) J. Schmidt and H. Wagner, *Ann.*, **387**, 164 (1912).