yielded 10.2 g. of unchanged 4-bromo-2-nitrotoluene. Addition of an excess of hydrochloric acid to the aqueous alkaline solution gave 10.1 g. (41%) of a crystalline precipitate of 4-bromo-2-nitrobenzoic acid, which was recrystallized from benzene and melted at 163.5–165°.

BATON ROUGE 3, LOUISIANA

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

Reactions of Hindered α-Bromo- and Hydroxysuccinic Acids[1a,b]

BY WYMAN R. VAUGHAN AND KIRBY M. MILTON[1c]

RECEIVED FEBRUARY 5, 1952

A number of dibenzo[2,2,2]bicycloöctadiene-2,3-dicarboxylic acids have been prepared and their reactions have been studied. The preparation of one such compound involves a well-defined *trans* addition of hydrogen bromide to the olefinic double bond of dibenzo[2,2,2]bicycloöctatriene-2,3-dicarboxylic acid. The resulting product in alkali undergoes, *inter alia*, *cis* elimination of bromide with the carboxyl beta to it thus suggesting that care must be used in invoking this reaction to establish structural geometry. The steric disposition of groups about the bromine and hydroxyl of the adducts is such as to inhibit completely intermolecular nucleophilic displacements, in place of which a number of anomalous reactions are observed. Infrared spectra for the adducts and their derivatives are given.

The observation that 2-bromodibenzo[2,2,2]-bicycloöctadiene - 2,3 - *cis* - dicarboxylic anhydride (*cis* - 9,10 - dihydroanthracene - 9,10 - *endo* - α-bromo - α,β-succinic anhydride) (IA) affords 2-hydroxydibenzo[2,2,2]bicycloöctadiene - *trans* 2,3 - dicarboxylic acid (*trans*-9,10-dihydroanthracene-9,10-*endo*-α-hydroxy-α,β-succinic acid) (IVB) led the investigators[2] to suggest that such substances might well prove excellent for study of the Walden inversion.

It seemed to the present authors, however, that such compounds would be still better suited for study of the reactions of hindered halides and alcohols since the substituents on C^α (C^2) are almost as inaccessible to external nucleophilic displacement as in apocamphyl chloride and apocamphanol.[3] Striking dissimilarities between the latter substances and those under investigation include the possibility of structural inversion owing to the absence of the complete "cage" and the presence of adjacent polar groups capable of participating in nucleophilic reactions. Hence the possibility of observing other than simple S_N2 reactions was anticipated.

Accordingly the preparation of a number of related substances was carried out, either by the addition of anthracene to the appropriate dienophile, or by subsequent reaction of the resulting adducts with the proper reagents. The *cis* and *trans* structures of the key compounds are illustrated by Figs. 1 and 2, respectively, and Table I lists the principal substances studied.

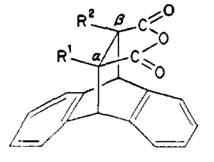

Fig. 1 (A series)

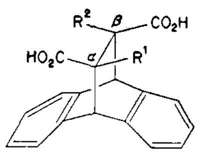

Fig. 2 (B series)

TABLE I

Compound	*cis*-Anhydride R¹	R²	Compound	*trans*-Acid R¹	R²
IA[2]	Br	H	IB	Br	H
IIA	Br	CH_3	IVB	OH[2]	H
IIIA	OH	CH_3	IIIB	OH	CH_3

In addition the anthracene adducts of propiolic, tetrolic and acetylenedicarboxylic acids were prepared and characterized (Fig. 3).

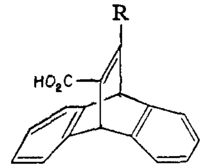

Fig. 3.

V, R = H
VI, R = CH_3
VII, R = CO_2H

Normal Reactions: The Bromoanhydrides

Examination of Stuart models of compounds IA and IIA reveals that the β-carboxyl is favorably situated for nucleophilic displacement of the α-bromine. Thus the previously reported[2] reaction: IA → IVB, and the presently reported reaction: IIA → IIIB, follow the usual course of behavior for β-haloacids[4]: after opening of the anhydride the β-carboxylate ion attacks the rearside of C^α displacing bromide ion, and the β-lactone thus produced does not survive but is cleaved by hydroxide which attacks the β-carbonyl carbon.[5] The resulting indirect inversion on C^α is in accord with the observations of others,[6] and the resemblance to the normal behavior of β-haloacids is strengthened by the concurrent production[6] of the olefinic compounds V and VI (Fig. 3) from IA and IIA (Fig. 1), respectively, by the simultaneous *trans* elimination of bromide ion and carbon dioxide. The structures of the unsaturated acids were established by comparison with independently synthesized V and VI.

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[1] (a) Abstracted from the Ph.D. dissertation of Kirby M. Milton, University of Michigan, 1951. (b) Presented before the Division of Organic Chemistry at the 119th Meeting of the American Chemical Society at Boston, Massachusetts, April 5, 1951. (c) Abbott Laboratories Fellow, 1949–1950.

[2] W. E. Bachmann and L. B. Scott, THIS JOURNAL, **70**, 1458 (1948).

[3] P. D. Bartlett and L. H. Knox, *ibid.*, **61**, 3184 (1939).

[4] H. Johansson and S. M. Hagman, *Ber.*, **55**, 647 (1922).

[5] T. L. Gresham, J. E. Jansen and F. W. Shaver, THIS JOURNAL, **70**, 998 (1948).

[6] A. R. Olson and R. J. Miller, *ibid.*, **60**, 2687 (1938); A. R. Olson and J. L. Hyde, *ibid.*, **63**, 2459 (1941); P. D. Bartlett and P. N. Rylander, *ibid.*, **73**, 4275 (1951).

The reaction of IIA with sodium methoxide in dioxane solution can follow one of only two reasonable paths: direct nucleophilic displacement of the bromine in the β-half-ester formed by alkoxide opening of the anhydride, or intramolecular transfer of the alkoxide group from the β-half-ester to C$^\alpha$ with simultaneous alkoxide attack upon the carbonyl function. The former is tentatively discarded in favor of the latter, precedent for which is to be found in the observation of Noyes that a methyl *trans*-3-aminocyclopentanecarboxylate on treatment with nitrous acid affords in part a *cis*-methoxycyclopentanecarboxylic acid.[7]

The structure of the major reaction product, the half-ester VIII (Fig. 4, R = CH_3) is assigned for the following reasons: (1) saponification affords a methoxy acid, IX (Fig. 4, R = H), which does not form an anhydride and whose infared spectrum in general resembles that of the unmethylated *trans*-acid IIIB (Fig. 2); and (2) any opening of the original anhydride ring which yielded other than a β-half-ester would result in β-lactone formation in the usual way, followed by cleavage on the β-carbonyl to an hydroxy *trans*-ester which is known. It is of course both reasonable and possible in view of the isolation of but 50% of the reaction product as VIII that an appreciable quantity of IIA did follow the latter course; however, all attempts to isolate the hydroxy *trans*-ester met with failure. Thus the reaction of IIA with sodium methoxide is tentatively pictured as

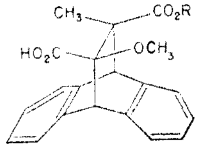
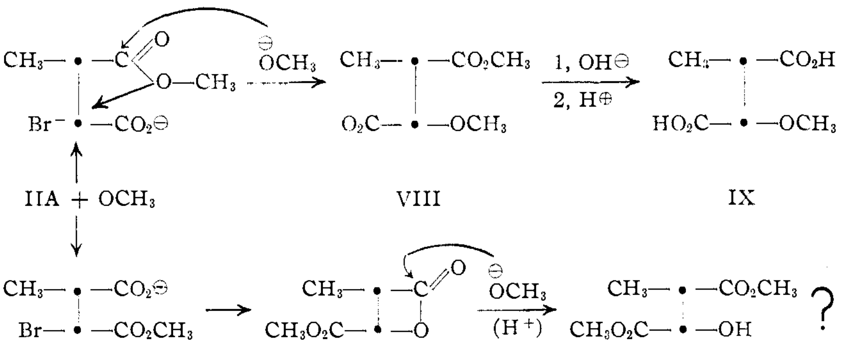


Fig. 4.—VIII (R = CH_3), IX (R = H).



It is also of course possible that methoxide is involved only in the anhydride opening reactions, with methanol replacing methoxide in the second stages of both series.

The reaction of IIA with ammonia in dioxane appears to give a near-statistical opening of the anhydride, since somewhat more than half the theoretical quantity of ammonium bromide was obtained and the only organic product actually isolated (in somewhat less than 50% yield) contained bromine. Initially the reaction product was alkali soluble, but drying and recrystallization evidently converted the β-half-amide X′ to the imide X. Inasmuch as the other organic product(s) have not been identified, only half of the reaction can be described with any certainty, but the fate of the remainder of the organic material tentatively may be inferred as above

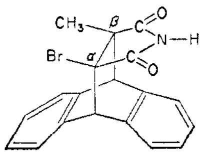
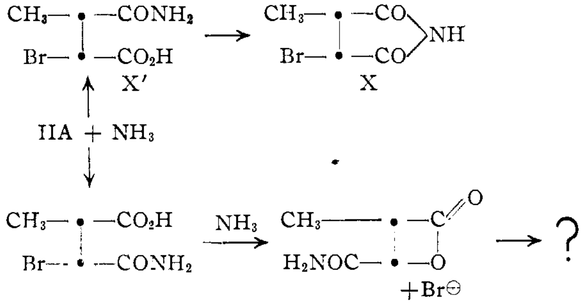


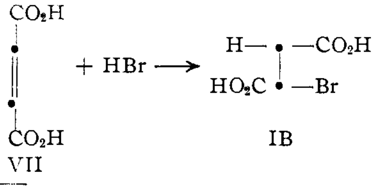
Fig. 5.—X.



Structure of the *trans*-Acids

The *trans* configuration of the hydroxy acids IIIB and IVB (Fig. 2) is inferred from the nature of the reactions producing them and from the fact that the independently synthesized *cis* compound IIIA (Fig. 1) which corresponds to IIIB does not exist as the free acid but in common with all of the *cis* compounds studied spontaneously forms the anhydride. The preparation of the *cis* compound corresponding to IVB has not yet been achieved. All attempts to add acetoxymaleic anhydride[8] to anthracene were unsuccessful, in sharp contrast to the facile reaction of acetoxycitraconic anhydride and in spite of the observation that acetoxymaleic anhydride will undergo the diene addition, albeit with the more reactive cyclopentadiene.[9] No appreciable reaction was observed at low temperatures, and above 80° extensive decomposition of the anhydride was evidently much faster than the addition reaction.

The *trans*-bromo acid IB (Fig. 2) was first obtained by the (apparent) diene reaction of anthracene with bromofumaric acid, but subsequently it was prepared by addition of hydrogen bromide to VII (Fig. 3). Again the structure is inferred from the nature



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[7] W. A. Noyes and G. S. Skinner, This Journal, **39**, 2692 (1917).

[8] E. Ott, *Ber.*, **47**, 2392 (1914).

[9] P. Nylén and A. Olsen, *Kgl. Norske Videnskab. Selskabs, Forh.*, **11**, 229 (1938).

of the reaction and from the non-identity of the product IB with IA. The production of V (Fig. 3) from both IA and IB supports the argument. The preparation of IB (Fig. 2) by *trans* addition of hydrogen bromide to VII (Fig. 3) in acetic acid at room temperature is thought to constitute the first demonstrable *trans* addition of hydrogen halide to an olefinic system.

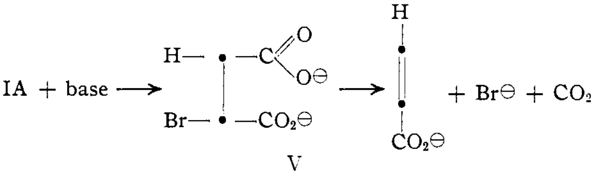
The assignment of *trans* configurations to IB, IIIB and IVB is supported by infared analysis. While far from close correspondence is observed, the general shapes of the curves for the A and B series are consistent, and examination of the curves for the individual geometric pairs IA, IB and IIIA, IIIB reveals possibly characteristic differences similar to those observed among the pairs of reference substances XIA, XIB (Figs. 1 and 2, $R^1 = R^2 = H$) and XIIA, XIIB (Fig. 1 and 2, $R^1 = H$, $R^2 = CH_3$),[10] in the carboxyl–carbonyl region just below 6 μ,[11] where the *cis*-compounds have bands at slightly shorter wave-lengths than the corresponding *trans* compounds.

Abnormal Reactions: Alkali

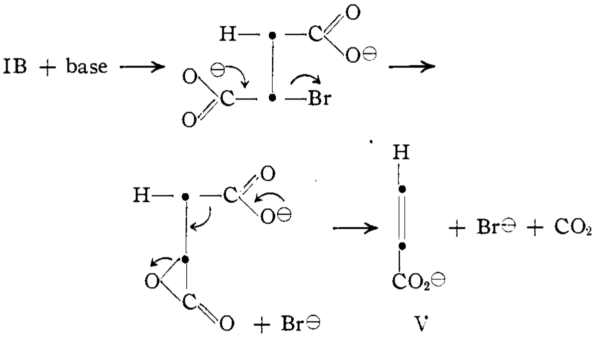
In IB (Fig. 2) internal nucleophilic displacement of bromide by the β-carboxylate group in the usual sense is impossible. Nevertheless, treatment of IB with alkali effects production of a dibasic acid, XIII, which is isomeric with IVB but which cannot be the acid corresponding to the unavailable anhydride IVA (Fig. 1) since it fails to form an anhydride and is readily attacked by cold alkaline permanganate, indicating the presence of a secondary (or primary) hydroxyl. An oxidizable function is incompatible with the original skeleton, and hence the reaction appears to involve Wagner–Meerwein rearrangement, analogous to the reaction of bornyl or isobornyl chloride with alkali to produce camphene hydrate.[12] The distinctly different shape of the infrared curve, especially beyond 7 μ where skeletal frequencies appear[11], supports the rearrangement hypothesis. However, any rearrangement which destroys the anthracene structure need not be considered, since vigorous alkaline or acid permanganate oxidation of XIII both afford anthraquinone.

A particularly interesting feature of the reaction of IB with alkali is the simultaneous production of the unsaturated acid V (Fig. 3). Heretofore it has been tacitly assumed[13] that the intramolecular elimination of bromide ion and carbon dioxide from a β-haloacid under the influence of alkali is *trans* elimination, even as the formation of the (often) accompanying β-lactone[4,6] is necessarily a *trans* phenomenon. Inasmuch as the kinetics of the reaction of β-haloacids in basic solution indicates two simultaneous reactions which are first order in the acid and independent of *p*H[4,14] (one producing olefin and the other a β-lactone or corresponding β-hydroxy acid), it is not necessary to assume rapid formation of a common intermediate, with different modes of decomposition as the rate-determining processes. Indeed, the evident impossibility of direct β-lactone formation and consequent absence of its hydrolysis product, IVB, in the reaction products, coupled with the production of V in the reaction of IV with alkali suggest very strongly that a common intermediate is not only unnecessary but actually improbable.

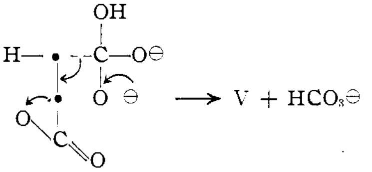
Thus a reasonable explanation of the unexpected formation of V from IB as well as from IA requires two different reaction paths. Incomplete kinetic studies[14] support the qualitative observation that IA eliminates bromide and carboxyl (*trans*) far more rapidly than does IB (*e.g.*, the latter *cis*-elimination is all but unobservable in aqueous bicarbonate but is rapid in concentrated alkali). The *trans* or normal elimination may be pictured most simply thus at moderate alkaline *p*H where there is independence of hydroxide ion concentration[4,14]



while the *cis* or abnormal elimination may be pictured most simply as involving an α-lactone structure (*i.e.*, participation by the α-carboxylate) such as is invoked to account for retention of configuration in the hydrolysis of α-haloacids[15]



The obvious dependence on hydroxyl concentration[4,14] at higher *p*H values may involve a somewhat more complex intermediate α-lactone, *e.g.*



which might be expected to eliminate bicarbonate ion more rapidly than the simpler intermediate eliminates carbon dioxide, thus accounting for the relative stability of IB in bicarbonate solution and its rapid decomposition by hydroxide.

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(10) Respectively, the adducts of anthracene with maleic anhydride, fumaric acid, citraconic anhydride and mesaconic aicd, kindly supplied by the late Professor W. E. Bachmann, *cf.* ref. 2.

(11) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 21.

(12) O. Aschan, *Ber.*, **41**, 1092 (1908).

(13) *Cf.* the assignment of the *exo* configuration to cantharidine; R. B. Woodward and R. B. Loftfield, THIS JOURNAL, **63**, 3167 (1941).

(14) W. R. Vaughan and R. Q. Little, unpublished observations.

(15) For discussion and leading references see L. P. Hammett "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 175–178.

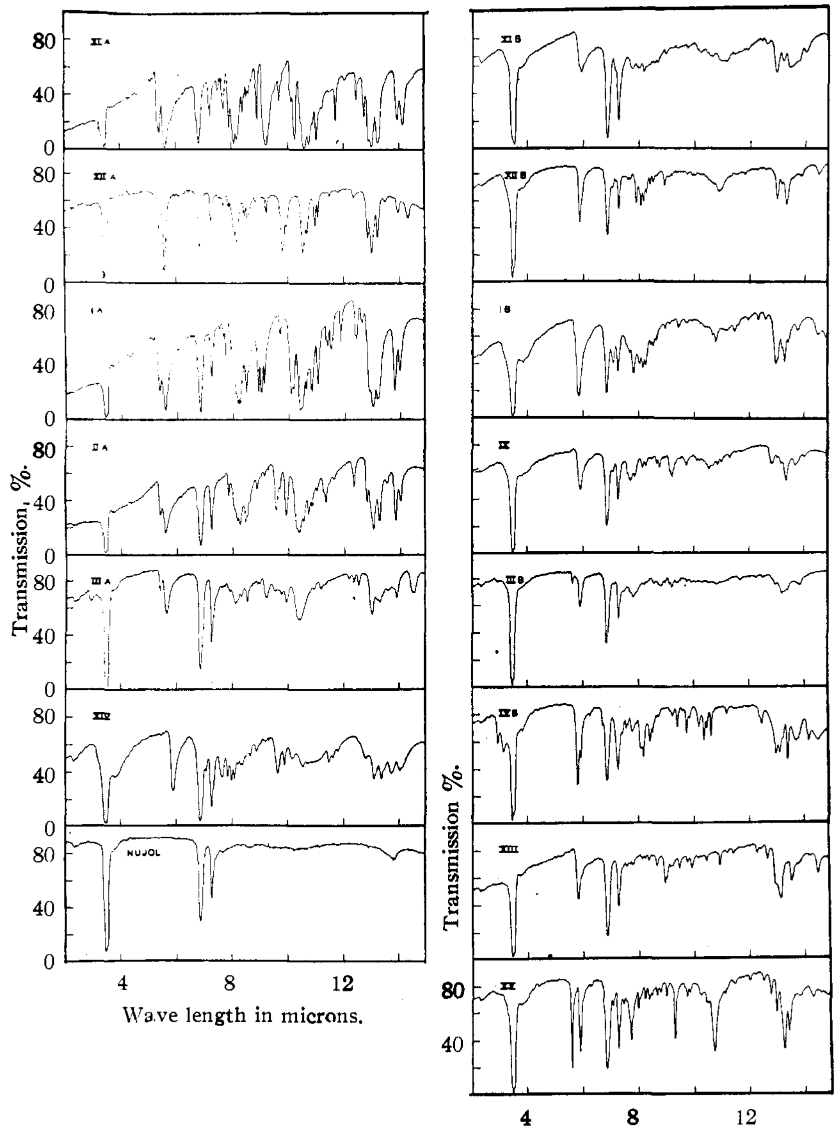

Plate. 1.—Infrared spectra: The spectra were obtained with the Perkin–Elmer double beam instrument of the Department of Physics. Mulls of 3–5 mg. of compound in a few drops of nujol were prepared and analyzed without the use of nujol in the compensating cell.

Except as noted the compounds are derivatives of *cis*- or *trans*-dibenzo[2,2,2]-bicyclooöctadiene-2,3-dicarboxylic acid: IA, 2-bromo-*cis*-anhydride; IIA, 2-bromo-3-methyl-*cis*-anhydride; IIIA, 2-hydroxy-3-methyl-*cis*-anhydride; XIA, *cis*-anhydride; XIIA, 3-methyl-*cis*-anhydride; IB, 2-bromo-*trans*-acid; IIIB, 2-hydroxy-3-methyl-*trans*-acid; IVB, 2-hydroxy-*trans*-acid; IX, 2-methoxy-3-methyl-*trans*-acid; XIB, *trans*-acid; XIIB, 3-methyl-*trans*-acid; XIII, dibasic acid from rearrangement of IB; XIV, 2-methyl-3-ketodibenzo[2,2,2]bicyclooöctadiene; XV, lactone from rearrangement of IIIB.

Normally this type of reaction should afford a hydroxy acid, but the hindrance to external nucleophilic attack coupled with the possibility of facile decarboxylation effect the unexpected *cis*-elimination.

Competing with elimination in each reaction is a second process, β-lactone formation as already discussed for IA, and molecular rearrangement in which the migrating β-bridgehead instead of the β-carboxylate's bonding electron pair provides the rearside displacement for IB. The results of a kinetic study[14] on these compounds will be reported in a subsequent paper.

Abnormal Reactions: Acid

The anomalous behavior of the hydroxy acids with hydrobromic acid is of considerable interest. When IIIA (Pl. 1) is allowed to stand with 30% hydrogen bromide–acetic acid, the only observable reaction is precipitation of a very unstable 1:1 complex which is readily destroyed with regeneration of IIIA by vacuum drying or by washing with water. Since the same complex is formed using acetic acid alone, the powerful hydrogen bromide solution is completely without effect on the hydroxyl. The *same* results obtain when sufficient hydrogen bromide–acetic acid is used to retain the product in solution until evaporation, thus precluding arguments as to inhibition of substitution by precipitation of an insoluble product.

When IIIA is treated with constant-boiling (48%) hydrobromic acid at the reflux temperature (126°) or in a sealed tube at 175°, besides tar, anthracene and starting material there is obtained (in higher yield at the higher temperature) an appreciable quantity of non-acidic material whose analysis and infrared spectrum clearly suggest that it is 2-methyl-3-ketodibenzo[2,2,2]bicyclooöctadiene (XIV).

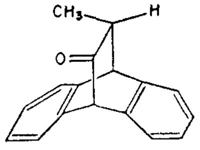

Fig. 6.—XIV.

The production of such a ketone resembles the formation of aldehydes or ketones from α-hydroxy acids, which is usually promoted by concentrated sulfuric acid (*e.g.*, acetonedicarboxylic acid from citric acid[16]).

The reactions of the corresponding *trans*-acid, IIIB (Fig. 2) with hydrogen bromide also fail to produce brominated products. With 30% hy-

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(16) R. Adams, H. M. Chiles and C. F. Rassweiler, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, second edition, p. 10.

drogen bromide–acetic acid the tertiary hydroxyl is acetylated. Failure to observe this with IIIA may be due to slightly less favorable steric disposition of the surrounding groups.

Still more striking is the effect of hot 48% hydrobromic acid on IIIB. There is formed in good yield a monobasic acid, XV, containing a slowly saponifiable group, which is instantly reformed upon acidification, thus indicating a γ-lactone. Oxidation of the compound with cold dilute acidic or alkaline permanganate is very slow, and vigorous alkaline permanganate oxidation affords no evidence of anthraquinone formation. Thus one must conclude that a rearrangement has occurred in which the anthracene structure has been destroyed and in which γ-lactone formation is possible. The presence of the lactone is supported by the appearance of a band at 5.6 μ (shifted from the 5.5 μ value for β-lactones,[11] thus indicating the less strained structure of a γ-lactone). The infrared spectrum offers no assistance in gross structure determination in view of the complexity of the problem; however, the present chemical evidence admits of no other explanation.

Until the results of degradative and synthetic studies now in progress on the rearranged products XIII and XV can be completed, it is impossible to assign structures to them with any certainty.

Conclusions

The nature of the hindrance to external nucleophilic attack on C^α is purely steric. The disposition of adjacent groups provides considerably more shielding than is encountered in neopentyl compounds, which have recently been shown to undergo normal displacement[17]; in fact the conditions at C^α approximate those at the apocamphyl bridgehead, with the same rigidity but lacking the restraint imposed by the bond to the opposite bridgehead and thus possessing the freedom to undergo inversion by either internal or external displacement. Rearrangement or other anomalous behavior is invariably observed instead of external displacement on C^α. Thus it may be argued that the most important single factor in determining the activation energy for the nucleophilic displacement process is steric inhibition of rearside approach, and that as long as no restraints such as exist at the bridgeheads of cage structures are present, the extent of stabilization of an intermediate complex by ordinary resonance or other phenomena (*e.g.*, B-strain) plays a secondary role.

Acknowledgment.—The authors wish to express their appreciation to Professor G. B. B. M. Sutherland of the Department of Physics for interpretation of the infrared spectra and to Mr. Richard Mara, Mr. Alexander Stuart and Mr. Gilbert Sloan for the preparation of the spectra.

Experimental[18,19]

2-Bromodibenzo[2,2,2]bicycloöctadiene-*cis*-2,3-dicarboxylic Anhydride (IA).—This compound was prepared according to the procedure of Bachmann and Scott[2] from purified anthracene and bromomaleic anhydride in toluene solution, maintained at the reflux temperature for three days. By evaporation of the solvent a total yield of 94% was obtained. The product was crystallized once from xylene and once from acetone; m.p. 170.5–171.5°, previously reported 169–170° cor.[2].

2-Bromo-3-methyl[2,2,2]bicycloöctadiene-*cis*-2,3-dicarboxylic Anhydride (IIA).—A solution of 6.42 g. (0.0337 mole) of bromocitraconic anhydride[20,21] and 6.00 g. (0.0337 mole) of anthracene in 25 ml. of sodium-dried xylene was refluxed for four days, cooled to 50° and filtered; yield 8.63 g. (69.4%), m.p. 214–221°. Two recrystallizations from excess ethyl acetate afforded 1.87 g. of irregular prisms, m.p. 231.8–232.4° cor.

Anal. Calcd. for $C_{19}H_{13}BrO_3$: C, 61.81; H, 3.55; Br, 22.6. Found[22]: C, 61.95; H, 3.77; Br, 22.1.

α-Acetoxycitraconic Anhydride.—On mixing 12.1 g. (0.0943 mole) of methyloxalacetic anhydride[23] (m.p. 117–119°), 20.5 ml. (0.188 mole) of isopropenyl acetate[24] and 0.188 g. of concd. sulfuric acid, the solution immediately began to darken. The flask, to which an upright air-condenser of sufficient length to prevent the escape of isopropenyl acetate at an upper bath temperature of 165° was attached, was placed in an oil-bath at 120°, and after about three minutes, acetone began to evolve.[25] The acetone was condensed by a downward water-cooled condenser attached to the top of the air condenser, about 8 ml. being collected over two hours while the temperature of the bath was gradually raised from 120 to 165°. The air condenser was then replaced by a downward condenser, and all of the liquid which would distil at a bath temperature of 165° (at atmospheric pressure) was collected. The residual black liquid was then distilled *in vacuo*, affording a colorless liquid collected in three fractions from 100–106° (3.5 mm.); yield 13.5 g. (84.2%). The middle fraction was redistilled under nitrogen; b.p. 77.0–77.5° (0.31 mm.), (86–87 (0.43 mm.)), $n^{25}\text{D}$ 1.4672 (unchanged from that of the original distillate).

Anal. Calcd. for $C_7H_6O_5$: C, 49.42; H, 3.56. Found: C, 49.42; H, 3.60.

The product darkens fairly rapidly when exposed to air but remains colorless for at least a week when sealed under nitrogen. It gives a dark red color with alcoholic ferric chloride and immediately decolorizes 2% aqueous permanganate. When a small sample was mixed with water at room temperature, 15 minutes were required for the formation of a homogeneous solution. When mixed with 5% aqueous sodium hydroxide, a yellow coloration was produced at once, but 10 minutes were required for complete solution to be effected.

2-Acetoxy-3-methyldibenzo[2,2,2]bicycloöctadiene-*cis*-2,3-dicarboxylic Anhydride.—A solution of 4.00 g. (0.0224 mole) of anthracene and 3.82 g. (0.0224 mole) of α-acetoxycitraconic anhydride in 10 ml. of sodium-dried xylene was refluxed for four days under nitrogen. The solution was then concentrated in an air stream, and the precipitated solid was collected and washed with 20 ml. of acetonitrile leaving 0.765 g. of anthracene (19.1%). The dark filtrate was treated with a liberal quantity of Norit which removed much of the color. A glass was obtained upon evaporation of the acetonitrile, and trituration of the glass afforded a solid which was then slurried with ether, filtered and washed with additional ether until nearly colorless; yield 4.70 g. (60.2%), m.p. 181–185°. The product crystallized from carbon tetrachloride in rectangular plates, m.p. 184.5–186.0°. Additional recrystallizations raised the melting point to 185.8–187.0° cor.

Anal. Calcd. for $C_{21}H_{16}O_5$: C, 72.40; H, 4.63. Found: C, 72.24; H, 4.66.

The ethereal washings were combined and evaporated to dryness, and the residue was warmed with 5 ml. of 25% aqueous alkali. The alkaline solution was thoroughly ex-

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[17] L. H. Sommer, H. D. Blankman and P. C. Miller, THIS JOURNAL, **73**, 3542 (1951).

[18] Microanalyses by Clark Microanalytical Laboratory, Urbana, Illinois, unless otherwise indicated.

[19] Melting points corrected to ±0.5°, where indicated.

[20] A. Angeli and G. Ciamician, *Ber.*, **24**, 74 (1891).

[21] W. R. Vaughan and K. M. Milton, THIS JOURNAL, **73**, 5497 (1951).

[22] Micro-Tech Laboratories, Skokie, Illinois.

[23] J. Schreiber, *Compt. rend.*, **218**, 464 (1944). *Cf.* "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, second ed., p. 272, for starting material.

[24] Kindly furnished by the Tennessee Eastman Corporation.

[25] *Cf.* H. J. Hagemeyer, Jr., and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

tracted with benzene and the combined extracts, after drying, were passed through an activated alumina column and then evaporated to give 0.093 g. of anthracene (2.3%). The extracted alkaline solution was acidified with hydrochloric acid and the gummy precipitate was taken up in ether, dried over calcium sulfate, decolorized with Norit and evaporated to dryness. Trituration of the residue with methanol afforded 0.631 g. of IIIA (9.7%), m.p. 198–199° dec. Thus the over-all yield of the diene reaction was 69.9%.

2-Hydroxy-3-methyldibenzo[2,2,2]bicycloöctadiene-*cis*-2,3-dicarboxylic Anhydride (IIIA).—A mixture of 0.320 g. (0.000918 mole) of the preceding acetoxy anhydride adduct and 0.88 ml. of 25% aqueous sodium hydroxide was warmed on the steam-bath, and immediately following the complete solution of the solid, a sodium salt began to separate. After 15 minutes 2 ml. of water was added to dissolve the salt, and the solution was acidified with hydrochloric acid. The initial white gummy precipitate upon stirring gradually became crystalline. It was collected by suction filtration and washed with water, affording a quantitative yield of the hydroxyanhydride IIIA, m.p. 195–197° dec. The product crystallized from methanol–water in elongated hexagonal plates; 0.262 g. (93%), m.p. 197.5–198° dec. After four recrystallizations from methanol (rectangular prisms), the melting point was raised to 204.2–204.8° dec. cor.

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.54; H, 4.80.

Dibenzo[2,2,2]bicycloöctatriene-2-carboxylic Acid (V).—A solution of 4.00 g. (0.0224 mole) of anthracene and 2.20 g. (0.0224 mole) of ethyl propiolate[26] in 10 ml. of sodium-dried xylene was heated at 145° under reflux for seven days. The solid which crystallized upon cooling was washed well with acetonitrile leaving 1.26 g. (31.5%) of anthracene. The residue obtained upon evaporation of the acetonitrile was triturated with ethanol to give 2.78 g. (44.7%) of the ethyl ester adduct, m.p. 107.5–110.0°. A second crop of 0.771 g. (12.4%) was obtained by concentration. Both crops were dissolved in ethanol, treated with Norit and crystallized to give 2.25 g., m.p. 111.5–112.5°. The last trace of color was removed from this product by solution in benzene and passage of the solution through a chromatographic column of activated alumina, followed by elution with additional benzene until the eluate no longer contained any solute. The oil obtained by further evaporation of the ethanol triturate was refluxed for 2 hours with 2 ml. of 25% aqueous potassium hydroxide and the resulting mixture was processed as for the isolation of IIIA in the preparation of IIIA acetate. In this manner there was obtained 0.316 g. (5.7%) additional V and 0.038 g. (0.9%) anthracene thus giving an over-all yield from the diene reaction of 62.8%.

Evaporation of the benzene eluate afforded a 99% recovery of colorless material which on recrystallization from ethanol formed elongated plates, m.p. 111.4–112.0° cor., of the ethyl dihydroanthracene-*endo*-α,β-acrylate.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.46; H, 5.87.

On standing for 16 hours in contact with the mother liquor, these plates completely passed over into rectangular prisms, m.p. 107.4–108.4° cor., 107.4–112.0° when mixed with the original plates.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.92; H, 6.06.

Saponification affords the free acid V, m.p. 249.2–250.2° dec. cor. from acetonitrile.

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.20; H, 5.04.

3-Methyldibenzo[2,2,2]bicycloöctatriene-2-carboxylic Acid (VI).—A solution of 2.00 g. (0.0112 mole) of anthracene and 0.943 g. (0.0112 mole) of tetrolic acid in 10 ml. of propionic acid was refluxed for seven days and then was evaporated to dryness. After treatment with excess 25% aqueous sodium hydroxide the unreacted anthracene was removed by filtration; 1.88 g. (94.0%). The alkaline solution was acidified with concd. hydrochloric acid, and the precipitated solid was collected and washed with water; 0.165 g. (5.6%) of VI, m.p. 254–257° dec. The product crystallized from acetonitrile in needles, m.p. (after several recrystallizations) 266.5–267.0° dec. on slow heating, 277.2–277.8° dec. cor. when placed in the bath at 272°; neut. equiv. calcd. 262, found 262. Microanalysis was made on a sample obtained by reaction of IIIA with base (*vide infra*) which showed no depression on mixed melting point determination with this material, and which in general exhibited identical melting point behavior with variation in conditions of heating.

Dibenzo[2,2,2]bicycloöctatriene-2,3-dicarboxylic Acid (VII).—This substance was prepared according to the directions of Diels and Alder[27] from the dimethyl ester of acetylenedicarboxylic acid and anthracene, followed by saponification. After recrystallization from water VII was dried, m.p. 262–263° dec. (melting point not previously reported). The identity of the product was proven by its conversion to the anhydride, m.p. 248–249° (previously 247°[27]) by treatment with acetic anhydride.

2-Bromodibenzo[2,2,2]bicycloöctadiene-*trans*-2,3-dicarboxylic Acid IB).—A mixture of 2.00 g. (0.0112 mole) of anthracene, 2.19 g. (0.0112 mole) of bromofumaric acid[20,28] and 10 ml. of sodium-dried xylene was refluxed for ten hours. After four hours, the reactants had completely dissolved, but after eight hours a considerable quantity of crystals had again formed in the solution. Hydrobromic acid fumes were noted on opening the system, although no precipitate had formed in the silver nitrate solution contained in a gas trap affixed to the top of the reflux condenser. The crystallized solid was filtered from the cooled mixture, washed with 10 ml. of benzene and then 10 ml. of water; yield 1.935 g., m.p. 210–213° dec. The residue was recrystallized from enough nitromethane (*ca.* 25 ml.) so that only prisms of IB formed on cooling; 0.960 g. (22.9%), m.p. 220–221° dec. Three recrystallizations from nitromethane and one from ether–petroleum ether raised the melting point to 221.6–222.0° dec., cor.

Anal. Calcd. for $C_{18}H_{13}BrO_4$: C, 57.93; H, 3.51; Br, 21.42. Found: C, 57.92; H. 3.45; Br, 21.63.

As much as 18% of VII was isolable from the nitromethane, while 40% of IA was obtained from the original xylene filtrate plus the benzene washings. Identification of VII was by conversion to its anhydride and mixed melting point determination of the latter with an authentic sample, no depression being observed. Identification of IA was by mixed melting point determination with an authentic sample, no depression being observed. In subsequent experiments it was found that solution of VII in 30% hydrogen bromide-acetic acid, which occurred slowly on shaking at room temperature, followed by 12 hours standing at room temperature, and evaporation to dryness in an air stream at 60° effects virtually quantitative conversion of VII to IB, the identity of the product being established by mixed melting point determination with directly produced IB, no depression being observed. Thus by such treatment of the VII produced simultaneously in the diene reaction, the yield of IB can be raised to more than 40%. No more than 2% of anthracene was recovered from the reaction. IB is readily soluble at room temperature in 5% bicarbonate from which it may be recovered, apparently unchanged, by acidification.

Reaction of IA with Potassium Hydroxide.—A mixture of 2.00 g. (0.00563 mole) of I and 6.12 ml. (0.0338 mole) of 25% aqueous potassium hydroxide was heated on the steam-bath for 30 minutes. The anhydride dissolved rapidly and a salt began to precipitate after about two minutes. At the end of the heating period, sufficient water was added to dissolve the salt, and upon acidification with hydrochloric acid there precipitated a mixture of IVB and V which was separated into its components by extraction of IVB by eight portions of boiling water, totalling 125 ml. The residue of V was 0.380 g. (27.2%), m.p. 243–245° dec. After two recrystallizations from acetic acid–water a constant melting point was obtained, which was not depressed on admixture with V formed by the diene reaction as above, 247.1–248.6° dec., cor.

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found[22]: C, 82.20; H, 5.04.

Upon cooling, the aqueous extracts deposited 0.960 g. (54.9%) of IVB (plates), m.p. 226–228° dec. After two recrystallizations from water a constant melting point was

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(26) Prepared by M. Boudakian.

(27) O. Diels and K. Alder, *Ann.*, **486**, 191 (1931).

(28) A. Michael, *J. prakt. Chem.*, **52**, 289 (1895).

obtained, slightly higher than previously reported,[2] m.p. 236.4–236.7° dec. cor. (previously 232.5–233.2° dec. cor.). However, a sample[29] of the previously prepared material failed to depress the melting point of the present sample.

The methyl ester of IVB was prepared by use of diazomethane. It crystallized from methanol in fine needles, m.p. 199.0–199.6° cor.

Anal. Calcd. for $C_{20}H_{18}O_5$: C, 70.99; H, 5.36. Found[22]: C, 70.88; H, 5.42.

Reaction of IIA with Potassium Hydroxide.—A mixture of IIA (1.00 g., 0.00271 mole) and 3.65 ml. (0.0201 mole) of 25% aqueous potassium hydroxide was warmed on the steam-bath for one hour. Enough water was added at the end of this time to dissolve the precipitated salt (25 ml.), and the solution was then acidified with concd. hydrochloric acid. As in the analogous reaction with IA two substances precipitated and were separated by extraction with boiling water, five portions totalling 110 ml. The insoluble portion, 0.207 g., m.p. 265.5–266.0° dec., crystallized from acetonitrile in needles, a total of 0.176 g. (25%) of VI being collected in several crops, m.p. 279.8–280.0° dec., cor. when placed in the bath at 278° and no depression when mixed with authentic VI.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38; neut. equiv., 262. Found[22]: C, 82.72; H, 5.63; neut. equiv., 262.

The melting point of VI varies greatly with the rate of heating, the above value being obtained at a carefully controlled rate of 2°/min.

The methyl ester, prepared in the usual manner using a limited quantity of diazomethane, crystallized from methanol in prisms, m.p. 136.9–137.3° cor., with immediate resolidification and remelting at 146.1–146.5° cor.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found[22]: C, 82.67; H, 5.75.

The aqueous extracts of the original precipitate were combined and cooled and afforded crystals of IIIB, apparently containing water of hydration. The filtrate was extracted with ether and the residue from evaporation of the ethereal extract was added to the precipitate. Water was removed azeotropically by addition and distillation of chlorobenzene from which there crystallized beautiful, fine silky needles of IIIB, 0.649 g. (73.9%) after two recrystallizations, m.p. 203.4–204.0° dec. cor.

Anal. Calcd. for $C_{19}H_{16}O_5$: C, 70.30; H, 4.97; neut. equiv., 162. Found[22]: C, 70.22; H, 4.86; neut. equiv., 162.

The methyl ester was obtained using diazomethane, and it crystallized from methanol in fine needles, m.p. 148.9–149.6° cor.

Anal. Calcd. for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found[22]: C, 71.92; H, 5.72.

An increase in the ratio VI/IIIB ($^1/_4$ to $^1/_3$) is observed by going from 0.05 *M* base to 5.5 *M* base when a large excess of base is present, and a marked decrease is observed (to $^1/_6$) where equimolar quantities are used and the concentration of base is 2.8 *M*. In the latter experiment, however, there was recovered 63.9% of the original IIA. In the first two experiments the products VI and IIIB account for 99% of the starting material. All experiments were processed as described above.

IIA Plus Sodium Methoxide.—A solution of 1.000 g. (0.00271 mole) of IIA in 7 ml. of peroxide-free, sodium-dried dioxane was added to a solution of 0.062 g. (0.00271 mole) of sodium in 1 ml. of absolute methanol under dry nitrogen. Microscopic crystals appeared after one hour, and although the mixture did not appear to change after 24 hours, it was allowed to stand at room temperature for eight days. The apparent *p*H was approximately 6. The crystals were collected, and the solution was concentrated somewhat and then diluted with ether to give a second crop. The two crops were combined (0.249 g.) and dissolved in water, and upon titration with silver nitrate and potassium thiocyanate proved to be 94.3% sodium bromide; thus 83.9% of the bromine of IIA had been removed as bromide ion.

The filtrate from which the salt has been filtered was extracted with water, and the aqueous extracts upon evaporation afforded a glassy residue from which was isolated 0.11 g. (1.5%) of VI, 0.063 g. (7.2%) of IIIB and 0.024 g. (2.4%) of starting material. The organic phase was then evaporated to dryness and the residue was extracted with benzene, leaving 0.467 g. (49.9%) of VIII, 2-methoxy-3-methyl dibenzo[2,2,2]bicycloöctadiene-*trans*-2,3-dicarboxylic acid 3-methyl ester, which crystallized from benzene in trapezoidal prisms, m.p. 220.5–221.0° dec. on slow heating, but when plunged into the bath at 190°, the substance melted with gassing, resolidified and remelted at 219–219.5° dec. After recrystallization from acetone–petroleum ether (60–75°) (rectangular prisms); m.p. 215.7–216.7° dec. cor. when placed in bath at 190°.

Anal. Calcd. for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72; neut. equiv., 352. Found: C, 71.42; H, 5.80; neut. equiv., 353.

The ester was saponified by means of aqueous methanolic potassium hydroxide at the reflux temperature, and the dibasic acid IX was recovered after concentration followed by acidification. It crystallized from acetone–petroleum ether (60–75°); m.p. 217.1–217.6° dec. cor., mixed m.p. with VIII 205.5–214.0°.

Anal. Calcd. for $C_{20}H_{18}O_5$: C, 70.99; H, 5.36. Found: C, 70.47; H, 5.37.

IIA Plus Ammonia.—A solution of 0.500 g. (0.00135 mole) of IIA and 0.0928 g. (0.00545 mole) of anhydrous ammonia in 8 ml. of peroxide-free, sodium-dried dioxane was allowed to stand at room temperature for 9 days, although crystals appeared after four hours and no further change was apparent after 30 hours. The crystals were collected and washed with dioxane and ether; 0.074 g. (56% calculated as ammonium bromide, since it liberated ammonia with alkali and afforded silver bromide with silver nitrate). The filtrate was concentrated, treated with cold 5% aqueous sodium bicarbonate for one hour and the resulting suspension was extracted separately with benzene and with ether. Acidification of the bicarbonate solution afforded almost no product, and the benzene extract on evaporation yielded 0.108 g. of halogen-free amorphous material, which has not been identified. The ethereal extract on evaporation gave 0.362 g. of residue from which 0.249 g. (47.5–49.9%) of a mixture of X, 2-bromo-3-methyldibenzo[2,2,2]bicycloöctadiene-*cis*-2,3-dicarboximide, and the corresponding 3-half-amide X′ was obtained by fractional crystallization from ethyl acetate–benzene and then from ether. Before crystallization much of the product was readily soluble in cold alkali, and it melted with gassing, solidification and remelting at 241–242° dec. when placed in the bath near the melting point. However, the final product after recrystallization from ethyl acetate–benzene was not readily soluble in cold alkali. It formed thick, rhombohedral plates (rods from ether) and melted without decomposition at 250.7–251.2° cor.

Anal. Calcd. for $C_{19}H_{14}BrNO_2$: C, 61.97; H, 3.83; Br, 21.70; N, 3.80. Found: C, 62.27; H, 3.94; Br, 21.52; N, 3.78.

Reaction of IB with Sodium Hydroxide.—A solution of 0.444 g. of IB (0.00119 mole) in 2 ml. of 25% aqueous sodium hydroxide was heated on the steam-bath for 45 minutes and then was cooled and acidified with concentrated hydrochloric acid. The gummy precipitate was extracted eight times with a total of 80 ml. of boiling water leaving a residue of 0.075 g. (25.4%) of V, m.p. 247–249° dec. cor., no depression being shown upon admixture with authentic V.

The aqueous extracts were cooled and extracted with three portions of ether totalling 100 ml., and the ethereal extracts were combined and dried over anhydrous calcium sulfate, filtered and evaporated to dryness. The resulting glass was dried for 24 hours *in vacuo* over silica gel and sodium hydroxide, after which it weighed 0.265 g. The solid formed upon trituration with 2–3 ml. of ether was collected by filtration; and additional material was obtained by concentration of the filtrate (decolorized with Norit), total weight 0.155 g., m.p. 193–197° dec. (42% yield, calcd. as XIII). This substance readily reduces cold, alkaline permanganate. It crystallizes from nitromethane in needles and from 30–40° petroleum ether–ether in prisms. A constant melting point was obtained only after five recrystallizations, 201.8–202.4° dec., cor.

Anal. Calcd. for $C_{18}H_{14}O_5$: C, 69.67; H, 4.55; neut.

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[29] Kindly furnished by the late Professor W. E. Bachmann.

equiv., 155. Found[30]: C, 69.58; H, 4.74; neut. equiv. 157.

The ethereal filtrate appeared to contain at least two substances as shown by the partial solubility in benzene of the residue left by evaporation, but no identification has been achieved as yet. Prolonged refluxing of the product, XIII, with either alkaline or acidic permanganate afforded anthraquinone, which was identified by the characteristic vat color with alkaline sodium hydrosulfite, and by mixed melting point with an authentic sample.

Reaction of IIIA with 30% Hydrogen Bromide–Acetic Acid.—A mixture of IIIA and 30% hydrogen bromide–acetic acid was stirred until solution was effected. Transparent prisms began to form after about five minutes, and after five hours the solution was evaporated to dryness in an air stream. The residue was dried for a day *in vacuo* over sodium hydroxide and calcium chloride to constant weight. The yield was quantitative, based on a product of composition IIIA·HOAc, m.p. 205.0–205.5° dec. All qualitative tests for halogen were negative, and drying at 65° and 0.04 mm. for three hours afforded a substance which showed no melting point depression with the original IIIA (204.2–204.8° dec.), whereas the original material did depress this value somewhat. The product from the reaction when washed with cold water also was quantitatively reconverted into IIIA. Similar results were obtained when enough reagent was used to retain IIIA in solution or when glacial acetic acid alone was used.

Reaction of IIIA with 48% Hydrobromic Acid.—A mixture of 0.400 g. (0.00130 mole) of IIIA and 70 ml. of constant-boiling (48%) hydrobromic acid was heated in a sealed tube at 175 ± 5°. The white solid which sublimed into the unheated portion of the tube was occasionally shaken up with the liquid, but neither this substance nor the starting material appeared to dissolve appreciably. At the end of ten hours the tube was removed from the furnace and cooled. A very considerable pressure was released upon opening the tube.

The white sublimate, which showed typical anthracene fluorescence in ultraviolet light, was washed from the tube with water, filtered and dried; 0.70 g., m.p. 170–195°. A single recrystallization from acetonitrile afforded 0.028 g. (12.2%) of anthracene, m.p. 212.5–213.5° alone and when mixed with an authentic sample. The oil resulting from evaporation of the acetonitrile filtrate was dissolved in benzene and chromatographed on alumina, thus affording 0.033 g. (14.2%) additional anthracene, or a total recovery of 26.4%.

The hydrobromic acid solution was decanted from a dark tar and was evaporated to dryness in an air stream, the residue then being combined with the tar and the mixture being dissolved in acetone and filtered. After drying over anhydrous calcium sulfate, filtration of the acetone solution followed by evaporation yielded 0.225 g. of a black oil. The oil was treated in acetonitrile solution with a large quantity of norit, filtered and evaporated to a halogen-free yellow glass, weight 0.147 g. Extraction of the glass with 5 ml. of hot 5% aqueous sodium bicarbonate followed by cooling and acidification of the extract afforded 0.059 g. (14.8%) of starting material, m.p. 200.5–201.5° dec. alone, and 201–202° dec. when mixed with IIIA.

The alkali insoluble material weighed 0.068 g. (22.2% calcd. as mol. wt. 234). It was dissolved in 60–75° petroleum ether, and the solution was dried over anhydrous calcium sulfate, filtered and evaporated to dryness. The residue was recrystallized from petroleum ether in needles, 0.029 g., m.p. 121.6–122.4° cor.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.10; H, 6.09.

This substance shows almost the same fluorescence in ultraviolet light as does anthracene, and it decolorizes acidic permanganate slowly. Almost no evidence of decomposition is observed on heating to 300°, and sublimation occurs readily at room temperature and 0.05 mm. The infrared curve clearly indicates the presence of a carbonyl group by the strong band at 5.8μ.[11] A similar experiment run at the reflux temperature (about 126°) for 16 hours afforded only 6.4% anthracene and 7.2% of the ketone, 78% of the starting material being recovered.

Reaction of IIIB with 30% Hydrogen Bromide–Acetic Acid.—A solution of 0.500 g. (0.00154 mole) of IIIB in 3 g. of 30% hydrogen bromide–acetic acid was allowed to stand at room temperature for 24 hours, crystals first being observed after three hours. The mixture was next evaporated in an air stream to a moist solid which was washed three times with a total of 10 ml. of water, leaving 0.376 g. (66.6%) of a product, m.p. 219.5–220.5° dec. This substance was obtained as fine white needles after several recrystallizations from nitromethane–benzene, m.p. 225.6–226.4° dec., cor.; Beilstein test negative.

Anal. Calcd. for $C_{21}H_{18}O_6$: C, 68.84; H, 4.95; neut. equiv., 183. Found: C, 68.74; H, 5.14; neut. equiv., 184.

Since IIIB was regenerated in 93% yield by warming this substance for two minutes with 25% aqueous potassium hydroxide, diluting and then acidifying the alkaline solution and recrystallizing the precipitate from chlorobenzene, it is evident that the product is the acetyl derivative of IIIB.

Additional product (1%) and some starting material (9%) were recovered from the original aqueous extracts and an intractable oil, comprising the unaccountable starting material, remained unidentified.

Reaction of IIIB with 48% Hydrobromic Acid.—A mixture of 0.413 g. (0.00127 mole) of IIIB and 70 ml. of constant-boiling hydrobromic acid was heated on the steam-bath for 24 hours, solution being complete after five hours. The solution was concentrated while hot in an air stream, and two crops of crystals were collected; 0.266 g., m.p. 228–229° dec., and 0.119 g., m.p. 220–222° dec.; yield calcd. as XV 98.8%. The two crops were combined, treated with Norit in glacial acetic acid, crystallized from acetic acid–water, four times from chlorobenzene and once again from both acetic acid–water (thick hexagonal plates) and chlorobenzene (needles). The product is tentatively identified as XV, m.p. 233.0–234.0° dec., cor.; neut. equiv. calcd. 306, found 333, with a single well-defined break. The substance gives no Beilstein test and decolorizes an acidic permanganate solution only after one hour. After heating for one hour with 10% aqueous sodium hydroxide the original product was regenerated by acidification.

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61; mol. wt., 306. Found: C, 74.11; H, 4.63; mol. wt. (Rast), 318.

The infrared curve shows the lactone band[11] at 5.6 μ. It was observed that when XV was dissolved in a limited volume of 5% aqueous sodium bicarbonate, a crystalline precipitate began to accumulate slowly, the original monosodium salt being readily soluble. Boiling with excess alkaline permanganate for three days afforded no anthraquinone, all organic products being readily soluble in water.

ANN ARBOR, MICHIGAN

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(30) Semimicroanalysis by W. J. Byrd.