

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.38. Found: C, 80.77; H, 6.43.

The bromide was recrystallized from absolute ethanol, m. p. 180–181°; yield 90%.

Anal. Calcd. for $C_{17}H_{16}O_2Br_2$: C, 49.51; H, 3.91. Found: C, 49.89; H, 4.07.

Treatment of the bromide with sodium iodide in acetone gave an 85% yield of the parent stilbene.

Summary

Carbomethoxystilbenes of the type $ArCH=$

$CHC_6H_4CO_2CH_3$ have been prepared from aromatic aldehydes and the appropriate methyl α -bromotoluates by the action of zinc.

Similar results have been obtained by condensing benzyl halides with methyl terephthalaldehyde.

For the unsubstituted carbalkoxystilbenes the method of Meerwein, Büchner and Emster was found to be excellent.

URBANA, ILLINOIS

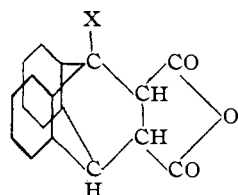
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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Bicyclic Structures Prohibiting the Walden Inversion. Some Bicyclo[2,2,2]octane Derivatives with Substituents at the Bridge-Head¹

BY PAUL D. BARTLETT AND SAUL G. COHEN

It has been shown in the laboratories of Barnett² and of Bachmann³ that maleic anhydride readily undergoes addition to 9-substitution products of anthracene, yielding dibenzobicyclo-octadiene derivatives such as I with substituents at the bridge-head position. These are among the few compounds known which are structurally incapable of replacement reactions with Walden inversion. In connection with our study of such compounds in the apocamphane series⁴ the substances I, II and III, in which X is Br, NH_2 and OH are of special interest.



I	X = Br
Ia	X = H
II	X = NH_2
III	X = OH
IV	X = $OOCCH_3$
V	X = NO_2
VI	X = $NHCOCH_3$
VII	X = $NHCOOC_2H_5$

These compounds have three principal features not found in the apocamphanes. The bridge-head carbon atom is directly bound to two phenyl groups, which in the acyclic analogs means an enhanced reactivity of the group X. The presence of two potential acid groups provides water-solubility in the salts, making these compounds quite different in manipulation from the apocamphanes. Finally, the dibasic acids show geometrical isomerism.

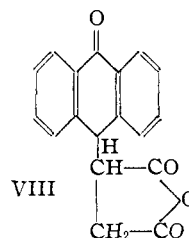
(1) Presented before the Organic Division of the American Chemical Society at its Boston meeting, September, 1939.

(2) Barnett, Goodway, Higgins and Lawrence, *J. Chem. Soc.*, 1224 (1934).

(3) Bachmann and Kloetzl, *J. Org. Chem.*, **3**, 55 (1938).

(4) Bartlett and Knox, *THIS JOURNAL*, **61**, 3184 (1939).

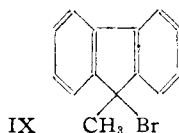
Barnett and his co-workers² observed that the addition product from 9-bromoanthracene (I) withstood treatment with alcoholic alkali for forty minutes without any replacement of the bromine. They also obtained only decomposition products from attempts to hydrolyze the corresponding acetate (IV). The direct reaction of maleic anhydride with anthranol or anthrone occurred only in the sense of a Michael condensation with the latter, yielding an uncyclized addition product (VIII).



From these results Barnett concluded that the compound III must be incapable of existence.

Where our experiments have duplicated those of Barnett and his co-workers, there is complete agreement. We subjected the bromo compound, I, in different experiments, to treatment for fifteen to eighteen hours with boiling 15 to 30% potassium hydroxide, with no other effect than to open the anhydride ring and isomerize the *cis*- into the *trans*-dibasic acid. The aqueous extract of the product, after acidification and shaking with ether, gave no precipitate with silver nitrate. As the nearest analogous compound without the bridged ring structure we

selected 9-methyl-9-bromofluorene (IX) for comparison. This compound, dissolved in ethyl alcohol at 25°, formed bromide ion at a unimolecular rate with a half-period of about five minutes. Although there is a possibility of elimination of hydrogen bromide from this compound, the isolation of impure 9-methyl-9-ethoxyfluorene in 52% yield shows that replacement of the bromine also was occurring. The corresponding half-period of the bridgehead bromine compound (I) at 83° is surely more than 1200 hours, since otherwise an easily detectable quantity of bromide ion would have been present in our experiments. Assuming a temperature coefficient of two for a ten degree rise in temperature, we find that at the same temperature there is at least a million-fold difference in reactivity between the bromine of I and that of IX. The difference is surely much greater than this, since the 50% aqueous medium in which the bicyclic compound was tested is much more favorable to bromine replacement reactions than the pure alcohol used for IX.⁵



This inertness of the bromine in I is subject to interpretation along the same lines as indicated by Bartlett and Knox,⁴ but the special structural features of this bromo compound make possible a new perspective on the problem. There is little opposition to the view that true and comparatively stable carbonium ions can be formed by the dissociation in appropriate solvents of diaryl and triarylmethyl bromides. The work of Walden⁶ has shown this by conductivity methods, and indeed Ziegler and Wollschitt⁷ have found that triphenylmethyl bromide is a completely strong electrolyte in liquid sulfur dioxide. Therefore even those who are unwilling to consider the ionization mechanism for the solvolysis of purely aliphatic tertiary halides must take it into account for highly arylated methyl bromides.

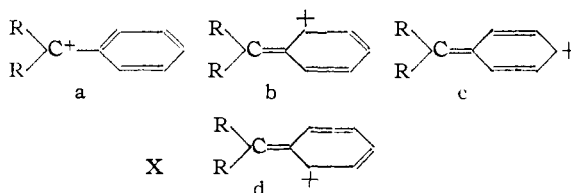
The source of the stabilization which facilitates such ionization in the arylated methyl halides is now well recognized in the contribution of the various bond structures Xa-d to the total (resonance) structure of the carbonium ion. It will be

(5) Hughes, *J. Chem. Soc.*, 255 (1935).

(6) Walden, "Chemie der freien Radikale," S. Hirzel, Leipzig, 1924.

(7) Ziegler and Wollschitt, *Ann.*, **479**, 90 (1930).

noted that three of these structures have double bonds to the central carbon atom and hence cannot be expected to contribute significantly to the resonance unless the geometry of the ion as a whole can be made compatible with such structures. This means that the central carbon atom, the three atoms directly connected to it, and in fact all the atoms of the phenyl group, must lie in the



same plane. This is obviously impossible in any carbonium ion that might be formed by the removal of Br⁻ from the compound I.

We thus derive, for carbonium ions stabilized by aromatic resonance, the generalization that the ion must approach a planar structure to be stable, and that any stereochemical conditions prohibiting a planar structure will markedly raise the energy barrier to the formation of the ion. Bartlett and Knox proposed that this might be the case for all carbonium ions, even those without aromatic resonance, taking the planar structure of trimethylborane (which, like the *t*-butyl cation, has a central atom with only six electrons) as an analogy.

With respect to reaction with metallic sodium, the bromine at the bridge-head is not wholly inert. In the reduction of 0.1 g. of I with a total of 4 g. of sodium in the presence of alcohol, 0.01 g. of the *trans*-reduction product was isolated and identified by mixed melting point with a synthetic sample prepared by boiling the addition product of maleic anhydride and anthracene with alkali. This seems to indicate that the hindrance to the momentary formation of a free radical at the bridge-head position is not as great as the hindrance to the formation of a carbonium ion. It is not purely the difference between a reagent which attacks the carbon and one which attacks the halogen, for the silver ion, which also must attack the bromine atom directly, fails to produce any silver bromide from this compound. Silver powder likewise gave no detectable reaction.

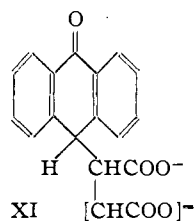
Experience in the apocamphane series suggested attempting the preparation of the hydroxy compound III or its *cis*- or *trans*-dibasic acid from the corresponding amino compound. Two

possible sources of this amino compound, the corresponding nitro and acetamino compounds (V and VI), were prepared with ease by the addition of maleic anhydride to 9-nitro- and 9-acetaminoanthracene, respectively. In neither case was the conversion into the amino compound achieved. The addition of maleic anhydride to ethyl N-9-anthrylcarbamate gave a bridge-head urethan (VII) which, as in the apocamphane series, was much more amenable to hydrolysis than the corresponding amide (VI). Sixteen hours of boiling with 35% alkali only converted the latter into the still acetylated *trans*-acid (in 80% yield), while the urethan was hydrolyzed in about an hour by 20% sodium hydroxide. Purification through the copper salt gave an amino-acid, m. p. 260–262°, of unknown configuration with respect to the two carboxyl groups.

When an acidified solution of this amino-acid was treated with sodium nitrite under controlled conditions, a variable yield of a white solid melting at 174–175° was obtained. Its analysis was correct for the dibasic acid from III, and although stable to heat its behavior in the presence of alkali was that to be expected from Barnett's results. In the presence of 10% sodium hydroxide it immediately acquired a deep orange color, and after thirty minutes of boiling, acidification and ether extraction, there resulted a mixture melting over a wide range above 130°. The results in preparing this compound were not reproducible and several other compounds were encountered in isolated runs but not satisfactorily identified.

The instability of the hydroxy compound to alkali probably is not uniquely related to the bicyclic ring structure. It is seen readily from the formula that III is a beta-hydroxy-anhydride, and its acid is an internal ketol condensation product of the acid of Barnett's compound, VIII. In the presence of a base this ketol condensation should be mobilized, and the equilibrium undoubtedly would be in favor of the uncyclized product. This is because the salt related to VIII can be enolized and converted into the alkali derivative of the corresponding anthranol. Actually, the compound VIII was never obtained from our hydroxy compound nor from Barnett's acetoxy compound (IV) with the bicyclic ring system. The only identifiable compounds which we obtained from the treatment of III with alkali were anthraquinone (obtained in the presence of

oxygen) and dihydroanthrone⁸ obtained from a reaction in the absence of air. Both these products were identified by mixed melting points. The compound VIII does not yield these products on similar treatment, and hence is not intermediate in their formation from III. The mechanism of the deketolization of the cyclic compound may be such as to yield an ionic modification of VIII especially well adapted to the Michael retrogression to anthrone and maleate or fumarate ion. The molecular species XI would be of this kind.



Experimental

Anthracene was brominated according to the directions of Barnett and Cook.⁹ The crude product was distilled *in vacuo* as was done by Bachmann and Kloetzel³ and crystallized several times from ligroin (b. p. 90–120°) and then from alcohol. The product was obtained as fine yellow needles melting at 101–103°.

9-Bromo-anthracene-9,10-endo- α,β -succinic Anhydride. (I).—The addition of maleic anhydride to 9-bromo-anthracene was carried out by refluxing equivalent quantities of the two reactants in dry xylene (5 cc. per gram of bromo-anthracene) for two and one-half hours. The product crystallized from the cooled solution in 94% yield, as white prisms, melting at 253–254°.²

Treatment of I with Alkali.—One-half gram of I was dissolved in 14 cc. of 21% aqueous potassium hydroxide and the solution was boiled for eighteen hours. The solution was acidified with chloride-free nitric acid, filtered and extracted with ether. Addition of a solution of silver nitrate to the water layer gave no precipitate or opalescence. Similar results were obtained when 50% aqueous alcohol was used as the solvent in this alkali treatment.

From this experiment a solid was recovered from the ether extract weighing 0.4 g., sintering at 210° and melting at 231°. Recrystallization from ether-petroleum ether gave white prisms melting at 238–240°; melting point, mixed with starting material, 224°. This product, not identical with either the starting material or the acid obtained from it by gentle treatment with alkali and acidification, is evidently the *trans*-dibasic acid.

*Anal.*¹⁰ Calcd. for C₁₈H₁₀O₄Br: C, 57.94; H, 3.51. Found: C, 58.20; H, 3.70.

Solution in acetic anhydride and seeding with the anhydride starting material produced a small quantity

(8) Houben, "Das Anthracen und die Anthrachinone," Verlag Georg Thieme, Leipzig, 1929, p. 179.

(9) Barnett and Cook, *J. Chem. Soc.*, **125**, 1086 (1924).

(10) Analysis was performed by H. S. Wight.

of this anhydride, which may have been produced by a slow isomerization to the *cis*-form followed by dehydration, or it may have been present as an impurity in the *trans*-acid.

In an attempt to carry the alkali treatment still farther, we boiled 0.2659 g. of the anhydride with 10 cc. of 50% aqueous potassium hydroxide in a copper vessel. On the ninth day a hole had been eaten through the vessel and the material ran out. From an extract of the bench-top we recovered 35% of the bromine-containing *trans*-acid.

The *cis*-acid from I was obtained in practically quantitative yield when 0.1 g. of the anhydride was dissolved in 10 cc. of 10% potassium hydroxide by boiling and the solution cooled and acidified. This acid melted at 106°, re-solidified and melted again at 253–254°, both alone and when mixed with the original anhydride. When this *cis*-acid was dissolved in warm acetic anhydride, the original anhydride immediately crystallized quantitatively.

cis-trans-Isomerism of the Acid from Ia.—The anhydride Ia, m. p. 258–260°, prepared according to Clar,¹¹ when boiled four hours with 2% potassium hydroxide, yielded a product which, after drying *in vacuo*, melted at 258–260° alone, and when mixed with the starting material. However, on boiling for sixteen hours with 3 g. of potassium hydroxide in 14 cc. of water, a product was obtained melting at 241°, which depressed the melting point of the original anhydride to 223°. Diels and Alder¹² prepared the *trans*-acid, m. p. 241–242°, by boiling 5 g. of the *cis*-dimethyl ester for twenty minutes in a solution of 0.5 g. of sodium in 100 cc. of alcohol. Treatment with the concentrated alkali for intermediate lengths of time gave mixtures of the *cis*- and *trans*-acids.

Treatment of I with Silver Nitrate.—A solution of 1.0226 g. of the anhydride and 1 g. of silver nitrate in 70 cc. of alcohol was heated to boiling for two and one-half hours on the steam-bath and allowed to stand for three days. There was a precipitate weighing 0.0248 g. Of this, 0.0118 g. was ignited in a porcelain crucible, leaving a residue of 0.0044 g. of silver which, after a second ignition, weighed 0.0042 g. These figures correspond to 37.3 and 35.5% of silver, respectively. Solution in nitric acid and precipitation gave 0.0054 g. of silver chloride. On the basis of 35.5% of silver the equivalent weight of the silver-containing precipitate was 304; calculated for C₁₈H₁₁O₄-BrAg₂, 293.5. The precipitate is therefore accounted for as the silver salt of the bromine-containing dibasic acid, and not as silver bromide.

Treatment of the Bromo Compound I with Silver Powder.—Four-tenths gram of silver powder was added to a solution of 0.1779 g. of the compound I in 25 cc. of acetone. The solution was kept at room temperature for two days, and was boiled for sixteen days. The mixture was filtered and the solvent was removed. The residue weighed 0.16 g. and was identical with the starting material. When this procedure was carried out in boiling xylene, again only starting material was recovered.

Reduction of I with Sodium.—The bromo-anhydride (0.1 g.) was dissolved in about 20 cc. of alcohol containing a little sodium ethoxide, and 1 g. of sodium was added.

When this had dissolved, the solution was acidified, diluted with water and extracted with ether. The ether was evaporated and the residue again dissolved in alcohol and treated with sodium. After four such treatments with a gram of sodium each time, 0.01 g. of *trans*-reduction product was recovered, m. p. 234–235°. Mixed with synthetic material of melting point 241°, the melting point was 234–237°, while a large depression was obtained on mixture with the *trans*-bromo-acid. In a number of such reduction runs, silver bromide was precipitated from the aqueous extract of the product, the maximum amount obtained being 95.4% of the theoretical, from a run in which the reaction mixture was boiled during the reduction. The reduction in most of the runs was less than 50%, and the organic product consisted of difficultly separable mixtures.

9-Methylfluoreneol was made in 94% yield of crude product by the method of Ullmann and von Wursterberger¹³ and melted at 172° after crystallization from benzene.

9-Methyl-9-bromofluorene.—0.87 g. of 9-methylfluoreneol was dissolved in 20 cc. of anhydrous ether. At 0°, hydrogen bromide was passed into this solution until it was fuming strongly, with anhydrous magnesium sulfate present to remove the water formed. After two hours at 0°, a yellow color had developed. The solution was then filtered and the ether was removed under reduced pressure in a stream of dry nitrogen. The oil residue was extracted with 10 cc. of petroleum-ether at room temperature, and a small quantity of red oil which did not dissolve readily was discarded. The solution was cooled in dry-ice and nearly colorless crystals were deposited, 0.92 g., 80% yield, melting at 48.5–49.5°. The recrystallized product melted at 50°. It has been reported previously by Keizo Nakamura.¹⁴ It was kept in dry-ice until used, since on standing at room temperature in the light, it was converted into a red oil with loss of hydrogen bromide.

Reaction of 9-Methyl-9-bromofluorene with Alcohol.—0.92 g. of 9-bromo-9-methylfluorene was dissolved in 10 cc. of absolute alcohol. After eleven hours at room temperature, the solution was poured into twice its volume of water. The mixture was cooled in an ice-bath, and the solid which formed was filtered off, 0.65 g., melting nearly completely at 75°, but with a small quantity of solid persisting until a much higher temperature. The solid was taken up in 25 cc. of ether, giving a yellow solution and a white insoluble solid, 0.10 g., which turned yellow on exposure to air, and decomposed over a wide range to about 250°. Evaporation of the ether gave a solid, 0.55 g., melting poorly to 77°. This was dissolved in petroleum ether (35–60°) and the solution was filtered from a small quantity of insoluble material, 0.02 g., decomposing over a range to 110°. Concentration of the petroleum ether gave 0.3 g. of solid melting 75–80°, and 0.11 g. melting 72–79°. Recrystallization from dilute alcohol gave fine white needles, melting at 82–83°.

Anal. Calcd. for C₁₈H₁₉O: C, 85.68; H, 7.20. Found: C, 85.63; H, 7.29.

Reaction of 9-methyl-9-bromofluorene with alcohol was followed kinetically by titrating aliquot portions of the

(11) Clar, *Ber.*, **64**, 2194 (1931).

(12) Diels and Alder, *Ann.*, **486**, 191 (1931).

(13) Ullmann and von Wursterberger, *Ber.*, **38**, 4107 (1905).

(14) Keizo Nakamura, *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **14**, 184 (1930).

reaction mixture against standard base: 0.6949 g. of 9-methyl-9-bromofluorene was dissolved in 50 cc. of absolute ethyl alcohol at 25.0° and 5-cc. portions were withdrawn at intervals. Each portion was pipetted into a 125-cc. glass-stoppered Erlenmeyer flask containing 50 cc. of water and 5 cc. of chloroform. By quick shaking the solution was cleared and the acid was then neutralized with 0.5525 N sodium hydroxide. The end-points were sharp.

TABLE I

Time in minutes	Cc. of base
4.5	2.29
22.08	3.73
33.33	4.21
51.17	4.56
∞	4.90

When the logarithms of the concentrations of bromo compound were plotted against time, the slope of the line gave a rate constant of 0.0442 min.⁻¹.

9-Nitroanthracene was made by the nitration of anthracene according to the directions of Dimroth.¹⁵ From 50 g. of anthracene was obtained 35 g. of 9-nitroanthracene, a 56% yield, orange needles, melting at 145–146°.

The nitrobicyclo compound V was obtained when a solution of 1.5 g. of 9-nitroanthracene and 1 g. of maleic anhydride in 5 cc. of xylene was boiled for two hours. The product, twice crystallized from xylene, weighed 1.2 g. (56% yield) and melted at 244–245°.

Anal. Calcd. for C₁₈H₁₁NO₃: C, 67.30; H, 3.45. Found: C, 67.54; H, 3.84.

Attempts to reduce this to the amino compound (II) by stannous chloride did not lead to the desired product.

9-Aminoanthracene was made by the reduction of 9-nitroanthracene with stannous chloride, the method of Meisenheimer and Connerade.¹⁶ We obtained, in 91% yield, a yellow product which rapidly became brown on exposure to air. It melted unsharply at 135–140°, after softening at 120°. The highest reported melting point is 145–150° after softening at 135°¹⁶ and it has also been reported as decomposing upward from 115°.¹⁷ On long standing in a desiccator it was converted to a compound melting at 216–217°. A solution of 9-aminoanthracene in benzene, on standing for several months, also deposited crystals of this high melting compound. We did not characterize it further.

The reactions of maleic anhydride with 9-aminoanthracene, and with 9-aminoanthracene hydrochloride, did not lead to the desired product.

N-9-Anthrylacetamide was made by the action of acetic anhydride on 9-aminoanthracene at room temperature, the method of Goldmann.¹⁷ The product is obtained, in practically quantitative yield, as slightly colored needles, melting at 272–274°.

The addition of maleic anhydride to N-9-anthryl acetamide was carried out by boiling a solution of 2.7 g. of the former and 4 g. of the latter in 20 cc. of xylene for four and one-half hours. The product (VI) was deposited from the cooled reaction solution in 91% yield, as white prisms, melting unsharply at 268°, after sintering from 257°.

(15) Dimroth, *Ber.*, **34**, 221 (1901).

(16) Meisenheimer and Connerade, *Ann.*, **330**, 165 (1904).

(17) Goldmann, *Ber.*, **23**, 2522 (1890).

*Anal.*¹⁰ Calcd. for C₂₀H₁₅O₄N: C, 72.05; H, 4.54. Found: C, 71.95; H, 4.51.

The bridge-head amide (VI) proved resistant to acid or base hydrolysis, and the bridge-head amine could not be prepared from it.

One-half gram of the amide was dissolved in a solution of 5 g. of sodium hydroxide in 14 cc. of water, and boiled for sixteen hours. Acidification of the black reaction solution gave 0.4 g., 76% yield, of a white solid, sintering at 250°, and melting at 253°, and depressed to 242° on mixture with the starting material. Analysis indicated that it was the dibasic acid, and the melting point depression that it was the *trans*-isomer.

*Anal.*¹⁰ Calcd. for C₂₀H₁₇O₄N: C, 68.38; H, 4.88. Found: C, 68.10, 68.39; H, 4.91, 4.87.

A solution of 0.2 g. of the amide VI in 10 cc. of concentrated sulfuric acid was allowed to stand at room temperature for one hour. Water was added until a slight turbidity formed, and the solution was warmed for one-half hour on the steam-bath. Color began to develop, so the heating was stopped. The solution was poured into water, and the product was extracted with benzene. We obtained 0.17 g., 85% yield, of starting material, sintering at 250° and melting at 263°. Its melting point was elevated on mixture with the starting material. Little or no hydrolysis had taken place.

Ethyl 9-Anthrylcarbamate.—Twenty-one grams of 9-nitroanthracene was reduced with stannous chloride as directed by Meisenheimer and Connerade.¹⁶ The tin double salt was decomposed with dilute ammonia, and the amine was extracted with ether. The amine was not isolated, but this ether solution was dried over magnesium sulfate, and treated with 20 cc. of ethyl chloroformate. The reaction was allowed to run for thirty-six hours at room temperature, and a precipitate of the urethan and the amine hydrochloride formed. This solid was filtered off, and evaporation of the filtrate gave a small quantity of the urethan. The solid was boiled for a few minutes in 500 cc. of xylene and filtered, and from the cooled filtrate the urethan crystallized. Combined with that obtained from the mother liquor, the yield was 9.4 g., 75%. The solid filtered from the boiling xylene was suspended in dilute alkali and extracted with ether. The ether extract was treated with ethyl chloroformate and more of the urethan was made. The urethan was crystallized twice from xylene, and was obtained as fine, light yellow needles, melting at 224–225°.

*Anal.*¹⁰ Calcd. for C₁₇H₁₅O₂N: C, 76.96; H, 5.70. Found: C, 77.15; H, 5.77.

The addition compound VII was obtained in 95% yield when 15 g. of maleic anhydride and 4.2 g. of ethyl 9-anthrylcarbamate were boiled in 60 cc. of dry xylene for 2.75 hours. There was a rapid development of an orange-red color, which slowly faded during the progress of the reaction. The product crystallized from the cooled reaction medium in colorless prisms, melting at 252–254°, with decomposition. It was washed with benzene and hexane, dried *in vacuo* and analyzed.

*Anal.*¹⁰ Calcd. for C₂₁H₁₇O₅N: C, 69.38; H, 4.72. Found: C, 69.38; H, 4.49.

Bridge-head Amine (II) Hydrolysis of the Urethan VII.—In one of a series of preparations, 0.3 g. of the bridge-

head urethan was boiled for 1.25 hours in 20 cc. of 20% sodium hydroxide. A yellow color developed. The solution was filtered, acidified and warmed until the carbon dioxide was removed. The solution was made neutral, the silica which formed was filtered off, and a solution of 1 g. of cupric acetate in a little water was added. The mixture was warmed for a few minutes, and the precipitated copper salt was filtered off. The calcium and mercuric salts were soluble, whereas the copper salt precipitated from even a weakly acidic solution. When the reaction is run on a larger scale, the copper salt is rather to be centrifuged than filtered. The copper salt was suspended in a little water and dissolved by addition of a few drops of concentrated hydrochloric acid. Hydrochloric acid was added, so that the solution was about 6 normal. The solution was cooled in ice and the product slowly crystallized. The product also crystallizes out if the copper salt is merely dissolved in concentrated hydrochloric acid. We obtained 0.15 g. of crude product, 51% yield. It was purified by solution in water and precipitation by addition of hydrochloric acid. It melted at 260–262° with decomposition.

*Anal.*¹⁰ Calcd. for $C_{18}H_{16}NClO_4$: C, 62.53; H, 4.66; N, 4.05. Found: C, 62.28; H, 4.74; N, 3.94.

Treatment of the Amine II with Nitrous Acid.—To a solution of 0.62 g. of the amine II in 40 cc. of 20% hydrochloric acid, a solution of 0.7 g. of sodium nitrite was added and the mixture allowed to stand at room temperature for several hours. A white turbidity appeared immediately. The mixture was extracted with ether, the ether dried and concentrated and petroleum ether added. There was obtained 0.37 g. (65% yield) of a product giving the correct analysis for the hydroxy compound III, m. p. 174–175°.

*Anal.*¹⁰ Calcd. for $C_{18}H_{14}O_3$: C, 69.68; H, 4.55. Found: C, 69.54; H, 4.83.

This product was later obtained without prior isolation of the amine II. A solution of 0.3 g. of the bridge-head urethan VII in 20 cc. of 20% sodium hydroxide was boiled for thirty minutes. The solution was acidified, and to the clear acidic solution 0.5 g. of sodium nitrite was added. After standing one-half hour at 0° and at room temperature for sixteen hours, the mixture was saturated with hydrogen chloride gas and extracted with ether. The ether was dried and concentrated, and on addition of petroleum ether this product was obtained in 62% yield.

Measurement of the Nitrogen Evolved in the Nitrous Acid Reaction.—One-half gram of the bridge-head urethan VII was hydrolyzed by boiling for one hour in 25 cc. of 20% sodium hydroxide. The solution was neutralized and 3 cc. excess of concentrated hydrochloric acid was added. The flask was immersed in an ice-bath, and a solution of 0.5 g. of sodium nitrite was admitted. The nitrogen, carried on

a stream of carbon dioxide, was passed through alkaline permanganate and collected over 50% potassium hydroxide. The reaction was complete in a few hours at 0°.

The gas gave no test for oxides of nitrogen with starch-iodide paper and it did not support combustion.

While the reaction was proceeding at 0°, a white solid precipitated. However, it turned to a yellow oil when it was filtered off, or when the solution was allowed to warm up to room temperature. In one instance, we filtered off the solid which formed, but could isolate from it only an impure compound (1.5%) melting 160–200°. From the filtrate, worked up as usual, we obtained, in 4% yield, an impure product, melting 175–200°, and, in 19% yield, the compound melting at 174–175°, and an oil residue.

The results of this nitrous acid reaction were not strictly reproducible, the yields varying over a wide range. Several other compounds, none of them identical with any prepared by Barnett and his co-workers,² were found in different runs, usually in small yields, but they have not yet been satisfactorily identified.

Behavior of the Product of the Nitrous Acid Reaction.—Thirteen milligrams was boiled in 0.8 cc. of xylene for fifteen minutes. The compound was slightly soluble and stable, and was recovered both from the undissolved residue and from the filtrate.

Treatment with Alkali.—(a) The orange solution of 0.2 g. of the hydroxy compound in 20 cc. of 10% sodium hydroxide was boiled for one-half hour. A red color developed and the solution became turbid. Acidification discharged most of the color, and precipitated 0.1 g. of a yellow solid which melted at 258–269°. After crystallization from acetic acid and from xylene it darkened at 270° and melted at 277–280°, and on mixture with anthraquinone it melted at 279°. The product was apparently anthraquinone, obtained in 75% yield.

(b) The solution of 0.1 g. of the hydroxy compound in 10 cc. of 10% sodium hydroxide was boiled for thirty minutes in a stream of nitrogen. The orange solution was cooled and acidified. The color was discharged and a yellow solid formed, weighing 0.06 g. This sintered at 130°, melted to a large extent at 160°, and completely at 198°. After standing in ether solution for several weeks, it was converted to a compound melting at 240–250°.

These same compounds were obtained from anthrone. One-fourth gram of anthrone was boiled for thirty minutes in 50 cc. of 10% sodium hydroxide. On acidification a yellow compound, sintering at 145°, melting to a large extent at 155° and fully molten at 198°, was obtained. This melting range was not affected on mixture with the compound obtained above. Oxidation of this by ferric chloride in acetic acid solution, the method of Dimroth,¹⁸ yielded dihydroanthrone, melting at 245–257°, and at 242–257° on mixture with the compound obtained above.

Summary

The addition product (I) of maleic anhydride to 9-bromoanthracene, which is structurally incapable of a Walden inversion in the replacement of the bromine, shows no replacement of this bromine on boiling for eighteen hours with 30%

(18) Dimroth, *Ber.*, **34**, 222 (1901).

TABLE II

Time, hours	Vol. N ₂ (unlevelled), cc. <i>t</i> = 30°
2	28
3.5	35
4	36
4.5	36.3, levelled vol. 34 cc.

Corrected for temperature, 30.6 cc.

Calculated, 31 cc.

potassium hydroxide in 50% aqueous ethyl alcohol. This extends the observations of Barnett and his co-workers to more drastic conditions.

Two interpretations of this and similar facts are considered, that a Walden inversion must attend such a replacement reaction, or that a carbonium ion must be formed in which the central carbon atom and the three atoms directly combined with it lie in a common plane. The latter concept, advocated previously by Bartlett and Knox by analogy to boron compounds, is here correlated with the resonance normally present in an arylated carbonium ion. This interpre-

tation is favored but not conclusively proved.

The bromine can be replaced by hydrogen by means of reduction with sodium and alcohol.

Maleic anhydride has been added to ethyl *N*-9-anthrylcarbamate to yield a bridged-ring urethan (VII) which is readily hydrolyzed to the amino-dibasic acid related to II. Nitrous acid converts this into a compound which is probably the dibasic acid with hydroxyl on the bridge-head. As expected by Barnett, this compound is very unstable to alkali. Its decomposition is interpreted as ketol cleavage.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CREIGHTON UNIVERSITY]

The Partial Pressure of Hydrogen Chloride from its Solutions in *o*-Nitrotoluene, *m*-Nitrotoluene and *n*-Hexane at 25°

BY S. JAMES O'BRIEN AND CHRISTOPHER L. KENNY

In an earlier paper¹ the partial pressure of hydrogen chloride from its solutions in various solvents was interpreted in terms of an acid-solvent reaction. The results so obtained may be taken as a measure of the relative basicities of the solvents used. It also has been pointed out^{2,3,4} that the problem of solvent basicity can be attacked by means of infrared absorption studies. In work of this type the position of a certain absorption band, which is attributed to the formation of a hydrogen bond and which shifts to longer wave lengths in the more basic solvents, is considered a measure of the basicity of the solvent. It seemed of interest to determine to what extent the conclusions concerning the basicities of solvents obtained from such infrared absorption data parallel those obtained from partial pressure experiments. It was decided, then, to measure the partial pressure of hydrogen chloride from its solutions at 25° in the ortho and meta isomers of nitrotoluene in order to compare these and other similar available data with those obtained from infrared absorption investigations.⁵

Also, a few measurements of the partial pressure of hydrogen chloride from *n*-hexane solutions at the same temperature were made in order to determine whether the deviation of hydrogen chloride from the law of Raoult in this solvent is positive, as might be anticipated from the results obtained with haloforms in hydrocarbon solutions,⁶ and from the fact that the rate of addition of hydrogen chloride to ethylenes is so very much greater in aliphatic than in aromatic hydrocarbons.⁷

Experimental

Apparatus and Method.—The apparatus and method were in general the same as those employed in the previous work.^{1,8} The time allowed for the establishment of the solution-vapor equilibria ranged from two to five days. In the analysis of the solutions of the nitrotoluenes it was found to be advantageous to add a drop or two of capryl alcohol to the solutions before titration with sodium hydroxide. The constant temperature bath was regulated at 25.00 ± 0.02°.

Materials.—The liquids used were Eastman Kodak Company products. The *m*-nitrotoluene and *n*-hexane were not further purified. Since the *o*-nitrotoluene had a slightly pink color which turned to a deep purple on the

(1) S. J. O'Brien, C. L. Kenny and R. A. Zuercher, *THIS JOURNAL*, **61**, 2504 (1939).

(2) W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 99 (1939).

(3) W. Gordy, *ibid.*, **7**, 93 (1939).

(4) W. H. Rodebush and A. M. Buswell, *J. Phys. Chem.*, **43**, 219 (1939).

(5) Since this paper was written, an article by W. Gordy and S. C. Stanford, *J. Chem. Physics*, **8**, 170 (1940), has appeared in which a study of this kind has been made. Gordy and Stanford relate the basicities of solvents as derived from shifts of the OD vibrational band of CH₃OD in these solvents, to those derived from

measurements of the solubilities of monofluorodichloromethane. This comparison seems to be in accord with the opinion, stated later in this paper, concerning the discrepancies between the basicities of solvents as intimated by infrared absorption and solubility studies.

(6) G. F. Zellhoefer, M. J. Copley and C. S. Marvel, *THIS JOURNAL*, **60**, 1337 (1938).

(7) S. F. O'Connor, L. H. Baldinger, R. R. Vogt and G. F. Hennion, *ibid.*, **61**, 1454 (1939).

(8) J. Saylor, *ibid.*, **59**, 1712 (1937).