The 52-min. component was ethyl *cis*-β-cyclobutylacrylate (XV), n^{28}D 1.4578. The infrared spectrum (chloroform) had absorption characteristic of an α,β-unsaturated ester at 1700 and 1635 cm.$^{-1}$.[16] The n.m.r. spectrum (135 mg./ml. in carbon tetrachloride, G in Fig. 3) showed cyclobutyl hydrogen signals from 239 to 293 p.p. 10^8 ethoxy hydrogen signals at 68 (quartet) and 357 (triplet) p.p. 10^8 and olefin hydrogen signals at −174, −152, −145, and −125 (quartet) and −88 and −58 (doublet) p.p. 10^8.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.49; H, 8.86.

Isolation of a Mixture of Cyclobutyl Ethyl Ether and Cyclopropylcarbinyl Ethyl Ether from a Photochemical Reaction of Diazocyclobutane.—In the workup of reaction mixtures from the irradiation of solutions of diazocyclobutane in *trans*-2-butene–ethanol,[17] a number of volatile fractions were obtained. One of these, b.p. 80° (130 mm.) to b.p. 110° (25 mm.), when it was further purified by vapor chromatography through a didecyl phthalate column (retention time 16.5 min. at 70° with a helium flow rate of 60 cc./min.) was found to have the properties of a mixture of cyclobutyl ethyl ether and cyclopropylcarbinyl ethyl ether, n^{25}D 1.4042 (lit.[30] n^{20}D 1.4050, b.p. 99.5–100.8° for cyclopropylcarbinyl ethyl ether). The infrared spectrum (chloroform) showed no absorption between 1500 and 2700 cm.$^{-1}$ or above 3150 cm.$^{-1}$. There was absorption at 3080, 2970, 2860 and 1115 cm.$^{-1}$.

Anal. Calcd. for $C_6H_{12}O$: C, 71.95; H, 12.08. Found: C, 71.74; H, 12.05.

The n.m.r. spectrum (215 mg./ml. in carbon tetrachloride, I in Fig. 3) showed a triplet at 353, 371 and 387 p.p. 10^8 and groups of signals from 114 to 181 p.p. 10^8, 273 to 314 p.p. 10^8 and 431 to 461 p.p. 10^8.

A sample of this ether mixture when fractionated through two didecyl phthalate columns at 70° with a flow rate of 50 cc./min. showed two peaks of about equal heights at 45.8 and 49 min.

Formation of Cyclobutyl Ethyl Ether and Cyclopropylcarbinyl Ethyl Ether in the Preparation of Diazocyclobutane.—To a solution of 4.5 g. (0.031 mole) of N-cyclobutyl-N-nitrosourea in 100 ml. of ether at −45° was added a solution of lithium ethoxide (from 0.5 g. (0.07 g. atom) of lithium) in 25 ml. of ethanol and 25 ml. of ether. The diazo compound formed immediately to give a cherry-red solution. The solution was turbid but homogeneous. Seventy-five ml. of the solution was transferred to another flask at −45°. A solution of 1.5 g. (0.015 mole) of benzaldehyde in 15 ml. of ether was added to this solution, and the color disappeared in 3 min. The remaining solution of diazo compound was allowed to warm to room temperature, by which time the color of the diazo compound had disappeared. The color was still present but faint at 0°.

Both reactions were washed with 4 portions of 25 ml. of water, dried over anhydrous calcium chloride and filtered. Twenty ml. of freshly distilled decalin was added to each of the solutions and they were distilled through a semimicro spinning band column to give, in addition to an ether fraction (b.p. 34°), a fraction b.p. 42 to 160°. The weight of the latter fraction was 0.833 g. for the reaction which included benzaldehyde and 0.727 g. for the reaction which did not.

Vapor chromatography of the foreruns through two didecyl phthalate columns at 80° showed only ether, at 6.6 minutes. Chromatography of the other fractions at 90° gave the following results. The yields are based on areas of the peaks.

Component	Benzaldehyde reacn., min.	%	Thermal reacn., min.	%
Ether	6.1	17	6.0	23
Ethanol	7.4	47	7.3	36
Mixed ethers	28.4, 29.2	11	28.0, 28.9	13
Decalin	120	25	120	28

The retention times of cyclobutyl and cyclopropylcarbinyl ethyl ethers from the photochemical reaction above at 90° were 27.8 and 28.8 min. The estimated yields of these ethers for the benzaldehyde and thermal reactions were 92 mg. (6%) and 94 mg. (6%), respectively.

URBANA, ILL.

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(30) C. G. Bergstrom and S. Siegel, THIS JOURNAL, **74**, 145 (1952).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AT THE UNIVERSITY OF TEXAS AND THE UNIVERSITY OF LONDON, QUEEN MARY COLLEGE]

The Synthesis and Properties of the Perinaphthenylium Cation

BY R. PETTIT

RECEIVED SEPTEMBER 16, 1959

The synthesis of perinaphthenylium perchlorate is described. This salt is thermodynamically stable; although very reactive, it can be stored under nitrogen. The salt is insoluble in non-polar solvents though it readily dissolves in nitromethane and 60% perchloric acid. The perinaphthenylium cation reacts with water to produce perinaphthene and perinaphthenone; it reacts with zinc dust to form peropyrene.

Simple L.C.A.O. molecular orbital calculations[1a] predict that the perinaphthenyl cation (Ia), anion (Ib) and radical (Ic) should all possess the same value of the π-electron delocalization energy, namely, 5.83β (β = 20 kcal.). This follows from the fact that like the allyl and triphenylmethyl systems, the perinaphthenyl system is an odd alternant hydrocarbon and the extra one and two electrons possessed by the radical and anion, respectively, occupy a molecular orbital of energy zero (with reference to the energy of an electron in the p_z-orbital of an isolated sp^2-hybridized carbon atom). Furthermore, similar calculations show that the gain in π-electronic energy in deriving each of the above species following loss of a hydride ion, hydrogen atom or proton from perinaphthene (II) should be 1.7 β or 34 kcal.[1b] These two facts together then predict that the perinaphthenyl cation, radical and anion might display unusual stability and, in a suitable environment, each may be capable of more than a transient existence.

The successful preparations of a salt of the perinaphthenylium cation and of the perinaphthenyl radical have recently been reported[2,3] and solutions containing the corresponding anion[4] have been made. Even prior to these reports there was considerable evidence supporting the

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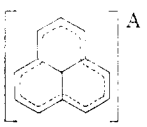
(1) (a) M. J. S. Dewar and R. Pettit, unpublished results. Other independent calculations have been reported by V. Gold and F. L. Tye, *J. Chem. Soc.*, 2184 (1956); (b) based upon a value of 4.13 β for the π-electron delocalization energy of 1-vinylnaphthalene as given by C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," Vol. III, p. 68.

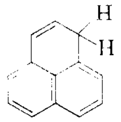
(2) R. Pettit, *Chemistry & Industry*, 1306 (1956).

(3) D. H. Reid, *ibid.*, 1504 (1956).

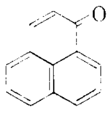
(4) V. Boekelheide and C. E. Larrabee, THIS JOURNAL, **72**, 1245 (1950).



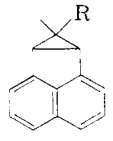
Ia, A = +
b, A = −
c, A = ·



II



III



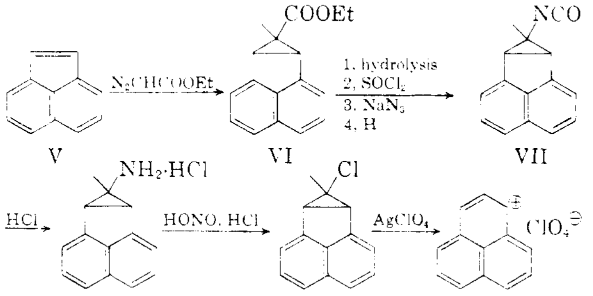
IV

molecular orbital predictions. Thus perinaphthenone (III), was found to be soluble in strong aqueous acids,[5] presumably due to the formation of the hydroxy derivative of the perinaphthenylium cation, a reaction entirely analogous to that of tropone with acids to form hydroxytropylium salts.[6] Clar had also accumulated evidence showing that several derivatives of the perinaphthyl radical were unusually stable.[7] Boekelheide and Larrabee[4] also showed that perinaphthene (II) reacted with phenyllithium and with triphenylmethyl to give presumably the anion Ib and the radical Ic, respectively.

The present paper is concerned with the preparation and properties of the perchlorate salt of the perinaphthenylium cation; a preliminary report of some of this work has appeared earlier.[2] A stable tribenz-derivative[8] and solutions containing an indeno-derivative[9] of the parent cation Ia have also been reported.

At the outset it seemed that the most suitable material which could be used for ascertaining the potential stability of the perinaphthenylium cation would be a halogen derivative of perinaphthene where the halogen atom was attached to the saturated carbon. However Boekelheide and Goldman had previously tried to synthesize the bromo derivative of II without apparent success.[10] The synthesis we therefore chose to follow was one similar to that employed by Dewar and Pettit[11] for their synthesis of the tropylium cation and aimed at preparing a molecule such as IV. It was hoped that if the group R in a molecule such as IV could be removed as an anion, a cationic system would remain which could be reasonably expected to give the perinaphthenylium cation upon electronic rearrangement.

The final successful synthesis is outlined in the accompanying scheme. Diazoacetic ester was treated with acenaphthylene in decalin to give 3′-carbethoxy-1:2-cyclopropanoacenaphthene (VI).



Hydrolysis of this ester followed by a Curtius rearrangement of the corresponding acid azide furnished the isocyanate VII. Unlike cycloheptatrienyl isocyanate, which can readily yield tropylium salts,[11] the isocyanate VII showed no potentially ionic properties at all, and attempts to remove an isocyanate ion from this molecule failed.

Hydrolysis of the isocyanate afforded the hydrochloride salt of 3′-amino-1:2-cyclopropanoacenaphthene (VIII). It was hoped that treatment of this amine with nitrous acid would furnish the alcohol IV (R = OH) and that this could yield the perinaphthenyl cation upon treatment with strong acids. However reaction of the amine hydrochloride with sodium nitrite in dilute acid yielded only high molecular weight material. Nevertheless, when the reaction was carried out in concentrated hydrochloric acid, 3′-chloro-1:2-cyclopropanoacenaphthene (IX) was formed in fair yield. This very fortunate result was a little unexpected; the most reasonable explanation seems to be that an intermediate diazonium chloride ion pair is formed in the concentrated hydrochloric acid and that this undergoes an SNi type reaction. There can be no free carbonium ion type intermediate involved, for, as will be seen, this would surely undergo immediate electronic rearrangement to the more stable perinaphthenylium cation. The formation of the chloride IX was fortunate in that it allowed the perinaphthenylium cation to be formed under anhydrous conditions and this greatly facilitated the isolation of a salt of the cation.

The chloro compound IX showed no ionic properties, it was readily soluble in non-polar solvents and gave no immediate reaction with silver nitrate. It also showed no unsaturated behavior and the molecule undoubtedly possessed the covalent structure IX. The ultraviolet spectrum was very similar to that of the carboxylic acid IV (R = COOH) and to that of acenaphthene itself, showing that no rearrangement had occurred. Attempts to prepare the corresponding bromo and iodo derivatives directly, utilizing a Hunsdiecker reaction on the acid IV (R = COOH), failed.

However, treatment of the chloro compound with silver perchlorate in dry nitromethane at 70° for two hours did result in almost quantitative precipitation of silver chloride. Addition of ether to the remaining deep green solution caused precipitation in good yield of a yellow microcrystalline solid which, from the following properties, was shown to be the required perinaphthenylium perchlorate.

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(5) J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 365 (1934).

(6) W. von E. Doering and F. L. Detert, THIS JOURNAL, **73**, 876 (1951).

(7) E. Clar, "Aromatische Kohlenwasserstoffe," 2nd Ed., Springer-Verlag, Berlin, 1952, p. 431.

(8) E. Clar and D. G. Stewart, *J. Chem. Soc.*, 23 (1958).

(9) D. H. Reid, *Angew. Chem.*, **67**, 761 (1955).

(10) V. Boekelheide and M. Goldman, THIS JOURNAL, **76**, 604 (1954). These workers isolated a yellow solid which underwent rapid decomposition. In view of the very facile decomposition of perinaphthenylium perchlorate it seems possible that the yellow solid above may have contained the perinaphthenylium cation.

(11) M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 2021 (1956).

The yellow solid contained the perchlorate anion, it readily decomposed in moist air but could be stored at room temperature under nitrogen without apparent change. It was insoluble in such non-polar solvents as benzene, chloroform and ether though it readily dissolved in nitromethane. Perinaphthenylium perchlorate readily dissolved in 60% aqueous perchloric acid to give stable yellow solutions; but on dilution the salt decomposed and perinaphthene (II) and perinaphthenone (III) were isolated from the decomposition products. These compounds probably arose following disproportionation of diperinaphthenyl ether or of perinaphthenol. Whatever their mechanism of formation, this decomposition has prevented the estimation of the pK_a value of the perinaphthenylium cation. The lowest value of the atom localization energy of the perinaphthenylium cation is 1.7 β, which would thus predict that the pK_a value of the cation should be somewhat less than that for the tropylium and benztropylium cations but greater than that for 1:2, 4:5-dibenztropylium cation.[12]

The ultraviolet spectrum of the salt taken in 60% H_2SO_4 was closely similar to that of perinaphthenone (III) in the same solvent, confirming the idea that the latter solutions contain the hydroxy derivative of the perinaphthyl cation.

In an attempt to prepare methylperinaphthene, perinaphthenylium perchlorate was treated with both methyllithium and methylmagnesium bromide, but although a reaction appeared to take place, in neither case could an identifiable product be isolated. In view of the ready rearrangements which seem to occur in the series of methylperinaphthenes[13] it would have been interesting to find which isomer was formed in such a reaction of the cation.

Peropyrene was isolated following reaction of perinaphthylium perchlorate with zinc dust. This hydrocarbon is also formed when the perinaphthenyl radical[3] is similarly treated and in the former reaction the same radical is presumably also formed as an intermediate following a one electron transfer from the metal to the cation.

Attempts have been made to isolate other salts of the perinaphthenylium cation, but due largely to the instability of the cation in water these have not been successful. Nitrobenzene solutions of the chloro compound IX, when treated with aluminum chloride, became deep green in color and also became conducting, suggesting that a salt was formed, but no solid could be isolated. Also when treated with boron trifluoride in ether, solutions of the chloride acquired the green color typical of the cation Ia, but again no solid salt could be isolated.

Experimental

1:2-Cyclopropanoacenaphthene-3′-carboxylic Acid (IV, R = COOH).—To a mixture of acenaphthylene (250 g.) and decalin (200 ml.) stirred at 140°, ethyl diazoacetate (130 g.) was added dropwise over a period of 3.25 hours. Heating and stirring were continued until evolution of gas ceased. (In a typical run about 20 l. of gas was collected.) The mixture was cooled, stirred with acetone (400 ml.) and the large amount of polymeric material which precipitated was filtered off. The acetone was evaporated from the filtrate and the crude ester VI was stirred vigorously under reflux with 10% NaOH solution (1000 ml.). The mixture was cooled to 5° and the slimy crystals of the sodium salt of the acid were filtered off. The salt was dissolved in hot water (500 ml.) and treated several times with charcoal until the filtrate appeared clear. The free acid (62 g., 20%) was obtained by treating the filtrate with excess HCl solution. The acid crystallized from ethanol in white plates, m.p. 199–201°. The material did not readily decolorize permanganate solution; ultraviolet spectrum: max. mμ (log ϵ) 288 (3.95), 300 (4.10), 314 (3.95), 320 (3.63); min. mμ (log ϵ) 258 (3.22), 292 (3.90), 210 (3.83), 319 (3.58).

Anal. Calcd. for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.59; H, 4.89.

The picrate derivative formed orange plates from alcohol; m.p. 158°.

Anal. Calcd. for $C_{20}H_{13}N_3O_9$: C, 54.67; H, 2.98; N, 9.57. Found: C, 55.21; H, 3.06; N, 9.76.

Curtius Rearrangement of Acid IV (R = COOH).—(a) The above acid (30 g.) was refluxed for 1.5 hours with thionyl chloride (20 g.) in dry benzene (1.80 ml.) containing six drops of pyridine. The solvent was removed and the residual acid chloride crystallized from petroleum ether. Treatment with ammonia afforded the amide derivative as white needles from alcohol, m.p. 248°.

Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 79.99; H, 5.29; N, 6.80.

(b) To the acid chloride (26 g.) dissolved in acetone (150 ml.) a solution of sodium azide (8.5 g.) in water (15 ml.) was added dropwise with vigorous stirring. The temperature was kept below 0° during the addition and the mixture was then stirred for a further 20 minutes. Water (300 ml.) was then added and the acid azide which separated was extracted with benzene and the solution dried over sodium sulfate. Most of the benzene was removed under reduced pressure, dry benzene (300 ml.) added and the solution then refluxed for 2.5 hours. The solvent was concentrated to a volume of about 50 ml., concentrated hydrochloric acid (150 ml., 35%) was added to the residue and the mixture then was stirred vigorously under reflux for 45 minutes. On cooling, the amine hydrochloride VIII (20.5 g.) separated as light brown plates. A sample was recrystallized from dilute hydrochloric acid.

Anal. Calcd. for $C_{13}H_{12}NCl$: C, 71.72; H, 5.53; N, 6.44. Found: C, 71.44; H, 5.59; N, 6.20.

3′-Chloro-1:2-cyclopropanoacenaphthene (IX).—The above amine hydrochloride (10.0 g.) was dissolved in a mixture of concentrated hydrochloric acid (80 ml.) and glacial acetic acid (40 ml.). Ether (200 ml.) was added, the mixture cooled to −5° and a solution of $NaNO_2$ (4.2 g.) in water (20 ml.) then added dropwise with vigorous stirring. After 15 minutes the mixture was stirred at room temperature for a further 30 minutes. Water was added and the mixture extracted several times with ether. The combined ether layers were washed first with water then with dilute ammonia solution. The crude product obtained after removal of the solvent was adsorbed on alumina and eluted with light petroleum ether. The chloro compound (5.0 g.) was thus obtained as colorless needles, m.p. 122–123°.

Anal. Calcd. for $C_{13}H_9Cl$: C, 77.8; H, 4.5; Cl, 17.7. Found: C, 77.7; H, 4.8; Cl, 17.5.

The chloro derivative is very soluble in benzene, hexane and chloroform; it gives no immediate reaction with ethanolic silver nitrate; ultraviolet spectrum: max. (log ϵ) 286 (3.92), 298 (4.00), 311 (3.88); min. (log ϵ) 256 (3.34); 290 (3.88), 308 (3.72).

Perinaphthenylium Perchlorate.—3′-Chloro-1:2-cyclopropanoacenaphthene (1.1 g.) was dissolved in dry nitromethane (30 ml.) and silver perchlorate (3.0 g.) added. The solution was kept at 70° for two hours, with occasional shaking. Silver chloride slowly precipitated during this time and the solution gradually became dark green. The silver chloride (0.79 g. 90%) was then filtered off. Dry ether (250 ml.) was added to the filtrate. The yellow micro-crystalline precipitate of perinaphthenylium perchlorate which appeared was collected, washed several times with dry ether and, while still wet, transferred under nitrogen to a weighed flask. The excess ether was removed under vac-

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(12) D. Meuche, H. Strauss and E. Heilbronner, *Helv. Chim. Acta*, **41**, 57 (1958).

(13) V. Boekelheide and C. E. Larrabee, THIS JOURNAL, **72**, 1240 (1950).

uum. The product weighed 1.2 g. (84%). The material can be successfully crystallized from warm nitromethane if the operation is carried out rapidly and in an inert atmosphere; ultraviolet spectrum: max. (log ϵ) 226 (4.51), 400 (4.67); min. 308 (2.67). There also occurs a shoulder at 378 mμ (4.21) and the spectrum "tails off" very slowly; the log ϵ value is still 2.56 at 540 mμ (in which area the curve also appears to have a broad shoulder).

Anal. Calcd. for $C_{13}H_9ClO_4$: ClO_4, 37.6. Found: ClO_4, 37.3, 38.0.

Deep green solutions were also formed when IX was treated with aluminum trichloride in nitrobenzene and with boron trifluoride in ether. Although the development of color probably indicated presence of the perinaphthenylium cation, only intractable materials could be isolated from these reactions.

The perchlorate salt was insoluble in all non-polar solvents; it dissolved in 60% aqueous perchloric acid, and in 35% hydrochloric acid, though the latter solutions became turbid on standing and both did so on dilution.

Reaction of Perinaphthenylium Perchlorate with: (a) **Water.**—The salt (0.47 g.) was added with stirring to a mixture of water (20 ml.) and ethanol (20 ml.). After 10 minutes the mixture was extracted with ether, the ethereal solution then washed and dried. After evaporation of the ether the residue was chromatographed over alumina, eluting first with petroleum ether followed by benzene. The colorless first fraction on evaporation yielded perinaphthene which crystallized from petroleum ether in white needles, m.p. 84°. From alcohol, the compound formed an orange-red picrate, m.p. 120° or 205° depending on the rate of heating.[14] The ultraviolet spectrum of the hydrocarbon was identical to that previously reported.[15]

The yellow benzene eluate gave yellow needles of perinaphthenone (0.17 g.) on evaporation, m.p. 156°. This material dissolved in concentrated hydrochloric acid and could be recovered unchanged on dilution.

Anal. Calcd. for $C_{13}H_8O$: C, 86.7; H, 4.4. Found: C, 86.7; H, 4.2.

(b) **Zinc Dust.**—A freshly prepared sample of the salt (approx. 0.50 g.) was stirred in ether (50 ml.) with zinc dust (5.0 g.) for 20 hours. The ether was evaporated and the residue extracted with boiling benzene (3 × 50 ml.). Evaporation of the benzene afforded crude peropyrene (0.14 g.). The compound was purified by sublimation followed by recrystallization from toluene. The substance dissolved in concd. sulfuric acid to give blue-green solutions. The ultraviolet spectrum in alcohol showed peaks at 230, 264, 277, 310, 324, 366, 388, 410 and 437 mμ, in agreement with the reported values.[16]

Attempted Hunsdiecker Reaction on the Acid IV, R = COOH.—Bromine (3.1 g.) in dry benzene (30 ml.) was added dropwise to a stirred suspension of the silver salt of the acid (6.3 g.) in dry benzene (200 ml.). The mixture was stirred and refluxed for 3 hours. The silver bromide was collected. The residue after evaporation of the benzene was almost completely soluble in sodium hydroxide. It crystallized from ethanol in white prisms, m.p. 220°.

Anal. Calcd. for $C_{14}H_9BrO_2$: C, 58.1; H, 3.1; Br, 27.7. Found: C, 57.9; H, 3.3; Br, 27.2.

The same compound was formed when the acid was treated with bromine in acetic acid. The material would thus appear to be the 5-bromo derivative of the acid IV (R = COOH) though no further work was done on this compound.

Only polymeric material was formed when iodine was substituted for bromine in the above reaction.

AUSTIN, TEXAS

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[14] G. Lock and G. Gergely (*Ber.*, **77**, 461 (1944)) report a value of approximately 110° for the m.p. of this picrate, while V. Boekelheide and C. E. Larrabee (see ref. 4) report a value of 205–207°.

[15] See ref. 7, p. 429.

[16] See ref. 7, p. 362.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

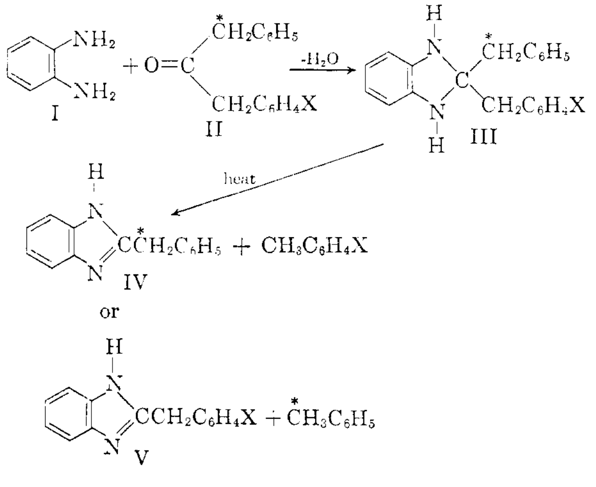
The Reaction of o-Phenylenediamines with Ketones. V. Further Studies with Dibenzyl Ketones[1,2]

BY ROBERT C. ELDERFIELD AND KENNETH L. BURGESS[3]

RECEIVED JULY 6, 1959

The thermal decomposition of a series of 2-benzyl-2-substituted benzylbenzimidazolines has been investigated. Analysis of the products by vapor phase chromatography or mass spectroscopy with the aid of C^{13} has shown conclusively that the decomposition is not subject to the Hammett equation as previously indicated on the basis of preliminary evidence. A definitive comparison of the accuracy of vapor phase chromatography *versus* use of C^{13} as a tracer in the analysis of mixtures of toluenes has been made. A critical study of optimum methods for the synthesis of a series of substituted phenylacetic acids and of a series of 1,3-diphenyl-2-propanones has been made.

In the preceding paper of this series[4] a study of the thermal cleavage of certain 2,2-dibenzylbenzimidazolines was reported. In particular, attention was devoted to the decomposition of products resulting from condensation of o-phenylenediamine with unsymmetrical dibenzyl ketones as typified by I–IV or I–V.[5]



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[1] The material presented in this paper is taken from a dissertation submitted by Kenneth L. Burgess in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, June, 1957.

[2] This investigation was supported in part by a contribution from Parke, Davis and Co., Inc., to the Michigan Memorial Pheonix Project.

[3] Procter and Gamble Fellow, 1955–1956.

[4] R. C. Elderfield and V. B. Meyer, THIS JOURNAL, **76**, 1887 (1954).

[5] The structure of the condensation products of o-phenylenediamine and the dibenzyl ketones is arbitrarily represented by III for convenience. This is probably an oversimplification. For a detailed discussion of the tautomerism involved see ref. 4.