Anal. Calcd. for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90. Found: C, 70.23; H, 7.71.

Ethylacetylaminomalonate (1.03 g.) was added to a solution of sodium (0.11 g.) in dry ethanol (11 ml.) with stirring at room temperature. 6-Methoxygramine (1.03 g.) was then added to the mixture which was then cooled to 0° and dimethyl sulfate (0.94 ml.) added. After stirring overnight at room temperature the mixture was added to ice and the product crystallized out (1.56 g.). The analytical sample was crystallized from ethanol to yield colorless prisms of ethyl-α-acetamido-α-carbethoxy-β-(3-(6-methoxyindole))-propionate, m.p. 147–148°.

Anal. Calcd. for $C_{18}H_{24}N_2O_6$: C, 59.33; H, 6.64. Found: C, 59.68; H, 6.38.

This ester (1.56 g.) was refluxed with 10% sodium hydroxide solution (10 ml.) for 1 hr., then cooled and acidified with concentrated hydrochloric acid and the malonic acid derivative filtered off and washed with cold water. The residue was refluxed with water (40 ml.) for 6 hr., then sodium hydroxide (3.0 g.) added and the mixture refluxed overnight. The solution was then made acidic with 2*N* sulfuric acid and then basic to phenolphthalein with barium hydroxide solution. The mixture was filtered and the filtrate evaporated to dryness *in vacuo*. The residue was dissolved in boiling acetic acid (40 ml.), filtered and benzene (40 ml.) added when 6-methoxytryptophan acetate (0.76 g., 42% yield from the formaldehyde-C^{14}) crystallized out as colorless plates, m.p. 277–278°.

Anal. Calcd. for $C_{12}H_{14}N_2O_3 \cdot C_2H_4O_2$: C, 57.13; H, 6.17. Found: C, 57.37; H, 6.22.

In an inactive run the α-acetamido-α-carboxy-β-(3-(6-methoxyindole))-propionic acid was isolated and crystallized from aqueous ethanol to afford colorless prisms, m.p. 175–176° dec.

Anal. Calcd. for $C_{15}H_{16}N_2O_6$: C, 56.25; H, 5.04. Found: C, 56.56; H, 5.00.

This malonic acid derivative was decarboxylated by heating in a nitrogen atmosphere at 160–180° for 30 min. The residue was crystallized from ethanol to yield N-acetyl-6-methoxy-tryptophan as colorless rhombic prisms, m.p. 209–210°.

Anal. Calcd. for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.48. Found: C, 61.13; H, 5.86.

[Contribution from the Department of Chemistry, University of Rochester, Rochester 20, N. Y.]

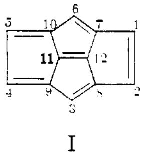
Syntheses of Bicyclo[3.3.0]octane Derivatives

By E. R. Hanna,[1] K. T. Finley, W. H. Saunders, Jr., and V. Boekelheide

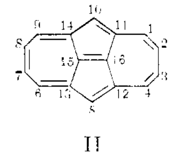
Received May 10, 1960

From calculations using simple molecular orbital theory, the hypothetical hydrocarbons I and II are predicted to be stable aromatic compounds. In an attempt to test these predictions the Diels-Alder reaction between bicyclo[2.2.1]heptadiene and cyclopentadiene has been utilized to prepare a series of 2,4,6,8-tetrasubstituted bicyclo[3.3.0]octane derivatives. Although their further conversion to I and II was not successful, a correlation between these derivatives and the Schroeter and Vossen "red salt" was made. Attempts to convert 2,4,6,8-tetraaminobicyclo[3.3.3]octane to pentalene are described.

Although the generalization from molecular orbital theory known as the "Hückel rule" is not applicable to polycyclic molecules containing fused rings,[3] previous studies would suggest that the detailed molecular orbital calculations following the standard Hückel method[4] do provide useful predictions concerning the properties of such polycyclic molecules.[5,6] To extend these studies it would be of particular interest to test the predictions of simple molecular orbital theory for polycyclic molecules having no benzenoid rings. In this communication the molecular orbital calculations for hydrocarbons I and II are presented and experiments directed toward their synthesis are described.



I



II

The calculations followed the standard Hückel method[4,7] with all coulomb integrals considered equal, as were all resonance integrals between adjacent carbons, and overlap was neglected. An I.B.M. 650 computer was employed for the calculations using a standard matrix-diagonalization program. The charge densities, bond orders and free valences for hydrocarbons I and II are summarized in Tables I and II. The delocalization (resonance) energy for I is 4.19 β whereas that of II is 6.03 β.

There are several points of interest with regard to these calculations, probably the foremost being the prediction of a high degree of thermodynamic stability for both I and II. This is in accord with the qualitative predictions deduced from other theoretical approaches. Thus, Platt used the box model with the free-electron network theory to arrive at the prediction that I (pyranene) would be a stable aromatic compound.[8] The predictions for I and II based on the symmetry requirements of Craig[9] are ambiguous. Although angle strain and bond compressions, which have been neglected in our calculations, would undoubtedly destabilize I, and to a lesser extent II, the predicted delocalization energies per π-electron are surprisingly high for I and II (0.35 and 0.38 β, respectively) and are in the same range as naphthalene (0.38 β) or anthracene (0.38 β). Furthermore, it is clear that the central bonds are involved in the resonance stabilization, since isolation of C_{11}–C_{12} in I leaves a system with a delocalization energy of 2.94 β (0.29 β per π-electron) and isolation of C_{15}–C_{16} in II leaves a sys-

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[1] Eastman Kodak Predoctoral Fellow, 1957–1958; the experimental portion of this publication is abstracted from the Ph. D. Thesis of E. R. Hanna, University of Rochester, 1958.

[2] Department of Chemistry, University of Oregon, Eugene, Ore.

[3] E. Hückel, *Z. Elektrochem.*, **43**, 752 (1937).

[4] E. Hückel, *Z. Physik*, **70**, 240 (1931).

[5] V. Boekelheide and G. K. Vick, This Journal, **78**, 653 (1956).

[6] R. J. Windgassen, W. H. Saunders, Jr., and V. Boekelheide, *ibid.*, **81**, 1459 (1959).

[7] (a) C. A. Coulson, "Valence," Oxford University Press, London, England, 1952, chapter IX. (b) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, chapter XIII.

[8] J. R. Platt, *J. Chem. Phys.*, **22**, 1448 (1954).

[9] D. P. Craig, *J. Chem. Soc.*, 3175 (1951).

tem with a delocalization energy of 3.98 β (0.28 β per π-electron).

The distribution of energy levels in I and II presents an interesting feature. For II there are eight bonding and eight antibonding levels. The eight bonding levels are just filled in the neutral molecule, so any additional electrons must go into antibonding orbitals. For I there are seven bonding and five antibonding levels. Only six of the bonding levels are filled in the neutral molecule, leaving one bonding orbital still available. The radical-anion and the bis-anion should thus have higher resonance energies than the neutral molecule (though interelectronic repulsions may reduce or reverse this advantage). This fact suggests that the radical-anion may be formed particularly easily in reactions of I with alkali metals or in electrolytic reductions.

From Tables I and II it can be deduced that electrophilic substitution should be favored at the 3-position in I and the 5-position in II. Nucleophilic attack would be favored at the 1-position in I and either 1 or 2 with about equal probability for II. Radical substitution, as predicted by free valences, should be essentially random for I, whereas in II position 5 is definitely favored. However, since both I and II are nonalternant hydrocarbons, these predictions, especially with regard to radical reactivity, may not be highly reliable.[10]

TABLE I

CALCULATED PROPERTIES OF I

Atom[a]	Charge density[b]	Free valence[b, c]	Bond[a]	Bond order[b]
3	1.13	0.54	3- 8	1.60
8	1.04	.18	1- 7	1.64
1	0.91	.54	1- 2	1.55
11	0.97	.32	7-12	1.32
			11-12	1.78

[a] See formula I for numbering. [b] Method of calculation described in ref. 7a. [c] Assuming $N_{(\max)} = 4.732$; see ref. 7a, p. 253.

TABLE II

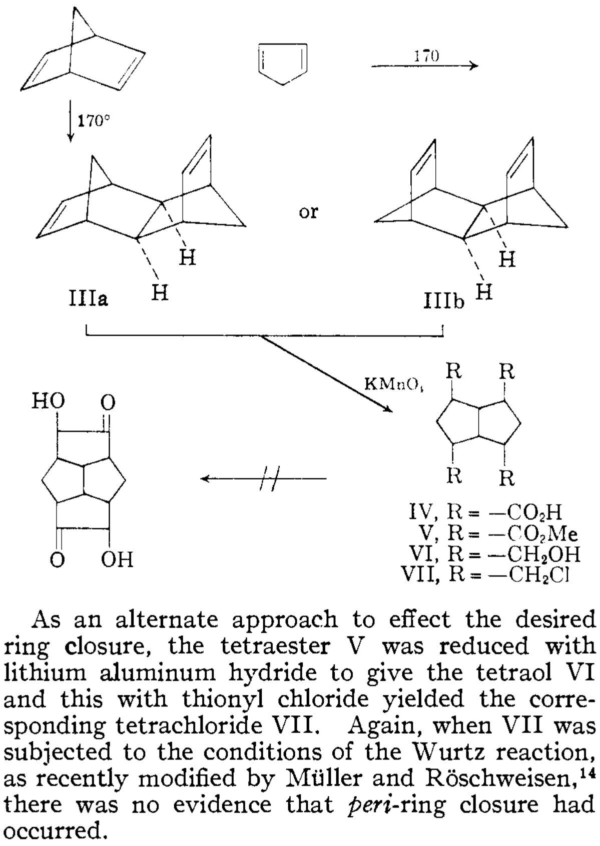
CALCULATED PROPERTIES OF II

Atom[a]	Charge density[b]	Free valence[b, c]	Bond[a]	Bond order[b]
5	1.17	0.53	5-12	1.60
11	0.97	.14	1-11	1.54
1	.94	.48	1- 2	1.71
2	.95	.44	2- 3	1.59
15	1.13	.15	11-16	1.45
			15-16	1.68

[a] See formula II for numbering. [b, c] See corresponding footnotes of Table I.

Bond orders around the periphery of I are quite even, suggesting little tendency toward bond localization. The same is true of II, with the exception of a moderately higher order for the C_1–C_2 bond. In both molecules the bonds from the periphery to the central atoms have low bond orders and the bonds between the central atoms high bond orders, though this pattern is more marked in I than in II. In valence-bond terminology, resonance forms placing double bonds between the central atoms of I and II would make large contributions to the respective resonance hybrids.

As starting material for syntheses directed toward I and II, the commercially-available bicyclo[2.2.1]heptadiene was chosen.[11] The Diels–Alder addition of cyclopentadiene and bicyclo[2.2.1]heptadiene occurred readily at 170° to give an adduct III for which either IIIa or IIIb seemed likely stereochemical formulations.[12] Oxidation of III with potassium permanganate led to the isolation of bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylic acid (IV) as a single crystalline isomer in 46% yield. This in turn was readily converted either by diazomethane or methanolic hydrogen chloride to the corresponding tetraester V. Thus, a *peri*-ring closure of the functional groups present in V would lead directly to the carbon skeleton required for I. Unfortunately, the acyloin condensation, using the liquid ammonia technique developed by Sheehan and his students for the formation of five-membered rings,[13] failed to give any useful product.



IV, R = —CO_2H
V, R = —CO_2Me
VI, R = —CH_2OH
VII, R = —CH_2Cl

As an alternate approach to effect the desired ring closure, the tetraester V was reduced with lithium aluminum hydride to give the tetraol VI and this with thionyl chloride yielded the corresponding tetrachloride VII. Again, when VII was subjected to the conditions of the Wurtz reaction, as recently modified by Müller and Röschweisen,[14] there was no evidence that *peri*-ring closure had occurred.

These negative results offered presumptive evidence that IIIa rather than IIIb was the correct stereochemical assignment for the adduct. Another test which should distinguish between structures IIIa and IIIb is their behavior on treatment with acid. Under these conditions IIIb should readily be converted to Winstein's "bird-cage" mole-

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[10] F. H. Burkett, C. A. Coulson and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).

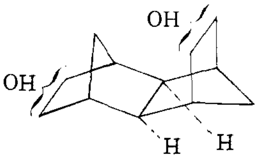
[11] We are indebted to the Shell Chemical Corporation for generous gifts of bicyclo[2.2.1]heptadiene.

[12] Subsequent to the completion of our experiments, J. K. Stille and D. A. Frey, THIS JOURNAL, **81**, 4273 (1959), have also reported the formation of this adduct, evidence for its formulation as IIIa, and its oxidation by ozonolysis to the tetraacid IV.

[13] J. C. Sheehan and R. C. Coderre, *ibid.*, **75**, 3997 (1953); J. C. Sheehan, R. C. Coderre and P. A. Cruickshank, *ibid.*, **75**, 6231 (1953).

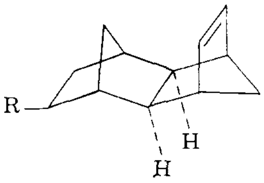
[14] E. Müller and G. Röschweisen, *Chem. Ber.*, **90**, 543 (1957).

cule,[15,16] whereas III should undergo simple hydration to give the diol VIII. When the Diels–Alder adduct was treated with perchloric acid in acetic acid or with formic acid, the product contained no hydrocarbon fraction and a crystalline diol having the correct composition for VIII was isolated.

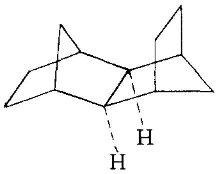


VIII

In the case of the Diels–Alder addition of cyclopentadiene and bicyclo(2.2.1)-2-heptene, Soloway has shown through oxidative degradation that the adduct is an unsymmetrical molecule and must therefore have the *exo-endo* configuration IX.[17a,b] In the course of this work, Soloway prepared the Diels–Alder adduct X of vinyl acetate with two molecules of cyclopentadiene and degraded it in an equivocal fashion to IX, proving that both adducts IX and X have the same configuration. We have repeated the reaction sequence described by Soloway leading to X. This, in turn, has been converted by hydrogenation followed by removal of the oxygen function to a solid hydrocarbon that must have structure XI. The same hydrocarbon resulted from simple hydrogenation of III and thus the original adduct must have structure IIIa, a conclusion reached earlier by Stille and Frey.[12]



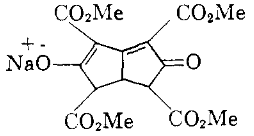
IX, R = H
X, R = OAc



XI

Since it would not be expected that the stereochemical relationships would be altered in the transformation of IIIa to the various bicycloöctane derivatives IV, V, VI and VII, the difficulties in the attempted *peri*-ring closures undoubtedly are a consequence of this adverse stereochemistry. Methods of obtaining a more suitable diastereoisomer of the tetramethyl bicyclo(3.3.0)octane-2,4,6,8-tetracarboxylate (V) were then investigated. When the crystalline diastereoisomer of V, m.p. 142–143°, obtained as described above, was boiled in absolute methanol containing sodium methoxide, it was converted to an oily mixture. Careful chromatography of this permitted the isolation in poor yield of two crystalline fractions: A, m.p. 88–89°, and B, m.p. 94–95°. Despite the sharpness of their melting points, it is not certain that either of these fractions is a pure compound. Similarly, a three-step sequence involving bromination of the tetraester V with N-bromosuccinimide, dehydrobromination with pyridine, and hydrogenation over Adams catalyst gave an oily mixture of isomers from which chromatography again gave A as white crystals, m.p. 87.5–89°.

The availability of these isomers of the tetraester V prompted us to attempt a correlation which might establish the structure of the Schroeter and Vossen "red salt."[18,19] Schroeter and Vossen had studied an unusual series of reactions in which chloral with excess dimethyl malonate yielded a "red salt." With remarkable intuitive insight they suggested that this "red salt" was the sodium enolate of tetramethyl 3,7-diketobicyclo-(3.3.0)oct-1-ene-2,4,6,8-tetracarboxylate (XII). This suggestion has received strong support from recent work.[20–22] In one of the outstanding contributions to this problem, Yates and Bhat described a series of reactions in which the "red salt" was reduced to the corresponding saturated diol, subjected to dehydration and then hydrogenated. If it is assumed that the Schroeter and Vossen "red salt" has structure XII, the final product in this series should have the same overall structure as the tetraester V. For comparison, this series of reactions was repeated.[23] The final product was a mixture similar in character to that obtained from the sodium methoxide equilibration of V. Likewise crystallization and chromatography led to the same crystalline fractions A and B as obtained previously. Their identities were confirmed by comparison of infrared spectra and by mixture melting point determinations.[24] These results provide independent synthetic proof for the correctness of the structures assigned the Schroeter and Vossen "red salt" and its derivatives,



XII

Another potential use for the tetraester V was its possible employment for a synthesis of pentalene. Treatment of V with hydrazine gave the corresponding tetrahydrazide XIII in essentially quantitative yield. The Curtius rearrangement of the tetrahydrazide proved difficult, but the tetracarbamate XIV could be isolated in about 30% yield after purification by chromatography. In several experiments the Curtius rearrangement was carried out in an inert solvent followed by addition of lithium aluminum hydride. It was hoped that this

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(15) S. Winstein, *Experientia*, Suppl. II, 137 (1955).

(16) See also R. C. Cookson and E. Crundwall, *Chemistry & Industry*, 1004 (1958), for the conversion of isodrin to a similar "bird-cage" molecule.

(17) (a) S. B. Soloway, THIS JOURNAL, **74**, 1027 (1952); (b) S. B. Soloway, Ph.D. Thesis, University of Colorado, 1955.

(18) G. Vossen, Doctoral Dissertation, University of Bonn, 1910.

(19) G. Schroeter, *Ann.*, **426**, 1 (1922).

(20) P. Yates and G. Bhat, *Chemistry & Industry*, 1237 (1954).

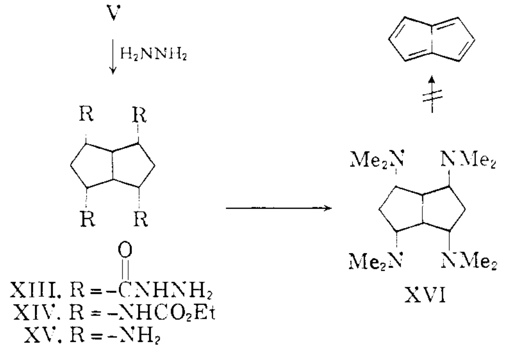
(21) H. Wanzlick, *Chem. Ber.*, **86**, 269 (1953).

(22) S. Tanaka, THIS JOURNAL, **80**, 5264 (1958).

(23) We would like to thank Professor Yates for his kindness in supplying us with experimental details of his procedures in advance of the full publication of this work.

(24) A sample of our pure diastereoisomer of V, m.p. 142–143°, was given to Professor Yates for spectral comparison with their product from the Schroeter and Vossen "red salt." In a private communication he has reported that they also have carried out a base-catalyzed equilibration of V and established a correlation with the Schroeter and Vossen "red salt."

would convert the hydrazide groups directly to methylamino groups, but the products were oils which could not readily be purified.



XIII, R = $-\overset{O}{\overset{\|}{C}}NHNH_2$
XIV, R = $-NHCO_2Et$
XV, R = $-NH_2$
XVI

Hydrolysis of the tetracarbamate XIV was accomplished using boiling concd. hydrochloric acid and gave the corresponding 2,4,6,8-tetraaminobicyclo[3.3.0]octane (XV) as its hydrochloride. Although methylation of the tetraamine proceeded in low yield using the Eschweiler–Clarke procedure, reductive alkylation with formaldehyde was satisfactory giving XVI in 45% yield. The final step in the series, the conversion of XVI to pentalene, was first tried using the elegant amine-oxide technique developed by Cope and his students.[25] Oxidation of XVI with hydrogen peroxide gave the tetraamine tetraoxide as a brown gum which readily decomposed on heating to give N,N-dimethylhydroxylamine, isolated as its hydrochloride. No volatile hydrocarbon was observed. The residue appeared to be polymeric and was neither soluble in organic solvents nor in aqueous acid. Attempts to trap pentalene as a Diels–Alder adduct by carrying out the decomposition in the presence of tetracyanoethylene were also unsuccessful. This behavior is reminiscent of that observed by Cope and Keller when they attempted to convert 3,7-bis-(dimethylamino)-bicyclo[3.3.0]oct-1(5)-ene to dihydro-pentalene.[26] Finally, attempts to degrade XVI to pentalene *via* the Hofmann exhaustive methylation procedure were also unsuccessful.

Experimental[27]

1,4,4a,5,8,8a-Hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene (IIIa).—The Diels-Alder addition of cyclopentadiene and bicyclo(2.2.1)heptadiene has been described by Stille and Frey.[12] In our hands the reaction was carried out at 170° for 27 hours using a threefold excess of bicycloheptadiene and gave in 49% yield a product having properties in accord with those given by Stille and Frey.[12]

The **bis-(phenyltriazoline)** derived from IIIa was prepared by adding 1.0 g. of phenyl azide to 0.5 g. of IIIa. After a few minutes the solution became warm and crystals began to separate. The mixture was then allowed to stand overnight at room temperature. The solid mass was triturated with benzene, the crystals were collected and, after recrystallization from pyridine, were obtained as white plates, m.p. 214–215° dec.

Anal. Calcd. for $C_{24}H_{24}N_6$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.49; H, 6.18; N, 21.25.

Hydrogenation of IIIa in ethanol using Adams catalyst at room temperature and atmospheric pressure led to a rapid uptake of two moles of hydrogen. After removal of the catalyst and solvent, the residue was sublimed to give crystals, m.p. 33.5–35°.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.81; H, 11.18.

Bicyclo(3.3.0)octane-2,4,6,8-tetracarboxylic Acid (IV).—A suspension of 10.0 g. of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene (IIIa) in 1 l. of water, was stirred rapidly while 54.0 g. of finely crushed potassium permanganate was added in small portions over a 2-hour period. The temperature of the solution did not exceed 50° during the addition. After an additional 2 hours of vigorous stirring, the solution had lost its permanganate color. The precipitated manganese dioxide was separated by filtration and washed with 200 ml. of hot water. The combined filtrate and wash water was concentrated to 60 ml. under reduced pressure and then acidified by cautious addition of 30 ml. of concd. hydrochloric acid. After the mixture had stood overnight, the precipitate was collected and air-dried to give 8.3 g. (46%) of the crude acid. Recrystallization from water yielded white needles, m.p. 263–264° dec. (evacuated tube).[28]

The dianhydride of IV was prepared by treating IV with boiling acetic anhydride. After recrystallization from acetonitrile, it was obtained as white crystals, m.p. 236–239.5° dec.

Tetramethyl Bicyclo(3.3.0)octane-2,4,6,8-tetracarboxylate (V).—To 130 ml. of absolute methanol there was added 8.3 g. of the crude tetraacid IV and anhydrous hydrogen chloride was bubbled through the mixture until the acid dissolved and the solution was saturated. Crystals of the tetraester began to separate immediately and, after the solution had been allowed to stand in the refrigerator overnight, the crystals were collected and washed with water. Recrystallization from methanol–water gave 7.7 g. (78%) of white needles, m.p. 142–143°. When the tetraacid IV was treated with an ether solution of diazomethane, the same tetraester was obtained as needles, m.p. 142.5–143°. Likewise the dianhydride of IV when treated with boiling methanol gave the same tetraester.

Anal. Calcd. for $C_{16}H_{22}O_8$: C, 56.13; H, 6.48. Found: C, 56.21; H, 6.71.

Attempted Acyloin Condensation with V.—To a solution of 400 mg. of sodium in 120 ml. of liquid ammonia there was added dropwise with stirring a solution of 400 mg. of V in 200 ml. of ether over a 30-min. period. The reaction mixture was then allowed to warm to room temperature and stand for an additional 6 hours with intermittent addition of ether to keep the volume roughly constant. When there was no longer ammonia in the exit gas, the excess sodium was decomposed by addition of 2 ml. of methanol in 30 ml. of ether and the mixture was acidified by addition of 50 ml. of 5% hydrochloric acid. After saturation of the water layer with sodium chloride, the ether layer was dried and concentrated to give 50 mg. of gum. This gave negative results with both Fehling solution and ferric chloride, characteristic tests for acyloins. Continuous extraction of the aqueous layer with chloroform yielded an additional 120 mg. of brown gum and this, likewise, gave negative tests for the acyloin group.

2,4,6,8-Tetra-(hydroxymethyl)-bicyclo(3.3.0)octane (VI).—To a solution of 700 mg. of lithium aluminum hydride in 70 ml. of ether there was added dropwise with stirring a solution of 2.0 g. of the tetraester V in 60 ml. of a 2:1 benzene–ether mixture. After the addition was complete, the mixture was boiled under reflux for 4 hours. The excess lithium aluminum hydride was then destroyed by addition of methanolic ether and a saturated aqueous solution of sodium sulfate was added until the organic layer became clear. The organic layer was separated and the aqueous slurry of inorganic salts was boiled with 50 ml. of methanol. Again the slurry was separated and the process repeated with 25 ml. of methanol. The combined methanol and ether extracts were concentrated to 20 ml. and passed over a column of ion-exchange resin (Dowex 50-X4) using methanol for elution. Concentration of the eluate gave a pale yellow solid which, after recrystallization from 1-butanol, yielded 0.95 g. (71%) of white crystals, m.p. 160–161°.

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(25) A. C. Cope and C. L. Bumgardner, THIS JOURNAL, **79**, 960 (1957), and earlier papers in this series.

(26) A. C. Cope and W. J. Keller, *ibid.*, **80**, 5502 (1958).

(27) All melting points are corrected. Analyses are by Micro-Tech Laboratories; W. Manser, E. T. H., Zürich; and Miss A. E. Smith.

(28) Stille and Frey (ref. 12) report that the tetraacid IV melts at 268–271° dec. and the corresponding dianhydride at 239–240°.

Anal. Calcd. for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.72; H, 9.69.

2,4,6,8-Tetra-(chloromethyl)-bicyclo(3.3.0)octane (VII).—To 1.15 g. of the tetraol VI and 1.8 g. of pyridine there was added 5 ml. of thionyl chloride with stirring and cooling of the reaction mixture. After addition was complete, the mixture was boiled under reflux for 3 hours. It was then cooled and the excess thionyl chloride was decomposed by addition of crushed ice. The resulting mixture was extracted three times with carbon tetrachloride and the combined extracts were washed successively with water, 5% aqueous sodium hydroxide, water, and a saturated sodium chloride solution. The carbon tetrachloride solution was then dried, concentrated to 20 ml. and passed over a column of activated alumina. After elution of the column with carbon tetrachloride, the eluate was concentrated to give white crystals, m.p. 86–90°. Recrystallization of these from *n*-hexane yielded 730 mg. (48%) of white crystals, m.p. 90–91°.

Anal. Calcd. for $C_{12}H_{18}Cl_4$: C, 47.38; H, 5.96. Found: C, 47.67; H, 6.18.

When the *peri*-ring closure of VII was attempted following the general procedure of Müller and Röscheisen,[29] the only products isolated appeared to be polymeric in nature.

Conversion of X to XI.—The preparation of X through the Diels–Alder addition of two moles of cyclopentadiene to vinyl acetate[30] followed by hydrolysis was carried out following the procedure described by Soloway.[31] The crude oil was purified by converting it to the corresponding acid phthalate, m.p. 165.5–167° (Soloway[31] gives 166–167°), purifying and saponifying. The regenerated alcohol was a crystalline solid, m.p. 104–106° (Soloway[31] gives 108°). The *p*-nitrobenzoate derivative of X was prepared and melted at 141–142° (Soloway[31] gives 144–144.5°).

The purified alcohol X was hydrogenated over Adams catalyst and the product was oxidized directly using pyridine and chromium trioxide to give the corresponding saturated ketone as an oil whose semicarbazone formed as white crystals, m.p. 206–207° (Soloway gives 206–207.5°).

Reduction of the ketone following Huang-Minlon's procedure[32] gave a hydrocarbon, XI, identical in its infrared spectrum and other properties to that obtained by the hydrogenation of IIIa.

Hydration of IIIa.—A solution of 1.0 g. of IIIa in 20 ml. of formic acid (90%) was heated on a steam-bath for 90 min. After the solution had been allowed to stand overnight at room temperature, it was diluted with 20 ml. of water and extracted with petroleum ether (50–60°). The combined extracts were washed successively with 5% aqueous sodium hydroxide, water and a saturated sodium chloride solution. Concentration gave 1.12 g. of a colorless oil. This was taken up in petroleum ether (50–60°) and chromatographed over neutral Woelm alumina. Nothing was eluted with petroleum ether or ether indicating the complete absence of a hydrocarbon such as the "bird-cage" molecule.[15] With a 2% methanol–ether mixture, there was eluted 900 mg. of an oil. This was treated with lithium aluminum hydride in ether to remove the formate ester groups and, on work-up, 660 mg. of a colorless gum resulted. This appeared to be a mixture of isomers but, by recrystallization from benzene, there was isolated 80 mg. of white crystals, m.p. 198–199°. The analytical data and infrared spectrum of these crystals are in accord with that expected for one of the possible isomers represented by VIII. When IIIa was treated with perchloric acid in acetic acid, the reaction mixture likewise gave no evidence of any hydrocarbon and the same crystalline diol, m.p. 198–199°, was isolated in poor yield.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.50; H, 9.51.

Equilibration of Tetramethyl Bicyclo[3.3.0]octane-2,4,6,-8-tetracarboxylate (V).—A mixture of 250 mg. of the tetraester V, 80 mg. of sodium methoxide and 15 ml. of absolute methanol was boiled under reflux for 5 hr. It was then acidified and concentrated under reduced pressure. The residue was taken up in 25 ml. of boiling benzene and chromatographed over Woelm neutral alumina. From the eluate fraction A was obtained as 70 mg. of an oil which crystallized on standing. Recrystallization from hexane gave white needles, m. p. 88–89°. Despite their sharp melting point, these crystals had a physical appearance more in keeping with a eutectic mixture than a pure isomer of V.

Anal. Calcd. for $C_{16}H_{22}O_8$: C, 56.13; H, 6.48. Found: C, 56.48; H, 6.56.

Fraction B was also an oil of approximately the same weight as A. Treatment with methanol–water gave crystals which, after recrystallization from hexane, melted at 94–95°. Its infrared spectrum is very similar to that of A but differing in its absorption at 8.08, 8.13, 10.76 and 10.92 µ.

Anal. Calcd. for $C_{16}H_{22}O_8$: C, 56.13; H, 6.48. Found: C, 55.84; H, 6.58.

Reaction of V with N-Bromosuccinimide.—A mixture of 1.8 g. of N-bromosuccinimide, 1.6 g. of V and 30 mg. of benzoyl peroxide in 45 ml. benzene was boiled under reflux for 12 hr. while being irradiated with a 60 watt lamp. The succinimide, which formed, was removed by filtration and the filtrate was washed with aqueous alkali, water, and then concentrated. The residual solid (2.0 g.) was taken up in benzene and chromatographed over Woelm neutral alumina. The development of the chromatogram indicated the presence of bromination products. However, the main fraction was eluted using a 1:1 benzene–ether mixture and amounted to 1.02 g. (52%) of crystals which melted over a wide range. On recrystallization from methanol–water, there resulted white crystals, m.p. 132–133°.

Anal. Calcd. for $C_{16}H_{21}O_8Br$: C, 45.62; H, 5.03. Found: C, 45.29; H, 5.16.

The monobromo derivative of V, obtained as above, was treated with boiling pyridine. The resulting unsaturated ester was purified by chromatography over alumina and then hydrogenated using Adams catalyst. From the work-up, after chromatography over alumina, there was isolated in good yield white crystals, m.p. 88–89°. Comparison of these crystals with those obtained as fraction A from equilibration of V with sodium methoxide showed both samples to have superimposable infrared spectra and mixtures of the two showed no depression of melting point.

Conversion of the Schroeter and Vossen "Red Salt" to a Mixture of Diastereoisomers of V.—The preparation of the Schroeter and Vossen "red salt" (XII) was carried out according to Vossen's directions.[18] Its reduction to tetramethyl bicyclo-(3.3.0)octane-3,7-diol-2,4,6,8-tetracarboxylate was accomplished in 80% yield using 500 mg. of platinum oxide for 4.2 g. of XII in 25 ml. of acetic acid.[20] Dehydration of the diol occurred on heating with concd. sulfuric acid on a steam-bath for 2 hours and, after the usual work-up followed by chromatography over Woelm neutral alumina using benzene for elution, gave the tetramethyl bicyclo(3.3.0)octadiene-2,4,6,8-tetracarboxylate as needles, m.p. 108–109° (Yates and Bhat[20] give 109–109.5°). Hydrogenation of 140 mg. of the diene in methanol using Adams catalyst was carried out at room temperature and atmospheric pressure. After removal of the catalyst and solvent, a waxy solid remained. Crystallization from methanol–water gave 35 mg. of crystals, m.p. 93–94°. Comparison of these crystals with fraction B from the sodium methoxide equilibration of V showed the two to have superimposable infrared spectra and mixtures gave no depression of melting point.

Evaporation of the methanol–water mother liquors gave a semi-solid residue which was taken up in benzene and chromatographed over Woelm neutral alumina. From the eluate there was isolated 25 mg. of crystals, m.p. 86.5–88.5°. Again, these crystals were shown to be identical with fraction A from the equilibration of V by comparison of infrared spectra and mixture melting points.

Bicyclo(3.3.0)octane-2,4,6,8-tetracarbohydrazide (XIII).—A solution of 4.0 g. of tetramethyl bicyclo(3.3.0)octane-2,4,6,8-tetracarboxylate (V) in 20 ml. of 95% hydrazine was heated on a steam-bath for 15 min. The solid cake, which separated, was then broken up by adding 50 ml. of methanol and heating the mixture under reflux for 1 hr. After the cooled mixture had been allowed to stand overnight, the solid was collected and air-dried to give 3.6 g. (90%) of a white powder, m.p. above 350°. A sample was prepared for analysis by dissolving it in dilute hydrochloric acid, treating it with charcoal, filtering, and carefully neutralizing the filtrate with base. The precipitate was collected, thoroughly washed with water and dried.

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(29) E. Müller and G. Röscheisen, *Chem. Ber.*, **90**, 543 (1957).

(30) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1940).

(31) S. B. Soloway, Ph.D. Thesis, University of Colorado, 1955.

(32) Huang-Minlon, THIS JOURNAL, **68**, 2387 (1946).

Anal. Calcd. for $C_{12}H_{22}N_8O_4$: C, 42.10; H, 6.48. Found: C, 42.03; H, 6.74.

Tetraethyl Bicyclo(3.3.0)octane-2,4,6,8-tetracarbamate (XIV).—To a solution of 500 mg. of the tetrahydrazide XIII in 20 ml. of 5% hydrochloric acid there was added 25 ml. of ether and the mixture was cooled in an ice-bath. A solution of 860 mg. of sodium nitrite in 10 ml. of water was added dropwise with stirring. After the mixture had been stirred with cooling an additional 20 min., the ether layer was separated and the aqueous layer was extracted twice with ether. The combined ether extracts were washed with a 5% aqueous bicarbonate solution and then dried. Absolute ethanol (25 ml.) was added and the solution was concentrated until a boiling point of 70° was reached. Then, the alcoholic solution was boiled under reflux for 5 hr. Removal of the ethanol gave a yellow solid which, on crystallization from acetone–water, gave 200 mg. (30%) of white leaflets, m.p. 250–252° dec.

Anal. Calcd. for $C_{20}H_{34}N_4O_8$: C, 52.39; H, 7.47; N, 12.22. Found: C, 52.22; H, 7.37; N, 12.19.

2,4,6,8-Tetra-(dimethylamino)-bicyclo(3.3.0)octane, (XVI).—A solution of 200 mg. of the tetracarbamate XIV in 16 ml. of concd. hydrochloric acid was boiled under reflux for 24 hr. Removal of the solvent under reduced pressure followed by drying in the presence of potassium hydroxide pellets in a desiccator gave 136 mg. (100%) of grainy white crystals, which darkened at 225° but did not melt below 350°. The tetraamine XV tetrahydrochloride was soluble in water and ethanol but not in organic solvents. Since attempts to purify it were not successful, it was converted directly to the corresponding dimethylamino derivative. To a solution of 136 mg. of the tetraamine XV tetrahydrochloride in 20 ml. of water there was added 2 ml. of 5% hydrochloric acid, 2 ml. of aqueous formaldehyde (35%) and 100 mg. of Adams catalyst. The mixture was subjected to hydrogenation at room temperature and 3 atm. pressure of hydrogen for 12 hr. After removal of the catalyst, the solution was made basic and extracted with ether. When the ether extracts had been dried over solid potassium hydroxide, concentration gave a gummy solid. This was taken up in petroleum ether and chromatographed over Woelm basic alumina. Elution with a 3:1 petroleum ether–ether mixture gave 135 mg. (45%) of white crystals, m.p. 92.5–93.5°. Attempts to convert XV to XVI using the conditions of the Eschweiler–Clarke procedure gave the same product but only in 10% yield.

Anal. Calcd. for $C_{16}H_{34}N_4$: C, 68.03; H, 12.13; N, 19.84. Found: C, 68.54; H, 12.15; N, 19.92.

Thermal Decomposition of the Tetroxide of XVI.—The preparation of the tetroxide of XVI and its thermal decomposition was carried out following the procedure described by Cope and Bumgardner for the preparation of 1,4-pentadiene.[25] Vigorous decomposition of the tetroxide of XVI occurred in the range of 95–120° under 10 mm. pressure of nitrogen. No evidence for a volatile hydrocarbon fraction was obtained. The contents of the first trap cooled with Dry Ice-acetone were washed out with 5% hydrochloric acid and extracted with pentane. The pentane solution was transparent in the ultraviolet region and left no residue on concentration. Evaporation of the aqueous layer gave a solid which, after recrystallization from ethanol-ether, was obtained as white needles, m.p. 98–101° (the melting point reported[33] for N,N-dimethylhydroxylamine is 104.5–106°). The residue in the flask from the thermal decomposition was a black solid insoluble in water, acid or the common organic solvents, suggesting that it is polymeric in nature. When the experiment was repeated in the presence of tetracyanoethylene using bis(2-methoxyethyl) ether as solvent, the outcome was essentially the same. It was hoped that an adduct might be formed to indicate the transient existence of pentalene. No such simple adduct was isolated although the black solid residue in this instance showed an altered infrared spectrum having absorption at 4.56 μ (nitrile) indicating that the tetracyanoethylene had become involved in the reaction product.

Attempted Degradation of XVI by the Hofmann Exhaustive Methylation Procedure.—Treatment of the tetraamine XVI (77 mg.) with methyl iodide (1.6 g.) and 1.5 ml. of methanol under nitrogen at 50° for 40 hrs. gave the quaternary tetramethiodide as a gum. A similar result was obtained when the mixture was heated at 100° for 23 hr. The tetramethiodide was somewhat unstable and attempts to purify it by recrystallization from methanol apparently led to some displacement by iodide giving material of continually increasing carbon content. Thus, after two crystallizations from methanol a yellow solid, decomposing about 205°, was obtained whose composition (C, 30.40; H, 5.90; N, 7.56) indicated it to be a mixture of tetramethiodide and presumably some trimethiodide. Because of this instability the crude tetramethiodide was converted directly to the corresponding tetrahydroxide by passage over an ion exchange column (Dowex 2) and the resulting gum was decomposed by heating it in a short path still under reduced pressure. Although trimethylamine was evolved, there was no indication of a volatile hydrocarbon. The residue in the distilling flask was again an insoluble black solid.

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[33] A. C. Cope, R. A. Pike and C. F. Spencer, THIS JOURNAL, **75**, 3212 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Schroeter and Vossen's "Red Salt" and Related Bicyclo[3.3.0]octane Derivatives[1]

BY PETER YATES,[2] ELLI SMAKULA HAND AND GARGI BHAT FRENCH

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The "red salt," $C_{16}H_{15}O_{10}Na$, obtained by the condensation of dimethyl (2,2,2-trichloroethylidene)-malonate (I) with dimethyl malonate in the presence of sodium methoxide has been shown to be tetramethyl sodio-3,7-dioxobicyclo[3.3.0]oct-1-ene-2,4,6,8-tetracarboxylate (II), as originally suggested by Schroeter and Vossen. Its transformation to a series of other bicyclo[3.3.0]octane derivatives has been effected and one of these, a bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylic acid (XII), has been correlated with an acid of the same structure, but different stereochemistry, obtained by other workers from the oxidation of the Diels-Alder adduct (XIV) of bicyclo[2.2.1]heptadiene and cyclopentadiene. A study of dianhydride formation in this series has permitted the assignment of the stereochemistry of the acid XII. The bromination products of tetramethyl bicyclo[3.3.0]octadiene-2,4,6,8-tetracarboxylate (X) and of the "red salt" have been investigated.

In 1910, Vossen,[3] working in Schroeter's laboratory, reported that dimethyl (2,2,2-trichloroethylidene)-malonate (I), gave with dimethyl malonate in the presence of sodium methoxide a red crystalline salt, $C_{16}H_{15}O_{10}Na$, to which he assigned the interesting structure II. Vossen made a careful

$$CCl_3CHO + CH_2(CO_2CH_3)_2 \xrightarrow[\text{ii, } H_2SO_4]{\text{i, } (C_2H_5)_2NH} CCl_3CH{=}C(CO_2CH_3)_2$$

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[1] A preliminary account of part of this work has appeared previously: P. Yates and G. Bhat, *Chemistry & Industry*, 1237 (1954).

[2] Department of Chemistry, University of Toronto, Toronto, Ontario, Canada.

[3] G. Vossen, Dissertation, Bonn, 1910.