stants derived from aliphatic compounds through the relationship

$$\sigma_m = \frac{1 - \alpha}{1 - \alpha m}\,\sigma_I + \frac{\alpha b}{1 - \alpha m}$$

Using the α-value of Roberts and Jaffé[10] this equation is simply $\sigma_m = 1.18\,\sigma_I + b/3$.

Finally, it should be stated that although σ-values were used, the identical plots would be obtained if pK_a- values had been plotted for the benzoic acid system. Plots of pK_a- values for phenols and anilinium ions show much greater deviations from linearity than found in the benzoic acid family. Resonance interactions seem to offer a possible explanation for some of these deviations. This suggests that of the dipolar groups shown in Fig. 1, only the oxygen substituents are strongly conjugated with the carboxyl group.

Department of Chemistry
University of Pittsburgh
Pittsburgh 13, Pa.

Added in Proof: Nathan L. Bauld presented at the 139th A. C. S. Meeting (March 1961) a relationship similar to that given in Fig. 1 accompanied with a theoretical approach differing from that given here.

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(10) J. L. Roberts and H. H. Jaffé, *J. Am. Chem. Soc.*, **81**, 1635 (1959).

Norbornadiene–Silver Nitrate Complexes[1,2]

James G. Traynham

Received March 20, 1961

Two descriptions of norbornadiene–silver nitrate complexes have been published.[3,4] On the basis of a silver analysis only, the complex precipitated from aqueous solution was first inferred to be $C_7H_8 \cdot AgNO_3$ (1:1 complex).[3] The later report described a product, recrystallized from ethanol, which gave carbon, hydrogen and silver analyses in agreement with the formula $C_7H_8 \cdot 2AgNO_3$ (1:2 complex).

Because of the implications of the composition of the complex for conjugative properties in the diene,[3] this system has now been reexamined and additional data have been collected. The white solid which is initially precipitated from 1*M* silver nitrate solution by the addition of norbornadiene gives analyses which are not in agreement with either the 1:1 or the 1:2 formula. Instead, the found values for carbon, hydrogen and silver lie in between those calculated for the 1:1 complex and the 1:2 complex. Different preparations have different compositions, and sometimes the silver analysis is close to that required by the 1:1 formula.[3] Contamination of the 1:2 complex by neither water nor silver nitrate would lead to both low silver and high carbon-hydrogen analyses. The most reasonable inference about this initially-precipitated material is that it is a mixture of 1:1 and 1:2 complexes whose exact proportions vary from preparation to preparation. On this assumption one may calculate the composition of the material. Two analyses, for example, indicate compositions of 51% and 32% of 1:1 complex, respectively.

When the initially-precipitated material is either recrystallized from ethanol[4] or is stirred well with water and then rinsed on a suction filter with cold alcohol and ether, the resulting white solid gives analyses for a 1:2 complex. Unlike the initial precipitate, which chars over a rather wide temperature range, the recrystallized material melts sharply. The 1:1 complex apparently is the more soluble and is readily removed by thorough washing with water or by recrystallization from ethanol.[5]

Attempts to prepare the pure 1:1 complex have been unsuccessful, but they have nonetheless provided evidence for the existence of such species in the mixture. When pure 1:2 complex was recrystallized from ethanol containing 10% of norbornadiene, the white needles gave analyses corresponding to a mixture of 27% of the 1:2 complex and 73% of the 1:1 complex. This mixture readily lost norbornadiene during extended suction filtration and subsequent standing in air; the composition returned to that of the 1:2 complex. It seems highly unlikely that the forming crystals would selectively occlude the minor component of the solvent mixture to the complete exclusion of the major component. It is possible however that the geometry of the norbornadiene molecule permits it to fit in holes in the crystal structure, without otherwise being chemically bound to the silver ions, and that ethanol molecules are unsuited for this. In order to examine this possibility, the pure 1:2 complex was recrystallized from a mixture of ethanol and norbornane. Achievement of exactly identical steric requirements for a diene and its saturated analog is not possible, of course, but norbornadiene and norbornane probably duplicate one another about as closely as possible. Were it merely a matter of shape and size, the nearly-identical norbornane molecules probably would substitute for the norbornadiene ones incorporated into the crystals in

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(1) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) A substantial part of this investigation was carried out at Eidg. Technische Hochschule, Zurich, Switzerland, while the author was on sabbatical leave from Louisiana State University during 1959–1960.

(3) J. G. Traynham and J. R. Olechowski, *J. Am. Chem. Soc.*, **81**, 571 (1959).

(4) E. W. Able, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, **1959**, 3178.

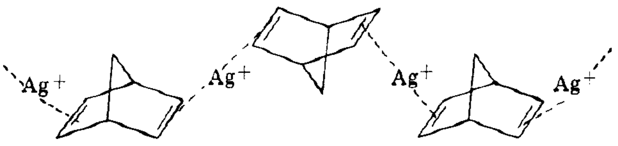
(5) The formation of cyclooctatetraene–silver nitrate complexes of different compositions by different methods of preparation has been described; A. C. Cope and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2515 (1950).

the previous experiment. The solid obtained however, gave analyses corresponding to the uncontaminated 1:2 complex. In like manner, the solid 1:2 complex, in evacuated apparatus, rapidly absorbs norbornadiene vapor but not norbornane vapor. Since the saturated analog is not incorporated into the complex either from solution or from vapor over solid, it seems certain that the additional norbornadiene is indeed chemically bound to the silver ions through pi-complex formation.

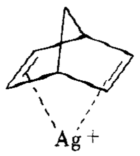
The 1:2 complex does not show infrared absorption bands characteristic of olefinic bonds (in the region 1550–1650 cm.$^{-1}$).[6] Since norbornadiene does show significant absorption in this region, the absence of such absorption in the complex probably means that both carbon-carbon double bonds in the diene are involved in pi-complex formation. Similar data and conclusions have been reported for platinum and palladium complexes of norbornadiene.[7] One would expect, *a priori*, that the 1:2 complex has structure *A*, in which the two silver ions occupy *exo* positions. The facile conversion of the mixture to the pure 1:2 complex in the solid state suggests that the two complexes are closely related to each other in structure. Structure *B* is one proposal that accommodates this requirement as well as the customary bivalent, linear complex formation by silver ion.[8,9] Loss of every other norbornadiene molecule from *B* would give *A*. Conversion of *C*, which is structurally similar to some other metal-norbornadiene complexes,[7,10] to *A* is less easily visualized.

Although it seems certain that two norbornadiene-silver nitrate complexes exist in the solid state, the earlier equilibrium data provide rather compelling evidence that only a single species exists in measurable concentration in aqueous solution.[3] The apparent equilibrium constant for complex formation is unchanging over a range of silver nitrate concentrations. Other dienes, both conjugated and unconjugated, give variable apparent formation constants and have been reported to form both the 1:1 and 1:2 complexes with silver nitrate in solution.[11] Since the equilibrium constants reported for the 1:2 complex formation are much smaller than those for the 1:1 complex formation,[11] it seems most probable that the norbornadiene-silver nitrate complex in aqueous solution is the 1:1 species. Structure *D* has already been proposed for this species.[3]

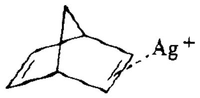
A



B



C



D

EXPERIMENTAL[12]

Norbornadiene was freshly distilled from lithium aluminum hydride before use. *Norbornane* was prepared by the atmospheric hydrogenation of norbornene in methanol with palladium-on-charcoal catalyst.

Preparation of complexes. To conserve space and provide convenience in evaluating the compositions found for the seven preparations described below, the calculated compositions for the 1:1 complex and the 1:2 complex are given here and will not be repeated.

Anal. Calcd. for $C_7H_8 \cdot AgNO_3$: C, 32.09; H, 3.08; Ag, 41.17. Calcd. for $C_7H_8 \cdot 2AgNO_3$: C, 19.46; H, 1.87; Ag, 49.95.

Preparation of I *and* II. Norbornadiene was added to 1*M* silver nitrate solution, with shaking, until a substantial amount of white precipitate had formed. The solid was collected by brief suction filtration and was dried over calcium chloride in a desiccator containing a small sample of norbornadiene.

Anal. Found, I: C, 26.10; H, 2.71; Ag, 45.68. II: C, 23.54; H, 2.36; Ag, 47.19.

On the assumption that the material is a mixture of the 1:1 and 1:2 complexes, the composition of I is calculated to be about 49% of 1:2 complex (47% based on *C*, 51% based on Ag) and that of II is calculated to be about 68% of 1:2 complex (68% based on *C*, 69% based on Ag).

Preparation of III. A portion of I was recrystallized from ethanol. The white needles melted at 153–154.5° (sealed tube, rapid heating).

Anal. Found, III: C, 19.64; H, 1.97; Ag, 50.05.

Preparation of IV. Another portion of I was washed thoroughly with water and then with ethanol and with ethyl ether.

Anal. Found, IV: C, 19.42; H, 1.89; Ag, 49.79.

Preparation of V. A sample of III was recrystallized again, this time from a mixture of ethanol (90%) and norbornadiene (10%). This solid did not melt sharply but instead darkened and decomposed over a rather wide temperature range (140–160°).

Anal. Found, V: C, 28.71; H, 2.76; Ag, 43.61. The composition of this mixture is calculated to be 27% of 1:2 complex (27% based on *C*, 28% based on Ag).

Preparation of VI. For about 1 hr., air was drawn through

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(6) The infrared spectrum of the mixed complex (Nujol mull) also lacked olefin absorption bands, but because of the possible loss of "extra" norbornadiene from the few milligrams of complex during mulling, this spectrum is not considered necessarily definitive.

(7) R. A. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Am. Chem. Soc.*, **82**, 535 (1960).

(8) L. Pauling, *The Nature of the Chemical Bond*, 2nd edition, Cornell University Press, Ithaca, N. Y., 1948, p. 89.

(9) A related structure has just been proposed for the cyclobutadiene–silver nitrate complex; H. P. Fritz, J. F. W. McOmie, and N. Sheppard, *Tetrahedron Letters*, No. 26, 42 (1960).

(10) R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).

(11) S. Winstein and H. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938).

(12) Microanalyses by W. Manser and associates, E. T. H., Zurich, Switzerland.

a portion of V while it was on a filter; it was then left standing overnight.

Anal. Found, VI: C, 19.56; H, 2.00; Ag, 49.25.

Preparation VII. A portion of the pure 1:2 complex (III) was recrystallized from a mixture of ethanol (90%) and norbornane (10%).

Anal. Found, VII: C, 19.47; H, 2.19; Ag, 50.44.

Infrared spectra were obtained for Nujol mulls of III and V. There was apparently no reaction between the silver salts and the sodium chloride cell windows.

Vapor pressure measurements. Solid 1:2 complex (0.1–0.5 g.) was placed in a small apparatus designed for vapor pressure measurements. The tube (A) containing complex was equipped with a differential manometer and two stopcocks. One stopcock opened to a vacuum pump and one to a tube (B) containing either norbornadiene or norbornane. The two tubes were frozen in Dry Ice–acetone, the stopcocks were opened, and the entire system was evacuated. The stopcocks were closed, and the apparatus was permitted to warm to room temperature. Vapor was admitted from B until the pressure in A was 50–90 mm. The stopcock was closed and the pressure in A was recorded from time to time during several hours. With norbornadiene vapor and powdered complex,[13] the pressure dropped rapidly (up to 65-mm. decrease with 0.5 g. of complex), but with norbornane vapor, the pressure did not change during 19 hr.

To insure that the drop in norbornadiene vapor pressure was not a result of simply replacing diene which had been removed from the 1:2 complex during evacuation, the complex which had been equilibrated with diene was refrozen, and the apparatus was again evacuated. After the apparatus had warmed to room temperature, the complex failed to absorb more diene vapor admitted from B. When the tube containing equilibrated complex was evacuated without freezing, fresh norbornadiene vapor was again absorbed rapidly.

Acknowledgment. The author is grateful to Professor V. Prelog, E.T.H., Zurich, for making the facilities of his laboratory fully available and to Dr. A. S. Dreiding, University of Zurich, for samples of norbornadiene and norbornene and for encouraging discussions.

COATES CHEMICAL LABORATORIES
LOUISIANA STATE UNIVERSITY
BATON ROUGE 3, LA.

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(13) Absorption of olefin seems to be related to the amount of surface available; the pressure decrease was greater with powdered complex than with larger sized crystals.

Substituted Phenylalanines and Phenylethylamines[1]

L. V. FENNOY[2]

Received March 28, 1961

The general synthesis of α-amino acids as employed by Erlenmeyer[3] has been used by many other workers. The initial step, the preparation of an azlactone, in almost all cases proceeds smoothly and in good yields. Carter[4] gives an excellent review of azlactone synthesis.

Methods of converting azlactones to the final α-amino acids have offered some difficulties. The azlactone or its hydrolytic product, an acylaminoacrylic acid, can be converted to an α-amino acid by reduction and hydrolysis.[4]

It has been found that some azlactones could be reduced and deacetylated in one step with Raney nickel and hydrogen in a mildly alkaline suspension. The resulting benzoylamino acids upon hydrolysis with hydrochloric acid yielded the corresponding phenylalanine hydrochlorides (Table I). In the case of Ic, its benzoylamino acid was not isolated (because of its instability under alkaline conditions); the reduction solution was hydrolyzed directly to IIIc.

Ramirez and Burger[5] have shown that nitrostyrenes (IV) can be reduced with lithium aluminum hydride to the corresponding β-phenylethylamines (V). This method was used successfully here.

The nitrostyrenes were prepared by the method of Crowder, Grundon and Lewis[6] (Table II).

EXPERIMENTAL

The following directions will serve as a general description of the preparative method for the compounds in Table I and Table II.

2-Phenyl-4-(3-methoxy-4,5-diacetoxybenzal)-5-oxazolone (Ic). A mixture of 5-hydroxyvanillin[10] (17 g., 0.1 mole), hippuric acid (18 g., 0.1 mole), freshly fused sodium acetate (15 g.) and acetic anhydride (35 ml.) was heated on a water bath for 15 min. and then allowed to stand at room temperature for 1 hr. The yellow solid was triturated with 250 ml. of ice water and then collected on a filter; yield 25 g. (65%), m.p. 184–185°. After two recrystallizations from glacial acetic acid, the m.p. was 189°.

3-Methoxy-4,5-dihydroxyphenylalaninehydrochloride (IIIc). A suspension of Ic (10 g., 0.025 mole), sodium hydroxide (8 g.) and Raney nickel (4 g.) in 200 ml. of water was hydrogenated at 5 atm. and 60° for 4 hr. The slightly reddish clear solution was filtered into 500 ml. of concd. hydrochloric acid. This mixture was then refluxed for 3 hr. When the mixture was cooled some benzoic acid crystallized. It was removed by filtration. The filtrate was extracted with three 150- ml. portions of ether to remove the remaining benzoic acid. The water fraction was evaporated on a steam bath under vacuum to dryness. The light tan solid (2.6 g., 50% yield) was recrystallized once from ethanol-ether; it melted at 229–230° dec.

3-Methoxy-4-hydroxy-α-aminobenzoylhydrocinnamic acid (IIa). A suspension of vanillin azlactone (16.8 g., 0.05 mole), 8 g. of sodium hydroxide and 4 g. of Raney nickel in 250 ml. of water was hydrogenated at 4 atm. and 60° for 4 hr. When the required amount of hydrogen had been absorbed,

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(1) This investigation was carried out during the tenuer of a Postdoctoral Fellowship from the National Institute of Neurological Diseases and Blindness, U. S. Public Health Service.

(2) Present address: Lab. di Chim. Terap., Instituto Superiore di Sanità, Rome, Italy.

(3) E. Erlenmeyer, *Ann.*, 175, 1 (1893).

(4) H. E. Carter, *Org. Reactions*, 198 (1946).

(5) F. A. Ramirez and A. Burger, *J. Am. Chem. Soc.*, 72, 2781 (1950).

(6) J. R. Crowder, M. F. Grundon, and J. R. Lewis, *J. Chem. Soc.*, 2142 (1958).

(7) F. Mauthner, *Ann.*, 370, 372 (1909).

(8) V. Deulofeu and O. Repetto, *Anales soc. espan. fis. quim.*, 32, 159 (1934).

(9) A. Challis and G. Clemo, *J. Chem. Soc.*, 1692 (1947).

(10) W. Bradley, R. Robinson, and G. Schwarzenbach, *J. Chem. Soc.*, 793 (1930).