spectrometer. In the case of VII and VIII no mass spectra were obtained. Melting points were determined on a Gallenkamp (design no. 889339) apparatus and are uncorrected.

A. 6,11-Diketo-5,12-dihydroxy-5b,6,11,11a-tetrahydrodibenzo[b,h]biphenylene (IV). 1. From II in Dioxane Containing Hydrochloric Acid.—A mixture of finely powdered II (1 g), dioxane (100 ml), and concentrated HCl (5 ml) was refluxed for 3 hr. The reaction product was precipitated with excess water, filtered, washed with water, and dried at 100°. The enolized product (0.56 g) was separated from unchanged II (0.185 g) by three successive extractions of the dried precipitate with 75-ml portions of boiling ethanol which were cooled to 20° and filtered. (II is practically insoluble in cold ethanol). The separate filtrates were rapidly concentrated until crystals began separating from the hot solution. After cooling, the crystalline product was filtered off.

a. The Anhydrous Diol (IV).—A boiling solution of the crude diol in anhydrous benzene was concentrated rapidly, whereupon IV separated as orange-red needles: mp 235° (blackening commencing at 220°); mass of molecular ion, *m/e* 316; ν_{max}^{KBr} 3410, 1668, 1640, 1589, 1274, 1248, 735 cm^{-1}; λ_{max} (in ethanol) 231 mμ (E 33,700).

Anal. Calcd for $C_{20}H_{12}O_4$: C, 75.95; H, 3.16. Found: C, 75.90; H, 3.20.

b. The Hydrated Diol (IVa).—A concentrated solution of the crude diol in ethanol (20 ml) was treated with water (4 ml). Upon cooling IVa separated as yellow needles: mp 235° (change in color to organge-red at 130–135°, blackening commencing at 220°); mass of molecular ion, *m/e* 316; ν_{max}^{KBr} 3440, 1672, 1639, 1633, 1590, 1275, 1242, 733 cm^{-1}.

Anal. Calcd for $C_{20}H_{12}O_4 \cdot H_2O$: C, 71.86; H, 4.19. Found: C, 71.81; H, 4.12.

2. From II in Acetic Acid.—A solution of II (0.5 g) in acetic acid (200 ml) was refluxed for 24 hr. The yellowish solution was concentrated to a small volume (25 ml) and left for 2 hr at 20°. Unchanged II was filtered off. The filtrate was concentrated to a smaller volume (5 ml), whereupon IV (0.015 g) separated as orange-red crystals.

3. From III in Dioxane Containing Hydrochloric Acid.—A mixture of III (0.1 g), dioxane (10 ml), and concentrated HCl (0.5 ml) was refluxed for 5 hr. The reaction mixture was treated as in procedure A1, yielding II (0.02 g) and IV (0.06 g), respectively.

B. 6,11-Diketo-5,12-dihydroxy-5b,6,11,11a-tetrahydrodibenzo[b,h]-biphenylenedihydrazone (VII).—A boiling solution of IV (0.2 g) in ethanol (40 ml) was treated with 80% hydrazine hydrate (1 ml). The yellow solution darkened rapidly and pale yellow needles of the dihydrazone (VII) separated. Compound VII (0.09 gm) was filtered from the hot reaction mixture and washed with cold ethanol: mp 231° (with violent decomposition); ν_{max}^{KBr} 3340, 1602, 1328, 765, 723 cm^{-1}.

Anal. Calcd for $C_{20}H_{16}O_2N_4$: C, 69.76; H, 4.65; N, 16.28. Found: C, 69.72; H, 4.60; N, 16.20.

C. 5,12-Diacetoxy-6,11-diketo-5b,6,11,11a-tetrahydrodibenzo[b,h]-biphenylene (VIII).—A boiling solution of IV (0.1 g) in dioxane (2 ml) was treated with acetic anhydride (0.065 g) and anhydrous sodium acetate (0.05 g), and the mixture refluxed for 3 min. Dilution with excess water led to the precipitation of VIII (0.064 g). Recrystallization from ethanol afforded colorless needles: mp 192–194°; ν_{max}^{KBr} 1768, 1688, 1356, 1281, 1194,1177 cm^{-1}.

Anal. Calcd for $C_{24}H_{16}O_6$: C, 71.99; H, 4.03. Found: C, 71.94; H, 3.97.

D. 5,6,11,12-Tetraacetoxydibenzo[b,h]biphenylene (IX).—A mixture of IV (0.02 g), acetic anhydride (5 ml), and anhydrous sodium acetate (0.5 g) was refluxed for 2 hr and cooled. The crystalline product was filtered off, and washed successively with acetic acid and water. Recrystallization of the crude IX (0.027 g) from acetic anhydride yielded yellow needles: mp 358–360° (lit.[2] mp 358–360°); the product was identified by ir spectroscopy.

E. Acetylation of VIII.—A mixture of VIII (0.02 g), acetic anhydride (5 ml), and anhydrous sodium acetate (0.5 g) was treated as in procedure D. Recrystallization of the crude product (0.025 g) produced yellow needles, identical with IX.

F. Ketonization of IV (or IVa). 1. In Concentrated Sulfuric Acid.—Compound IV (0.025 g) was dissolved in cold concentrated H_2SO_4 (2 ml), and the solution poured into ice cold water (20 ml). The greyish precipitate was washed with water and recrystallized from acetic acid, yielding colorless plates of II (0.019 g), mp 246–248° (lit.[1] mp 246–248°), identified by ir spectroscopy.

2. In Dioxane Containing Hydrochloric Acid.—A solution of IV (0.05 g) in dioxane (10 ml) was treated with concentrated HCl (1 ml). The mixture was refluxed for 5 hr, cooled, and treated with excess water. The precipitate was treated as in procedure A1, whereby II (0.007 g) and IVa (0.025 g) were obtained.

G. Ketonization of III. 1. In Dioxane Containing Hydrochloric Acid.—A solution of III (0.05 g) in dioxane (20 ml) was treated with concentrated HCl (1 ml). The reaction mixture was treated as in procedure F2, whereby II (0.01 g) and IV (0.026 g) were obtained.

2. In Ethanol.—A solution of III (0.025 g) in ethanol (30 ml) was refluxed until the blue fluorescence disappeared (5 hr). Concentration of the solution yielded crystalline IV (0.021 g). In dilute ethanolic solution (0.002 g/25 ml) complete conversion of III into IV at room temperature (20°) was established within 4 hr. In a similarly concentrated solution of III in dioxane ketonization was completed within 12 hr.

H. 5a,5b,11a,11b-Tetrabromo-5,6,11,12-tetraketo-5,5a,5b,6,11,11a,11b,12-octahydrodibenzo[b,h]biphenylene (X).—Bromine (0.1165 g, 0.00073 mol) was added to a stirred suspension of III (0.05 g, 0.00015 mol) in benzene (12 ml). The mixture was stirred at room temperature for 1.5 hr. The crystalline product (X) (0.04 g) was filtered off and washed with ether: mp 255–258° dec; ν_{max}^{KBr} 1692, 1591, 1250, 1005 cm^{-1}.

Anal. Calcd for $C_{20}H_8O_4Br_4$: C, 38.01; H, 1.28; Br, 50.59. Found: C, 38.00; H, 1.28; Br, 50.94.

I. 5a,11b-Dibromo-5,6,11,12-tetraketo-5,5a,5b,6,11,11a,-11b,12-octahydrodibenzo[b,h]biphenylene (XI).—Bromine (0.21 g, 0.0013 mol) was added to a solution of IV (0.2 g, 0.00063 mol) in boiling ethanol (20 ml). The colorless crystals of XI (0.2 g) which quickly separated were filtered off, washed with cold ethanol, and recrystallized from ethanol: mp 165–170° dec; ν_{max}^{KBr} 1704, 1686, 1591, 1254, 717 cm^{-1}; mass of molecular ion, *m/e* 472.

Anal. Calcd for $C_{20}H_{10}O_4Br_2$: C, 50.66; H, 2.13. Found: C, 50.63; H, 2.11.

Registry No.—I, 14734-20-4; II, 14734-19-1; IV, 19817-49-3; VII, 19817-50-6; VIII, 19817-51-7; X, 19817-52-8; XI, 19817-53-9.

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Hydrazine Derivatives. II. Side Reactions in the Preparation of 1,1′-Azobisformamides[1]

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During the preparation of a series of 1,1′-azobis(N-substituted formamides)[2] from dialkyl azodiformates and amines, 1,6-dialkylbiureas were frequently isolated as by-products. It is the purpose of this note to discuss the competitive and consecutive reactions occurring when dialkyl azodiformates (1) and amines react and to consider the sources of various by-products.

The first two reactions (1 and 2) are a facile lab-

(1) Part I: C. M. Kraebel, S. M. Davis, and M. J. Landon, *Spectrochim. Acta*, **23A**, 2451 (1967).

(2) C. M. Kraebel and S. M. Davis, *J. Chem. Eng. Data*, **14**, 133 (1969).

TABLE I

REDUCTION OF 1,1′-AZOBISFORMAMIDES

RNHCON=NCONHR

R	Solvent	Reducing agent	Molar ratio reducing agent: azobisformamide	Time, hr	Temp, °C	% redn
H	EtOH	EtOH	15	143.5	75	None
H	EtOH	$C_4H_9NH_2$	2	2	75	30
H	$C_4H_9NH_2$	$C_4H_9NH_2$	8	2.5	80	100
c-C_6H_{11}	EtOH	EtOH	25	64	45–50	None
n-C_3H_7	EtOH	EtOH	20	192	25	<2
n-C_3H_7	EtOH	$C_6H_5NH_2$	2	51	25	<2[a]
n-C_3H_7	EtOH	Piperidine	2	28.5	25	4
n-C_3H_7	EtOH	Piperidine	2	95	25	18
n-C_3H_7	EtOH	$C_4H_9NH_2$	2	51	25	20
n-C_3H_7	EtOH	$C_4H_9NH_2$	2	195	25	42
n-C_3H_7	EtOH	Allylamine	2	24	25	28
n-C_3H_7	EtOH	Allylamine	2	72	25	46
n-C_3H_7	EtOH	$(C_4H_9)_2NH$	2	4	25	10
n-C_3H_7	EtOH	$(C_4H_9)_2NH$	2	20	25	66

[a] No Michael addition was observed.

oratory synthesis for 1,1′-azobis(N-substituted formamides), particularly when diethyl azodiformate (**1a**, R′ = C_2H_5) is treated with unhindered aliphatic amines.

$$\underset{\mathbf{1}}{R'OCON{=}NCOOR'} + RNH_2 \longrightarrow R'OCON{=}NCONHR + R'OH \quad (1)$$

$$R'OCON{=}NHCONHR + RNH_2 \longrightarrow \underset{\mathbf{2}}{RNHCON{=}NCONHR} + R'OH \quad (2)$$

The by-product biureas can arise by three possible routes: reduction of 1,1′-azobisformamides (**2**) by the by-product alcohol (reaction 3), reduction by the amine used originally (reaction 4), or aminolysis of a dialkyl bicarbamate (reaction 5). Possible sources of dialkyl bicarbamate (**3**) include reduction of **1** by an alcohol (reaction 6), which has been reported by Yoneda, *et al.*,[3] or by an amine (reaction 7).

$$\mathbf{2} + R'OH \longrightarrow \underset{\mathbf{4}}{RNHCONHNHCONHR} \quad (3)$$

$$\mathbf{2} + RNH_2 \longrightarrow \mathbf{4} \quad (4)$$

$$\underset{\mathbf{3}}{R'OCONHNHCOOR'} + 2RNH_2 \longrightarrow \mathbf{4} + 2R'OH \quad (5)$$

$$\mathbf{1} + R'OH \longrightarrow \mathbf{3} \quad (6)$$

$$\mathbf{1} + RNH_2 \longrightarrow \mathbf{3} \quad (7)$$

Although Witkop, *et al.*,[4] have also cited **1a** as a selective oxidant, the oxidation reactions of **2** have not been studied. The data in Table I show that the amides are less potent dehydrogenating agents than **1a**. The amides are not reduced by ethanol after 192 hr at room temperature [for **2a**, R = *n*-C_3H_7] or even after 143.5 hr under reflux (for 1,1′-azobisformamide). These conditions are far more rigorous than those which Yoneda reports; thus, reaction 3 is insignificant in this system. However, **2** are reduced with varying degrees of ease by amines (Table I) to give **4** (reaction 4). The order of reducing activity is $(C_4H_9)_2NH$ >> allylamine > $C_4H_9NH_2$ > piperidine >> $C_6H_5NH_2$ ≃ EtOH.

Since reactions 1 and 2 are not quantitative,[2] amine is available for reaction 4 even when initial ratio of **1**:amine is 1:2. Moreover, Yoneda's data[3] indicate that reaction 6 can remove **1** as the amount of alcohol produced by reactions 1 and 2 increases. When **1** is removed by this process, the amine present can react *via* reactions 4, 5, or 7. In view of the relative potency of amines as hydrogen donors, reaction 7 can compete with reactions 1 and 2 and can, in fact, be another reason that compounds **2** are not obtained quantitatively. Although the procedure used to prepare **2** does not allow for the isolation of compounds **3**, which are soluble, we found reaction 5 so sluggish [<20% yield of 1,6-di-*n*-butylbiurea (**4a**, R = *n*-C_4H_9) from diethyl bicarbamate (**3a**, R′ = C_2H_5) and *n*-butylamine after 64 hr under reflux] that it can be excluded as a possible source of **4**. Thus, reaction 4 is the source of **4** in this system.

Dibenzyl azodiformate (**1b**, R′ = $CH_2C_6H_5$), which is about as reactive as **1a** toward amines,[2] is also active as a dehydrogenating agent. In methanol **1b** is rapidly decolorized at room temperature. The color change from orange-red to pale yellow is characteristic of **1a** during its dehydrogenation reactions. Diisopropyl azodiformate (**1c**, R′ = *i*-C_3H_7), which is less reactive than **1a** or **1b** toward amines, is also less easily hydrogenated. Even after several days of standing at room temperature in methanol, **1c** is incompletely decolorized. Isopropyl alcohol decolorized **1b** less rapidly than methanol; in isopropyl alcohol–heptane at 45°, the purity of **1b** falls from 100 to 97% in 5 hr.[5]

Reactions between secondary amines and azo esters are less predictable than those involving primary amines. Azobisformamides were obtained (Table II) from both dimethylamine and piperidine. However, excess piperidine under reflux gave reduction product. Pyrrolidine gave only the reduction product, whereas dibutylamine gave no azobisformamide, but reduced both **1a** and **1c** to **3**. This result is consistent with the relative position of dibutylamine among the reducing agents used in Table I. Thus, secondary amines can react according to eq 1, 2, 4, and 7. The poor material balances observed suggest that several processes do, in fact, compete.

(3) F. Yoneda, K. Suzuki, and Y. Nitta, *J. Org. Chem.*, **32**, 727 (1967).

(4) R. Axen, M. Chaykovski, and B. Witkop, *ibid.*, **32**, 4117 (1967).

(5) These results were obtained by Dr. E. C. Sabatino.

TABLE II
REACTIONS BETWEEN DIALKYL AZODIFORMATES AND SECONDARY AMINES

Amine	Ester	Molar ratio amine/ester	Solvent	Results
$(CH_3)_2NH$	**1a**	3.0	Et_2O–MeOH	$(CH_3)_2NCON{=}NCON(CH_3)_2$,[a] >98% purity, ~20% yield
Piperidine	**1a**	2.0	Ligroin	$(CH_2)_5NCON{=}NCON(CH_2)_5$,[b] ~80% purity, 14% yield
Piperidine	**1a**	10.0	Et_2O (reflux)	$(CH_2)_5NCONHNHCON(CH_2)_5$, >10% yield[c]
Pyrrolidine	**1a**	2.0	Ligroin	$(CH_2)_4NCONHNHCON(CH_2)_4$, >8% yield[d]
$(C_4H_9)_2NH$	**1a**	2.0	Ligroin	EtOCONHNHCOOEt, 34% yield
$(C_4H_9)_2NH$	**1c**	2.0	Et_2O	i-$C_3H_7OCONHNHCOOC_3H_7$-i, 36% yield

[a] R. J. Crawford and R. Rapp, *J. Org. Chem.*, **28**, 2423 (1963). [b] O. Diels and R. Fritzche, *Ber.*, **44**, 3020 (1911). [c] After repeated crystallization from aqueous EtOH, mp 188–190°, lit.[7] mp 188°. [d] After chromatographic purification.

$$1 + RNH_2 \longrightarrow R'OCONHN(COOR')NHR \quad (8)$$

$$2 + RNH_2 \longrightarrow RNHCONHN(CONHR)NHR \quad (9)$$

Aniline and **1a** yield the Michael addition product, diethyl 1-phenyltriazan-2,3-dicarboxylate,[6] by reaction 8. Aniline also reduced 1,1′-azobis(N-methylformamide) to 1,6-dimethylbiurea after 3 hr at 115°.[6] Under our milder conditions (Table I), aniline did not react to any detectable extent with **2a** according to either 4 or 9.

Experimental Section

Microanalyses were performed on a Fisher micro combustion apparatus. Melting points were determined in capillaries and are uncorrected.

1,1′-Azobis(N-*n*-heptylformamide).—*n*-Heptylamine (9.0 g, 0.08 mole) was added to a stirred solution of **1c** (8.0 g, 0.04 mole) in 40 ml of ether over 1.5 hr at room temperature. Stirring was continued for 0.5 hr after which the slurry was filtered with suction and the solid product was washed with ether until the washings were nearly colorless. The yield was 7.9 g (64%), mp 153–156° dec.

Anal. Calcd for $C_{16}H_{32}N_4O_2$: C, 61.50; H, 10.33; N, 17.93; equiv wt, 156.2. Found: C, 61.53; H, 10.54; N, 17.72; equiv wt (iodine titration),[2] 159.0.

1,6-Di-*n*-heptylbiurea.—Mothers liquors from the preparation of 1,1′-azobis(N-*n*-heptylformamide) from **1c** and *n*-heptylamine were left at room temperature for 10 days, after which the white solid which precipitated was removed by filtration and washed with ethanol (1.5 g, 12%), 222–238° dec. Its ir spectrum was indistinguishable from that of other 1,6-dialkylbiureas[1] in the NH and C=O stretching regions; ir (Fluorolube fluorocarbon mull on Perkin-Elmer 521 instrument), 3290, 3205, 3090 (NH), 1665 (C=O), 1565 (CNH) cm^{-1}.

Anal. Calcd for $C_{16}H_{34}N_4O_2$: C, 61.08; H, 10.90; N, 17.84. Found: C, 60.84; H, 10.70; N, 17.53.

Attempted Reduction of 2a by Ethanol (Table I).—A slurry of 5.0 g of **2a** in 100 ml of ethanol in a stoppered flask was left in the dark (cupboard). After 192 hr at room temperature, the color of the slurry was unchanged. The solid collected (1.6 g) had an equivalent weight of 100.4 (theoretical for **2a** in 100.1). Evaporation of the mother liquors to dryness yielded 3.2 g of residue with an equivalent weight of 102.0.

Reduction of 2a by *n*-Butylamine (Table I).—A slurry of 5.0 g of **2a** in 4.0 g of *n*-butylamine and 100 ml of ethanol was left in the dark (cupboard) for 51 hr at room temperature. The slurry was washed repeatedly with ethanol until a white solid (1.0 g), 1,6-di-*n*-propylbiurea (**4b**, R = n-C_3H_7), remained; ir (in Fluorolube), 3300, 3200, 3090 (NH), 1660 (C=O), 1570 (CNH) cm^{-1}.

Anal. Calcd for $C_8H_{18}N_4O_2$: C, 47.49; H, 8.95; N, 27.73. Found: C, 47.21; H, 8.95; N, 27.65.

The ethanol-soluble material was unreduced **2a**, not **4b**.

Aminolysis of 3a. A. In Ethanol.—Diethyl bicarbamate (**3a**, 10 g, 0.085 mole), 20 ml (0.2 mole) of *n*-butylamine, and 100 ml of ethanol were stirred and heated under reflux for 64 hr. Volatile materials were evaporated from the clear solution and the residual material was crystallized from aqueous ethanol and identified as **3a**, mp 132–134° (58% recovery after crystallization). Its ir was identical with that of **3a**.[1]

B. In Water.—A mixture of *n*-butylamine, water, and **3a** (4:4:1 molar ratio) was heated under reflux for 1.3 hr, after which 80% of the **3a** was recovered unchanged. A similar mixture, after 18 hr under reflux, gave 8% of an insoluble material, **4a**: ir (in Fluorolube), 3300, 3200, 3090 (NH), 1665 (C=O), 1570 (CNH) cm^{-1}.

Anal. Calcd for $C_{10}H_{22}N_4O_2$: C, 52.18; H, 9.62; N, 24.32. Found: C, 51.94; H, 9.46; N, 24.27.

After 64 hr under reflux, the yield of **4a** was 18%.

Attempted Preparation of 1,1′-(Azodicarbonyl)dipyrrolidine. Isolation of 1,2-Bis(1-pyrrolidinylcarbonyl)hydrazine.—To a stirred solution of 26.7 g (0.15 mole) of **1a** in 50 ml of ligroin was added 21.3 g (0.3 mole) of pyrrolidine in 50 ml of ligroin. After an exothermic reaction, a pale orange solid was precipitated by adding ether. The soluble portion was not worked up. The solid did not liberate iodine from potassium iodide solution; 210–215° dec (chars).

The solid was chromatographed on acid-washed alumina; the major fraction (2.9 g, 8%), eluted with benzene, was a white solid: mp 235–237; lit.[7] mp 176°; nmr ($CDCl_3$), multiplets at τ ~6.7 and ~8.2 and a singlet at 2.77 with relative intensities of 4.0:4.0:1.0; ir (Fluorolube mull), 3230 (shoulder at 3300, NH), 1650 and 1630 (C=O), and 1545 and 1525 (broad doublet, CNH) cm^{-1}.

Anal. Calcd for $C_{10}H_{18}N_4O_2$ [1,2-bis(1-pyrrolidinylcarbonyl)-hydrazine]: C, 53.07; H, 8.02; N, 24.76. Found: C, 52.72; H, 7.81; N, 24.74.

1,1′-Azobis(N,N-dibutylformamide). Attempted Preparation.—Dibutylamine (25.8 g, 0.20 mole) was added dropwise to a stirred solution of 20.2 g (0.10 mole) of **1c** in 100 ml of ether. The resulting colorless mixture was evaporated to dryness and the semicrystalline mass was triturated with hexane to give a white solid melting at 105–110° (7.3 g, 36%). Its ir spectrum (in Fluorolube) was very similar in the NH and C=O regions to that of **3a**: 3250, 1755, 1690, 1525 cm^{-1}.

Anal. Calcd for $C_8H_{16}N_2O_4$ (diisopropyl bicarbamate): C, 47.00; H, 7.90; N, 13.72. Found: C, 46.73; H, 7.81; N, 14.06.

A similar reaction using **1a** in ligroin as solvent gave **3a** (34% isolated).

Registry No.—1,1-Azobis(*N*-*n*-heptylformamide), 19740-68-2; 1,6-di-*n*-heptylbiurea, 19740-69-3; **4a**, 16314-55-9; **4b** (R = n-C_3H_7), 17696-84-3; 1,2-bis(1-pyrrolidinylcarbonyl)hydrazine, 19740-71-7; diisopropyl bicarbamate, 19740-72-8.

(6) K. E. Cooper and E. H. Ingold, *J. Chem. Soc.*, 1894 (1926).

(7) W. Reid, H. Hillenbrand, and G. Oertel, *Ann.*, **590**, 126 (1954).

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Synthetic Approaches to Oxygen-Bridged Cyclooctyl Compounds[1]

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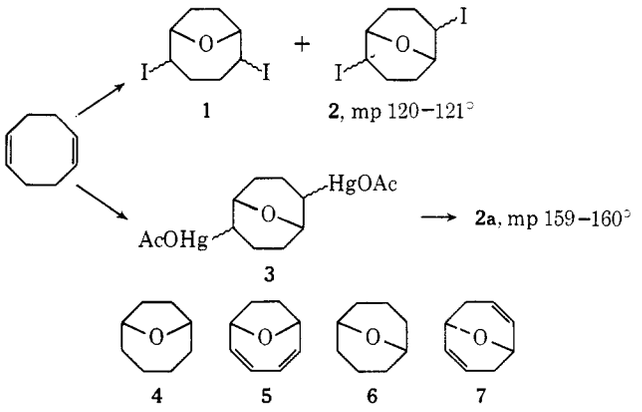
During our studies on transannular reactions in cyclooctyl compounds we observed that treatment of *cis,cis*-1,5-cyclooctadiene with mercuric oxide and iodine produced two new substituted 9-oxabicyclononanes. Since this structural feature is common to several products isolated from other transannular reactions,[3] we have investigated this reaction as a synthetic route to various substituted 9-oxabicyclononanes.

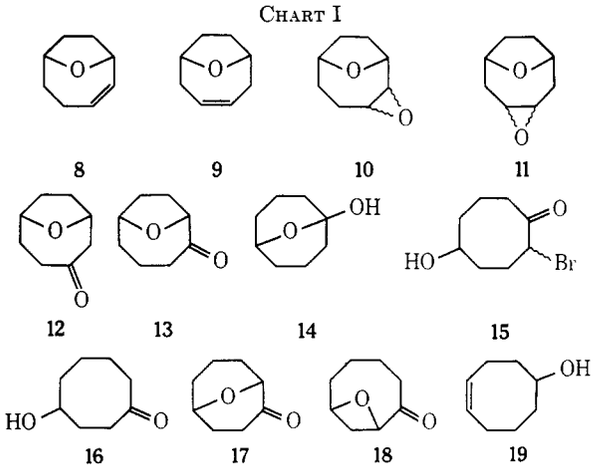
Addition of iodine to a mixture of the diene and mercuric oxide in chloroform at 35–45° led to the formation of mercuric iodide and a crystalline solid. Elemental and mass spectral analysis of the solid indicated the molecular formula $C_8H_{12}I_2O$. The molecular ion peak at *m/e* 378 in the mass spectrum was followed by intense peaks at *m/e* 251 and 124, indicating the successive loss of two iodine atoms. Glpc analysis showed the presence of two components in the ratio 2:3. Attempts to obtain pure samples of the individual components by preparative glpc were not successful although a pure sample of one was eventually obtained by selectively removing the other. Thus treatment of the mixture with potassium *t*-butoxide in ether gave a liquid and a crystalline solid. Support for structure **5** for the liquid product was obtained from spectroscopic measurements (see the Experimental Section) and from its transformation into 9-oxabicyclo[4.2.1]nonane (**4**)[4] on catalytic hydrogenation. The crystalline product, mp 120–121°, which had a glpc retention time identical with that of one of the components of the original mixture, gave (a) 9-oxabicyclo[3.3.1]nonane (**6**)[5] on exposure to tri-*n*-butyltin hydride and (b) 9-oxabicyclo[3.3.1]nona-2,6-diene (**7**)[6] on heating with potassium *t*-butoxide in tetrahydrofuran. From these experiments it was concluded that the products of the initial reaction were 2,5-diiodo-9-oxabicyclo[4.2.1]-nonane (**1**) and 2,6-diiodo-9-oxabicyclo[3.3.1]nonane (**2**) (Scheme I). Stetter and Meissner[6] have prepared an isomer of **2**, mp 159–160°, starting also with 1,5-cyclooctadiene. Treatment with aqueous mercuric acetate gave the bisacetoxymercuri compound **3** which yielded diiodide **2a** on exposure to iodine in chloroform.

SCHEME I



Diene **5** was a useful intermediate for the synthesis of other substituted 9-oxabicyclo[4.2.1]nonanes. Hydrogenation in aqueous potassium pentacyanocobaltate[7] gave a mixture of **8** and **9** in the ratio of 4:1 (Chart I).

CHART I



These olefins were separated by preparative glpc and their nmr spectra confirmed the assigned structures. Epoxidation of the olefin mixture with *m*-chloroperbenzoic acid in methylene chloride gave the isomeric epoxides **10** and **11** which on reduction with lithium aluminum hydride followed by chromic acid oxidation gave 9-oxabicyclo[4.2.1]nonan-3-one (**12**) and 9-oxabicyclo[4.2.1]nonan-2-one (**13**) in the ratio 1:3. Partial separation of these ketones was achieved by adsorption chromatography over alumina and subsequent preparative glpc gave the pure isomers.

In an attempt to find a more direct route to ketone **13** we investigated the bromination of 5-hydroxycyclooctanone.[8] This compound, which exists almost exclusively in the hemiketal form **14** (the infrared spectrum shows no carbonyl absorption), on treatment with pyridinium bromide perbromide in aqueous acetic acid at 60° gave a brominated product which showed a strong carbonyl absorption in the infrared spectrum and is therefore formulated as **15**. When this com-

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