above experiments were repeated with dried silica gel Grade "A" in place of activated alumina, the color of the adsorbates on the silica gel was deep red (after 24 hours) and the benzene solution acquired a deep, orange color. In a parallel experiment without silica gel, the color of the benzene solution was a very pale yellow and yellow in the case of (IIa) and (IIIa), respectively.

GIZA, CAIRO, EGYPT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

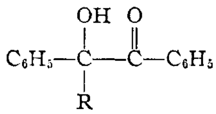
The Rearrangement and Cleavage of Benzoin and α-Substituted Benzoins by Alkali[1]

BY DEXTER B. SHARP[2] AND EDSEL L. MILLER

RECEIVED JULY 23, 1952

The cleavage by alkali of benzoin and six α-substituted benzoins has been examined in detail. α-Phenylbenzoin gave quantitative yields of benzhydrol and benzoic acid. α-(*o*-Tolyl)-benzoin gave quantitative yields of benzhydrol and *o*-toluic acid. Benzoin, α-methyl-, α-benzyl-, α-(*m*-tolyl)- and α-(*p*-tolyl)-benzoin each gave varying quantities of four products, which indicated partial rearrangement prior to cleavage. Mechanisms are suggested for these reactions.

Acree[3] observed that α-phenylbenzoin (I, R = C_6H_5) was cleaved by hot alcoholic alkali and gave benzhydrol (II) and benzoic acid (III) in unspecified amounts.



$$C_6H_5-\underset{R}{\overset{OH}{C}}-\overset{O}{\overset{\|}{C}}-C_6H_5$$

I

He reported also[3b] that α-(1-naphthyl)-benzoin gave benzoic acid and α-naphthylphenylcarbinol upon alkaline cleavage. Roger and McGregor[4] reported similar scissions in which R was *o*- and *m*-tolyl and methyl. Pascual and Cerezo[5] reported the alkaline cleavage of α-benzylbenzoin to benzoic acid and phenylbenzylcarbinol. The results of Roger and McGregor[4] suggested that a rearrangement may have occurred, but more complete studies of this reaction were lacking in the literature. In contrast, Temnikova[6] reported that trisubstituted α-ketols ($R_2COHCOR'$, R and R' alternatively methyl and phenyl) did not isomerize in alkali. Our interest in this reaction developed when Acree's[3] cleavage of α-phenylbenzoin was repeated and found to give quantitative scission into benzhydrol and benzoic acid. Since detection of rearrangement is impossible with α-phenylbenzoin, attention was directed toward an examination of the cleavage of representative examples of I.

Preparation of α-Substituted Benzoins.—Excepting benzoin itself, the starting compounds (I) were prepared by addition of the appropriate Grignard reagent to benzil. Benzoin, α-methyl-, α-benzyl-, α-phenyl- and α-(*o*-tolyl)-benzoin were crystalline solids and appeared to be single molecular species. The samples of α-(*m*-tolyl)- and α-(*p*-tolyl)-benzoin were viscous liquids obtained by fractional distillation at reduced pressure. It seemed unlikely that the crystalline α-substituted benzoins were mixtures of isomeric α-ketols formed during the Grignard reaction, and benzoin itself is known to be one molecular species only. Reduction products of α-(*o*-tolyl)- and α-(*m*-tolyl)-benzoin corresponded with compounds previously reported, and Zerewitinoff determinations of active hydrogen and carbonyl group content checked reasonably well for α-ketol structures. The homogeneity of the liquid α-substituted benzoins is probably subject to question.

Cleavage Reaction.—The α-arylbenzoins were cleaved easily in refluxing methanolic alkali and gave total product quantities accounting for 70–100% of the initial amount of α-ketol. Benzoin, α-methyl- and α-benzylbenzoin were unaffected under these conditions, but were cleaved at 160° in alkali-containing diethylene glycol with total product quantities accounting for 80–100% of the initial amount of α-ketol. The following formulation represents the general cleavage reaction, and all corresponding products were obtained from five of the seven compounds examined (R = H, CH_3, $C_6H_5CH_2$, *m*- and *p*-$CH_3C_6H_4$). The products

$$\text{I} \xrightarrow{OH^{\ominus}} \underset{\text{II}}{(C_6H_5)_2CHOH} + \underset{\text{III}}{C_6H_5CO_2H} + \underset{\text{IV}}{C_6H_5CHOHR} + \underset{\text{V}}{RCO_2H}$$

from α-phenylbenzoin were mentioned above. Cleavage of α-(*o*-tolyl)-benzoin gave only benzhydrol and *o*-toluic acid, confirming the report by Roger and McGregor.[4] This suggests that complete rearrangement occurred, or that the starting compound was diphenyl-*o*-toluylcarbinol rather than the expected α-(*o*-tolyl)-benzoin. The identities and relative quantities of the cleavage products from each reaction are summarized in Table I.

The cleavage of benzoin itself to give benzhydrol, benzoic acid, benzyl alcohol and formic acid is evidence indicating partial rearrangement prior to cleavage. Knoevenagel and Arndts[7] reported the cleavage of benzoin to benzoic acid and benzyl alcohol in concentrated alkali, but apparently did not obtain benzhydrol or formic acid.

Roger and McGregor[4] reported that α-methylbenzoin gave only trace amounts of benzhydrol, whereas our results indicate that approximately

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[1] Abstracted in part from the Ph.D. thesis submitted by Edsel L. Miller to the Graduate Faculty of Kansas State College, January, 1952. Contribution no. 281 from the Department of Chemistry.

[2] Monsanto Chemical Co., Dayton, Ohio.

[3] (a) S. F. Acree, *Am. Chem. J.*, **29**, 588 (1903); (b) *Ber.*, **37**, 2753 (1904).

[4] R. Roger and A. McGregor, *J. Chem. Soc.*, 442 (1934).

[5] J. Pascual Vila and J. Cerezo, *Anales. soc. espan. fis. quim.*, **24**, 395 (1926); *C. A.*, **21**, 3798 (1927).

[6] T. I. Temnikova, *Vestnik Leningrad Univ.*, 138 (1947); *C. A.*, **42**, 4155f (1948).

[7] E. Knoevenagel and J. Arndts, *Ber.*, **35**, 1982 (1902).

TABLE I

PRODUCTS FROM THE CLEAVAGE OF α-KETOLS IN ALKALI

α-Ketol PhCR(OH)-COPh R	Moles × 10^3	Products, moles × 10^3 Ph₂-CHOH	Ph-CO_2H	PhCH-OHR	RCO_2H	Mole balance,[a] %
H	28.3	7.5	24.0	7.5	8.3	82.5
CH_3	8.9	4.1	4.7	4.5	4.3	99.0
$C_6H_5CH_2$	9.9	3.9	10.1[b]	4.8	...[b]	95.1
p-$CH_3C_6H_4$	10.1	1.3	5.8	5.6	1.2	68.3
m-$CH_3C_6H_4$	16.6	12.2	5.8	7.0	6.6	95.2
	9.9	7.2	4.4	2.7	1.0	76.9
o-$CH_3C_6H_4$	4.2	3.9	...	...	3.7	90.6
	6.6	6.5	...	...	6.0	93.9
C_6H_5	1.74	1.7	1.8	...	...	100.0

[a] Percentage ratio of one-half the sum of the moles of product to the mole of starting α-ketol. [b] Odor of phenylacetic acid, not isolated.

half of the neutral fraction was benzhydrol. The formation of acetic acid was not observed by Roger and McGregor.[4]

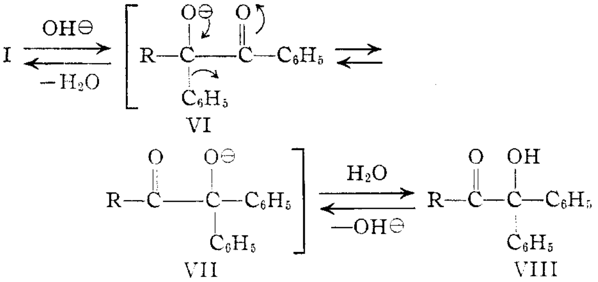
α-Benzylbenzoin gave three identified products, benzhydrol, benzoic acid and benzylphenylcarbinol. No phenylacetic acid was isolated but the characteristic odor was noted. These results are at variance with those of Pascual and Cerezo[5] in that they did not obtain benzhydrol but did isolate benzoic acid and benzylphenylcarbinol.

α-(*p*-Tolyl)-benzoin gave all four · products. Cleavage of this compound by alkali was not reported in the literature. α-(*m*-Tolyl)-benzoin gave four products, whereas Roger and McGregor[4] reported only two, benzoic acid and phenyl-*m*-tolylcarbinol. α-(*o*-Tolyl)-benzoin gave *o*-toluic acid and benzhydrol, corroborating the results of Roger and McGregor.[4]

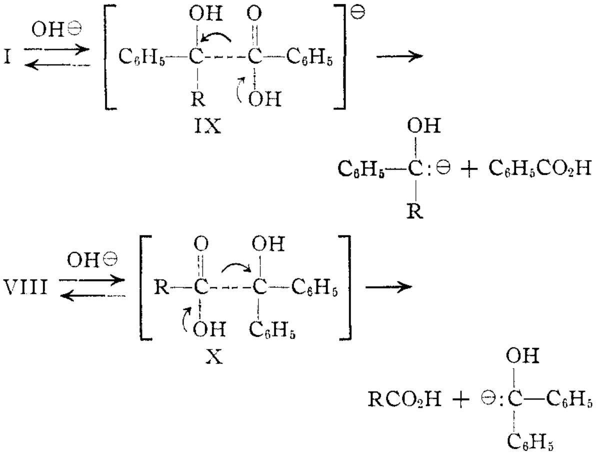
Because of the great similarities of physical and chemical behavior of the homologous pairs of neutral and acidic compounds obtained in several of these cleavage reactions, quantitative separation by physical means was virtually impossible. In order to obtain accurate estimates of the quantities of each component in a given homologous pair, it was necessary to resort to chromium trioxide oxidation techniques. The method was tested with known mixtures and gave satisfactory recoveries of the oxidation products of the two homologous components. Thus, several pairs of the homologous cleavage products were isolated as oxidized derivatives.

Discussion

In general, the scission reaction resembles those reported for aryl triarylmethyl ketones[8] and trihalomethyl ketones.[9] The formation of the abnormal products in several of the alkaline cleavage reactions suggested that a partial or complete rearrangement of the initial α-ketol to one of isomeric relationship was occurring. The scission and rearrangement reactions may be caused by hydroxyl ion attack on the carbonyl carbon or on the hydroxyl group proton, respectively. It is postulated that the rearrangement may proceed



It is conceivable that the high electron density and formal negative charge of the anionic oxygen in VI (or VII) could supply the driving force required for the shift of a pair of electrons and attached group to the adjacent, potentially electrophilic carbon of the carbonyl group. This rearrangement may be analogous to the benzil–benzilic acid rearrangement. The cleavage of I or VIII is postulated as a nucleophilic displacement reaction by hydroxyl ion at the carbonyl group and might involve the transition complexes suggested below.



Subsequent equilibration of the carbanions with solvent would give the corresponding carbinols. From a resonance viewpoint, the cleavage of VIII should require less energy than cleavage of I when R is not aryl, since greater resonance stabilization of the postulated transition complex X may be provided by the two phenyl groups. This conclusion is supported, perhaps, by the fact that the α-arylbenzoins (R = aryl) cleaved readily at 65–70° (each transition complex of type X) but the other benzoins required higher temperatures (one transition complex of type IX where R is hydrogen, alkyl or aralkyl).

Experimental Details

Benzoin and Substituted Benzoins.—Student preparation benzoin was recrystallized from alcohol–water mixtures, m.p. 132–133° (reported[10] 133°). The α-substituted benzoins were prepared by dropwise addition of the appropriate Grignard reagent to an equivalent amount of benzil in ether solution. Aqueous sulfuric acid or saturated ammonium chloride was used to decompose the addition complex, and the viscous yellow products were purified by crystallization from suitable organic solvents, or by fractionation at reduced pressure through a 4-foot 20-mm., i.d. glass helices-packed column. Table II summarizes the yields

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(8) W. E. Bachmann, THIS JOURNAL, **54**, 1969 (1932); W. E. Bachmann and E. J. Chu, *ibid.*, **57**, 1095 (1935).

(9) R. C. Fuson and B. A. Bull, *Chem. Revs.*, **15**, 275 (1934).

(10) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948.

obtained and the physical constants of the several compounds. The active hydrogen and carbonyl values (calculated as number of groups per molecule) were estimated by the Zerewitinoff[11] method.

TABLE II

α-SUBSTITUTED BENZOINS

$C_6H_5CR(OH)$- COC_6H_5 R	Prepn. ref.	Yield, %	M.p. (m) or b.p. (b), °C. Obsd.	Reptd.
CH_3[a]	*b*	47	m 68–69°	m 65–66°[b]
$C_6H_5CH_2$[c]	*d*	26	m 120–121°	m 120–121°[d]
C_6H_5	*e*	..	m 77–82°	m 87–88°[e]
p-$CH_3C_6H_4$[f]	*b*	27–30	b 216–219° (2.7 mm.)	b 220–230°[b] (high vac.)
m-$CH_3C_6H_4$[g]	*b*	40	b 200–204° (0.65 mm.)	b 210–240°[b] (high vac.)
o-$CH_3C_6H_4$[h]	*b*	39	m 116.5–117°	m 116–117°[b]

[a] Active hydrogen 0.92, carbonyl 1.27 per molecule (theory 1.00 each); sapn. equiv., 225 (calcd. 226). [b] Ref. 4. [c] Calcd. for $C_{21}H_{18}O_2$: C, 83.44; H, 5.96; act. hydrogen, 1.00; carbonyl, 1.00. Found: C, 83.46; H, 5.96; act. hydrogen, 1.08; carbonyl, 0.97. [d] Ref. 13. [e] Ref. 3b. [f] Active hydrogen 0.95, carbonyl 0.73 per molecule (calcd. 1.00 each). [g] Reduction product (HI–P) m.p. 80–81°, reported 84–85° (ref. 4). [h] Calcd. for $C_{21}H_{18}O_2$: C, 83.44; H, 5.96; act. hydrogen, 1.00; carbonyl, 1.00. Found: C, 82.59; H, 5.87; act. hydrogen, 0.97; carbonyl, 1.06. Reduction product (HI–P), m.p. 46°, reported 47.5–49° (ref. 4).

Cleavage Procedure.—Samples of the α-arylbenzoins (2–5 g.) were heated to reflux for three hours in methanolic alkali, prepared by dissolving 4.0 g. of potassium hydroxide in 5.0 ml. of water and diluting with 30 ml. of methanol. After the reflux period the methanol was removed by distillation, the residue was diluted to 100 ml. with distilled water, and the solution was extracted with three 30-ml. portions of ether. Removal of the ether yielded the neutral fraction which was heated on a steam-bath for two hours with 8.0 g. of chromium trioxide in 20 ml. of glacial acetic acid and 5.0 ml. of water. This oxidation mixture was diluted with water and extracted with three 30-ml. portions of ether. The ether solution was extracted with saturated sodium bicarbonate solution, the ether was removed and the residue was shown to be benzophenone. The sodium bicarbonate extract was acidified with hydrochloric acid and extracted with four 25-ml. portions of ether. Removal of the ether gave the acid formed by oxidation of one of the neutral components. The original ether-extracted alkaline solution was acidified and extracted with three 30-ml. portions of ether, the ether extract was evaporated, and the residue was heated on a steam-bath for two hours with 8.0 g. of chromium trioxide in 20 ml. of glacial acetic acid and 5 ml. of water. The oxidation mixture was diluted to 100 ml. with distilled water and the terephthalic or isophthalic acid was removed by filtration (from α-(*p*-tolyl)- or α-(*m*-tolyl)-benzoin). The filtrate was extracted with two 30-ml. portions of ether and two 40-ml. portions of one-to-one ether–ethyl acetate. Evaporation of the solvent yielded benzoic acid.

The samples of benzoin, α-methyl- or α-benzylbenzoin (2–6 g.) were heated at 155–160° for two hours in a solution of 4.0 g. of potassium hydroxide in 20 ml. of diethylene glycol and 5 ml. of water. The cooled mixture was diluted to 100 ml. with distilled water and extracted with five 20-ml. portions of ether. Removal of the ether yielded the neutral fraction which was subjected to chromium trioxide oxidation as described above. The oxidized components of the neutral fraction were separated by the usual procedure, since one was neutral and the other acidic. The original alkaline cleavage solution was acidified with hydrochloric acid and extracted with four 30-ml. portions of ether. Evaporation of the ether yielded benzoic acid in all cases. The acidified cleavage solution then was steam distilled to give 600–900 ml. of distillate. Duclaux numbers were obtained with these distillates and derivatives were prepared, thereby identifying acetic and formic acid from cleavage of α-methylbenzoin and benzoin, respectively. Quantities of these acids were estimated by titration of each steam distillate with standard alkali.

Individual Cleavages. A. Benzoin.—A 6.0-g. sample of benzoin was cleaved in the diethylene glycol–potassium hydroxide solution, and the neutral fraction (3.24 g.) was oxidized as described above. The oxidation mixture gave 1.37 g. of benzophenone, 2,4-dinitrophenylhydrazone, m.p. 237° alone or mixed with authentic derivative (reported[10] 239°), and 0.92 g. of benzoic acid, m.p. 120–121° alone or mixed with authentic benzoic acid. The acid was assumed to arise from benzyl alcohol formed during cleavage. The acidified cleavage solution was extracted with ether and yielded 2.93 g. of benzoic acid, m.p. 120–121° alone or mixed with authentic benzoic acid. The extracted solution was steam distilled to give 860 ml. of distillate containing 0.38 g. of formic acid (by titration). Duclaux numbers of a portion of the distillate were 3.93, 4.57 and 4.78 (reported[10] for formic acid 3.95, 4.40 and 4.55). The *p*-bromophenacyl ester was prepared, m.p. 135° (reported[10] 140°).

B. α-Methylbenzoin.—A 2.0-g. sample of α-methylbenzoin, m.p. 68–69° (reported[4] 65–66°), was cleaved by the procedure described above. The neutral fraction (1.58 g.) was separated by repeated crystallization from petroleum ether–cyclohexane into 0.75 g. of benzhydrol, m.p. 67° alone or mixed with authentic benzhydrol (reported[10] 68°), and 0.54 g. of methylphenylcarbinol which was converted to the 3,5-dinitrobenzoate, m.p. 95° alone or mixed with authentic derivative (reported[10] 95°). The ether-extracted cleavage solution was acidified and extracted with ether, giving 0.57 g. of benzoic acid, m.p. 120–121° alone or mixed with authentic benzoic acid. The extracted solution was steam distilled to give 680 ml. of distillate containing 0.26 g. of acetic acid (by titration). Duclaux numbers of a portion of the distillate were 6.0, 6.9 and 7.4 (reported[10] for acetic acid 6.8, 7.1 and 7.4). The *p*-bromophenacyl ester was prepd., m.p. 82° (reported[10] 85°).

C. α-Benzylbenzoin.—A 3.0-g. sample of α-benzylbenzoin, m.p. 120–121° (reported[12] 120–121°), was cleaved by the procedure described above. Chromic acid oxidation of a 0.52-g. portion of the neutral product (1.8 g.) gave 0.20 g. of benzophenone, 2,4-dinitrophenylhydrazone, m.p. 239° alone or mixed with authentic derivative (reported[10] 239°), and 0.33 g. of benzoic acid, m.p. 121–122° alone or mixed with authentic benzoic acid. The benzoic acid was assumed to arise by oxidation of the phenylbenzylcarbinol formed by the cleavage reaction. The mole portion of carbinol, therefore, would be one-half the mole portion of benzoic acid obtained. The ether-extracted cleavage solution was acidified and yielded 1.3 g. of benzoic acid, m.p. 120–121° alone or mixed with authentic benzoic acid. The odor of phenylacetic acid was noticeable, but none of this compound could be isolated.

D. α-Phenylbenzoin.—A 0.5-g. sample of phenylbenzoin, m.p. 77–82° (reported[3] 87–88°), was refluxed for two hours with 1.0 g. of potassium hydroxide in 20 ml. of methanol and 15 ml. of water. Separation of the products gave 0.31 g. of benzhydrol, m.p. 65–67° alone, 65–68° mixed with authentic benzhydrol (reported[10] 68°), and 0.22 g. of benzoic acid, m.p. 120–122° alone or mixed with authentic benzoic acid.

E. α-(*p*-Tolyl)-benzoin.—A 3.07-g. sample of α-(*p*-tolyl)-benzoin, b.p. 216–219° at 2.7 mm. (reported[4] 220–230° at high vacuum), was cleaved in methanolic alkali. The neutral fraction (1.96 g.) was oxidized with chromic acid and gave 0.30 g. of benzophenone, 2,4-dinitrophenylhydrazone m.p. 236° alone or mixed with authentic derivative (reported[10] 239°), and 1.26 g. of *p*-benzoylbenzoic acid, m.p. 193–194° (reported[13] 194°). The acid fraction was oxidized with chromic acid and gave 0.22 g. of terephthalic acid, sublimed at 300° alone or mixed with authentic terephthalic acid (reported[10] 300° subl.), and 0.70 g. of benzoic acid, m.p. 120–121° alone or mixed with authentic benzoic acid. As a check upon the chromic acid oxidation procedure, a mixture of 1.0 g. of benzhydrol and 1.0 g. of phenyl-*p*-tolylcarbinol was oxidized by the procedure outlined above

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(11) S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949.

(12) A. G. Banus and J. P. Vila, *Anal. soc. espan. fis. quim.*, **19**, 326 (1921); *C. A.*, **16**, 3479 (1922).

(13) I. M. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, London, 1934.

and gave 1.0 g. of benzophenone, 2,4-dinitrophenylhydrazone, m.p. 238° (reported[10] 239°) and 0.98 g. of *p*-benzoylbenzoic acid, m.p. 193–194° (reported[13] 194°).

F. α-(*m*-Tolyl)-benzoin.—A 5.0-g. sample of α-(*m*-tolyl)-benzoin, b.p. 200–204° at 0.65 mm. (reported[4] 210–240° at high vacuum), was cleaved by the procedure described above. A 2.0-g. portion of the neutral fraction (3.42 g.) was oxidized with chromic acid and gave 1.3 g. of benzophenone, 2,4-dinitrophenylhydrazone, m.p. 225–226° alone or mixed with authentic derivative (reported[10] 239°), and 0.93 g. of *m*-benzoylbenzoic acid, m.p. 163–164° (reported[14] 161–162°). The ether-extracted cleavage solution was acidified and the acid fraction was extracted with ether. Oxidation with chromic acid gave 1.1 g. of isophthalic acid, m.p. 300° (reported[10] 300°), and 0.7 g. of benzoic acid, m.p. 120–121° alone or mixed with authentic benzoic acid.

G. α-(*o*-Tolyl)-benzoin.—A 1.28-g. sample of α-(*o*-tolyl)-benzoin, m.p. 116.5–117° (reported[4] 116–117°), was cleaved in the usual manner. The neutral fraction (0.73 g.) proved to be benzhydrol, m.p. 65–66° alone or mixed with authentic benzhydrol (reported[10] 68°). The acid fraction (0.50 g.) proved to be *o*-toluic acid, m.p. 102–103° (reported[10] 102°). A second cleavage of 2.0 g. of α-(*o*-tolyl)-benzoin gave a neutral fraction which was oxidized with chromic acid and gave 1.1 g. of benzophenone, 2,4-dinitrophenylhydrazone, m.p. 234–240° alone or mixed with authentic derivative (reported[10] 239°). No acid compound was found as an oxidation product. The acid fraction (0.82 g.) from the cleavage was *o*-toluic acid, m.p. 100–101° (reported[10] 102°).

MANHATTAN, KANSAS

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[14] P. Senff, *Ann.*, **220**, 225 (1883).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

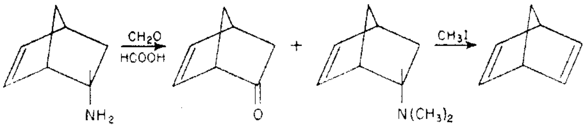
Studies of the Bicyclo[2,2,1]heptene-2 Ring System. II

BY WILLIAM E. PARHAM, WILLIAM T. HUNTER, ROBERTA HANSON AND THOMAS LAHR

RECEIVED APRIL 16, 1952

The reaction of *endo*-5-aminobicyclo[2,2,1]heptene-2 with formaldehyde and formic acid gives the corresponding ketone (24%) as well as the expected tertiary amine (30%) and trimethylamine. The formation of the ketone has been attributed to steric factors and not participation of the double bond, since the saturated amine, *endo*-5-aminobicyclo[2,2,1]heptane, behaves similarly. Methylation of *d*-(β-phenylisopropyl)-amine by the Clarke procedure resulted in no racemization, thus intermediates of the type $R_2C{=}N{-}CH_3$ are not involved. When the quaternary base of *endo*-5-dimethylamino[2,2,1]-heptene-2 was pyrolyzed, the amine was regenerated. Other reactions are cited which indicate that bicyclo[2,2,1]2,5,heptadiene is not easily formed by elimination reactions involving the bicyclo[2,2,1]heptene-2 ring system.

During a previous study of compounds[1] containing the bicyclo-(2,2,1)-heptene-2 ring system, one of us observed that the action of formaldehyde and formic acid on *endo*-5-aminobicyclo-(2,2,1)-heptene-2 (I) resulted in 24% yield of ketonic material, a 30% yield of a tertiary amine and an undetermined quantity of trimethylamine. The quaternary hydroxide derived from the tertiary amine (III) did not give the expected products when subjected to the Hofmann degradation (trimethylamine and IV), but decomposed to give the original amine III and a volatile alcohol (presumably methanol). The results of the methylation reaction and the Hofmann degradation reaction were both unexpected; therefore, these reactions have been reinvestigated and additional evidence concerning the structures of the resulting compounds has been obtained.

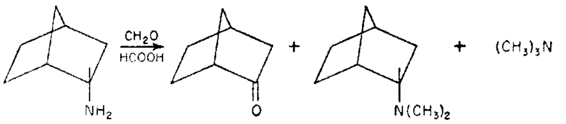


I II III IV

The unstable ketonic product II gave a 2,4-dinitrophenylhydrazone and a semicarbazone which were difficult to purify by crystallization. The ketonic product was shown to be principally 5-ketobicyclo-(2,2,1)-heptene-2 (II) by reduction (0.925 double bond) to the known 2-ketobicyclo-(2,2,1)-heptane (VI). The reduced ketone (VI) was isolated as its 2,4-dinitrophenylhydrazone and its semicarbazone. These derivatives did not depress the melting points of the corresponding derivatives prepared from an authentic sample of VI. The reduction of nortricyclanone under conditions used for the reduction of II did not result in the formation of VI by hydrogenolysis; consequently, nortricyclanone cannot be present in large amounts as an impurity in II.

The infrared spectrum of III revealed no broad absorption band near 800 cm.$^{-1}$, indicating[2] the absence of the nortricyclane ring structure. When III was reduced (Pt, H_2), 90% of one mole of hydrogen was absorbed and the product was *endo*-2-dimethylamino-(2,2,1)-heptane (VII).

The reaction of *endo*-2-aminobicyclo-(2,2,1)-heptane (V) with formaldehyde and formic acid was investigated in order to ascertain whether or not the formation of ketones during the methylation of I could be attributed to participation of the carbon–carbon double bond. The products of the reaction were: 2-ketobicyclo-(2,2,1)-heptane (VI, 40% yield), *endo*-2-dimethylaminobicyclo(2,2,1)-heptane (VII, 27% yield) and trimethylamine.



V VI VII

The formation of carbonyl compounds during the methylation of amines with formaldehyde and formic acid has been explained as outlined in the following equation.[3]

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[1] W. E. Parham, W. T. Hunter and R. Hanson, THIS JOURNAL, **73**, 5068 (1951).

[2] J. D. Roberts, E. R. Trumbull, W. Bennett and R. Armstrong, *ibid.*, **72**, 3117 (1950).

[3] H. T. Clarke, H. B. Gillespie and S. Z. Weishaus, *ibid.*, **55**, 4571 (1933).