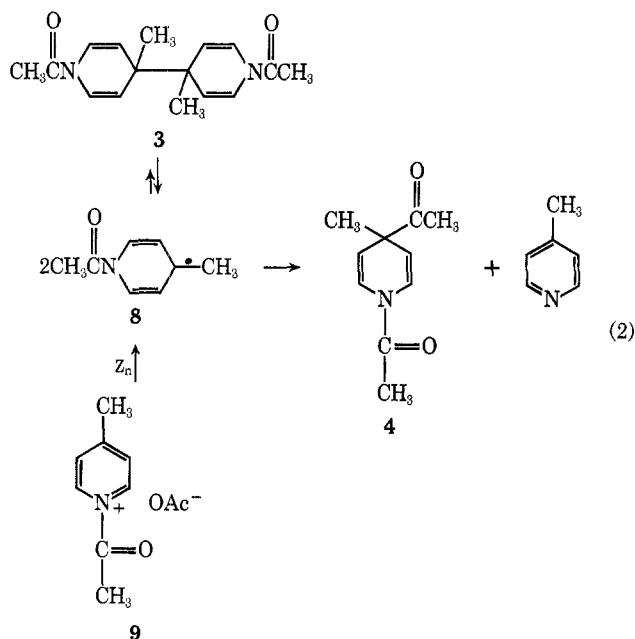
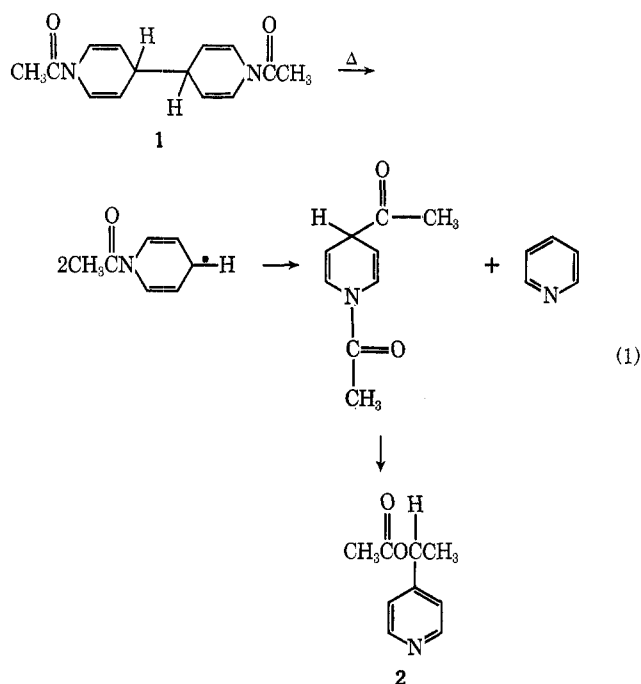


the corresponding pyridinium ions with sodium amalgam, are unstable upon storage and form compounds of lower molecular weight. The instability of **1** to heating with the resultant formation of **2**,<sup>3</sup> presumably by a disproportionation reaction shown in eq 1, strongly suggests that **3**, if formed, would disproportionate to **4** via **8** as shown in eq 2.



#### Experimental Section

**Materials.**—4-Methylpyridine, acetic anhydride, and 40 mesh zinc were reagent grade materials from Fisher Scientific Co.

**Preparation of 4.**—The procedure of Dimroth and Heene<sup>2</sup> was used with the substitution of 4-methylpyridine for pyridine. 4-Methylpyridine (50 ml) and 200 ml of acetic anhydride were mixed together in an erlenmeyer flask. After the addition of 50 g of zinc the reaction mixture was agitated in the stoppered flask with a magnetic stirrer for 16 hr–14 days at 30–35°. The only color change which was noticeable was a yellowing of the reaction mixture. The early precipitate formed was very soluble in water and is  $Zn(OAc)_2$  based upon its nmr spectrum in  $D_2O$  and the presence of a residue upon burning. The flask and its contents

were treated with 200 ml of water and heated to 85° in a water bath in order to dissolve the precipitate. The zinc was separated by filtration using hot acetic anhydride to wash the filter. The filtrate was refrigerated overnight and crystals of **4** were collected and recrystallized from methanol, mp 80–81°. A yield of 15–17% was obtained independent of the time of work-up. *Anal.* Calcd for  $C_{10}H_{13}NO_2$ : C, 67.02; H, 7.31; N, 7.81; O, 17.85. Found: C, 67.02; H, 7.44; N, 7.77; O, 17.77 (by difference). The molecular weight of **4** was determined in chloroform by vapor phase osmometry to be 181, agreeing well with the value of 179 calculated for  $C_{10}H_{13}NO_2$ .

**Physical Measurements.**—The spectral determination of **4** was made with a Beckman IR-4 infrared spectrometer, a Cary 14 ultraviolet-visible spectrophotometer, and a Varian A-60 nuclear magnetic resonance spectrometer.

**Registry No.**—**3**, 34803-87-7; **4**, 25463-04-1; 4-methylpyridine, 108-89-4.

#### The Reaction of Dilithium Cyclooctatetraenide with Phosgene. Preparation of Bicyclo[4.2.1]nona-2,4,7-trien-9-one<sup>1</sup>

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Although the chemistry of bicyclo[4.2.1]nonatrienes has been explored to a considerable extent,<sup>4</sup> the corresponding parent ketone, bicyclo[4.2.1]nona-2,4,7-trien-9-one (**1**), has not been described. This system has been synthesized by the reaction of dilithium cyclooctatetraenide with phosgene.<sup>5</sup> Cyclooctatetraene was converted into its dianion, which was treated with excess ethereal phosgene at  $-40^\circ$  and then quenched with water. The resulting mixture, containing two main products, was subjected to tlc. The component of shorter  $R_f$  was formed in about 19% yield and established to be the desired **1** on the basis of the mass spectrum [parent peak,  $m/e$  132 ( $C_9H_8O^+$ )] and nmr spectrum [ $\tau$  4.29 (6 H) and saturated bridgehead proton absorptions centered at  $\tau$  7.09 (2 H)]. The ir spectrum shows weak absorption at  $3045\text{ cm}^{-1}$  (olefinic C–H) and strong absorption at  $1755\text{ cm}^{-1}$  (C=O, similar to that of bridgehead ketones<sup>6</sup>). The addition of  $CH_3MgI$  to **1** resulted in the formation of one alcohol, indistinguishable from an authentic sample of *syn*-9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (**2**)<sup>4a</sup> on the basis of vpc comparison on two columns and nmr and ir spectral comparison. The component of longer  $R_f$ , formed in 22% yield, was 3-chloroindene (**3**).<sup>7</sup>

(1) Part of this work was described in a Communication to the Editor: M. Sakai, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4452 (1970).

(2) Address correspondence to this author at Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

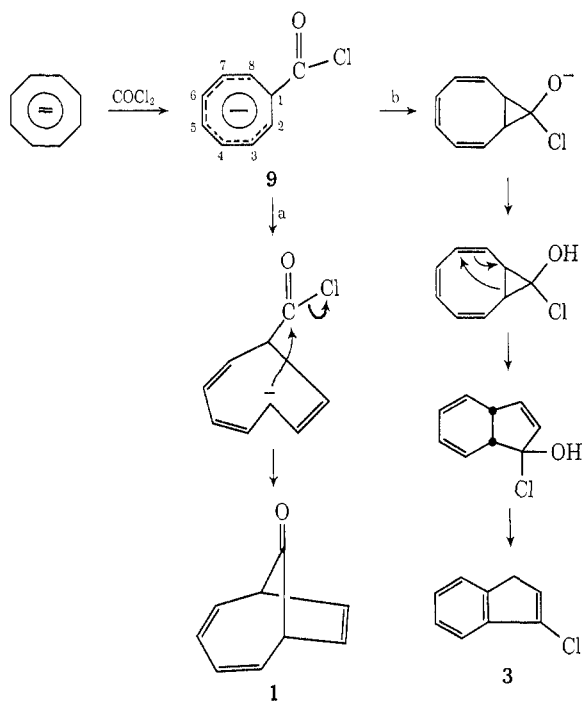
(3) Deceased Nov 23, 1969.

(4) (a) T. S. Cantrell and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 5868 (1967); (b) L. G. Cannell, *Tetrahedron Lett.*, 5947 (1966); (c) A. S. Kende and T. L. Bogard, *ibid.*, 3383 (1967); (d) M. Sakai and S. Winstein, unpublished results.

(5) After the present method had been perfected, we learned that Professor H. Shechter and coworkers made **1** by the reaction of dilithium cyclooctatetraenide with dimethylcarbamoyl chloride.

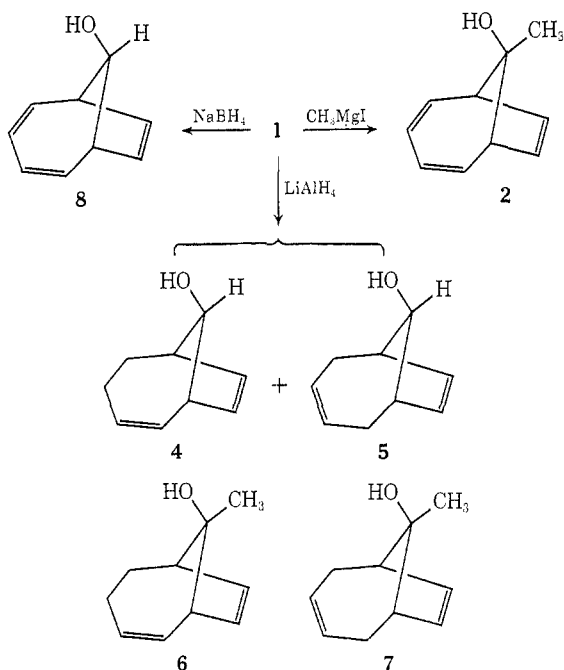
(6) (a) C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, **82**, 4067 (1960); (b) H. K. Hall, Jr., and R. Zhinden, *ibid.*, **80**, 6428 (1958); (c) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964); (d) C. F. H. Allan, T. Davis, D. W. Stewart, and J. A. VanAllan, *ibid.*, **20**, 306 (1955).

(7) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 3337 (1955).



Formation of **1** and **3** from the dianion and phosgene can be envisaged as proceeding *via* paths a and b. The intermediate **9** undergoes intramolecular reaction at C-4 (a) of the eight-membered ring to give **1**. Compound **3** is derivable *via* ring closure (b) of **9** at C-2, followed by dehydration of 1-chloro-1-hydroxy-8,7-dihydroindene and prototropic rearrangement.

Reaction of **1** with  $\text{LiAlH}_4$  in ether furnishes *syn*-9-hydroxybicyclo[4.2.1]nona-2,7-diene (**4**) and *syn*-9-hydroxybicyclo[4.2.1]nona-3,7-diene (**5**). The structure of **4** and **5** are assignable from their spectral properties. The nmr spectra are quite similar to those of the analogous alcohols **6** and **7**,<sup>4d</sup> except for the disappearance of methyl absorptions and formation of  $\alpha$ -proton absorption. It is probable that **4** and **5** have *syn* stereochemistry.



The reaction of **1** and  $\text{NaBH}_4$  in methanol at room temperature has been briefly investigated and found to yield only *syn*-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (**8**). The identification of **8** rests on its analysis, its ir spectrum, its mass spectrum, and, in particular, its nmr spectrum. The stereochemistry of the hydroxyl group in **8** is assigned as *syn* to the four-carbon bridge on the basis that the side of the carbonyl group facing the two-carbon bridge is considerably less hindered than the side facing the four-carbon bridge. Hydride attack should occur predominantly from the side of the carbonyl group *syn* to the two-carbon to give **8**.

#### Experimental Section

**Reaction of Dilithium Cyclooctatetraenide with Phosgene.**—Lithium (4.0 g) was added in small pieces to dry DME (250 ml, freshly distilled from  $\text{LiAlH}_4$ ) at  $-78^\circ$  in nitrogen atmosphere. Freshly distilled COT (26 g) was added, and the mixture was stirred vigorously for 20 hr, allowed to warm to room temperature, and stirred for an additional 48 hr. The deep green solution of  $\text{LiCOT}$  in DME was added over a 1-hr period to vigorously stirred cold ( $-40^\circ$ ) phosgene (100 g) in 200 ml of DME under helium. After further stirring for 3 hr at  $-40^\circ$ , the mixture was allowed to warm to room temperature and stirred for 5 hr more. The reaction mixture was filtered, water added, and extracted with pentane ( $3 \times 500$  ml) to give a red solution. The combined organic layers were washed with water (200 ml) and saturated  $\text{Na}_2\text{CO}_3$  solution (100 ml) and then dried ( $\text{MgSO}_4$ ). Evaporation of the solvent gave a red oil which was chromatographed on 100 ml of neutral alumina (activity III).

The first elution with pentane was 3-chloroindene (9.0 g, 22%): mass spectrum  $m/e$  150 ( $\text{M}^+$ ); nmr  $\tau_{\text{TMS}}^{\text{CS}_2}$  2.67 (m, 4, aromatic), 3.62 (t, 1, vinyl), and 6.67 (d, 2, allyl); ir  $\nu_{\text{max}}^{\text{neat}}$  759  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_9\text{H}_7\text{Cl}$ : C, 71.78; H, 4.68. Found: C, 71.92; H, 4.91.

The second elution with 12% ether-pentane was almost pure **1**, yield 6.2 g (19%).

Anal. Calcd for  $\text{C}_9\text{H}_8\text{O}$ : C, 81.79; H, 6.10. Found: C, 81.56; H, 6.09.

Some modification of the preparation of **1** gave the results shown in Table I.

TABLE I  
YIELDS OF **1** AND **3**

Solvent	Temp. $^\circ\text{C}$	Time, hr	Yield, %	
			<b>1</b>	<b>3</b>
DME	-40	4	19	22
Ether	-30	3	17	20
Ether	0	1	18	25
THF	-30	4	20	?

**Reaction of **1** with Methylmagnesium Iodide.**—A solution of **1** (100 mg) in ether (2 ml) was added at  $0^\circ$  to stirred methylmagnesium iodide (3 mol excess) in ether (2.5 ml). The mixture was refluxed for 20 min and then poured onto a slurry of ice and saturated aqueous  $\text{NH}_4\text{Cl}$ . The aqueous layer was washed with ether. The combined ether solution was washed with water, dried, and evaporated to give 95 mg of **2** as an oil: ir  $\nu_{\text{max}}^{\text{neat}}$  1394, 1372, 1180, 860, 751 and 687  $\text{cm}^{-1}$ ; nmr  $\tau_{\text{TMS}}^{\text{CS}_2}$  4.01 (m, 4, vinyl), 4.82 (m, 2, vinyl), 7.32 (m, 2, bridgehead), 8.13 (s, 1, OH), and 8.67 (s, 3, methyl).

**Reaction of **1** with  $\text{LiAlH}_4$ .**—A solution of 1.5 g of **1** in 20 ml of ether was added to a solution of 0.8 g of  $\text{LiAlH}_4$  in 5 ml of ether dropwise at  $-78^\circ$ . After the solution was stirred for 2 hr at this temperature, it was decomposed with 10 ml of 20% KOH solution. The ether solution was washed with water and dried ( $\text{K}_2\text{CO}_3$ ), and evaporation of the ether gave 1.6 g of a pale yellow oil. Examination by vpc revealed two components, **4** (81.5%) and **5** (18.5%) in order of increasing emerging time. Preparative vpc of a 1.0-g quantity of the above mixture gave 0.4 g of **4** [nmr  $\tau_{\text{TMS}}^{\text{CDCl}_3}$  4.07 (m, 2, vinyl), 4.43 (m, 2, vinyl), 5.78 (t, 1,  $\alpha$ -H), 6.83 (m, 1, bridgehead), 7.33 (m, 1, bridgehead), 8.06 (s, 1, OH), and 8.14 (m, 4, methylene)] and 0.1 g of **5** [nmr  $\tau_{\text{TMS}}^{\text{CDCl}_3}$  4.22 (m, 2, vinyl), 4.55 (m, 2, vinyl), 5.53 (t, 1,  $\alpha$ -H),

7.24 (m, 2, bridgehead), 7.69 (m, 4, methylene), and 8.28 (s, 1, OH)].

**Reaction of 1 with NaBH<sub>4</sub>.**—A solution of 0.5 g of 1 in 30 ml of methanol was cooled to 0°. NaBH<sub>4</sub> (0.4 g) was added in small portions. After 30 min, the ice bath was removed and the solution was allowed to stir for 1 hr. The reaction mixture was cooled and hydrolyzed with 10 ml of water and 15 ml of 20% KOH solution. The mixture was poured into ice-water and extracted with ether. Evaporation of the ether yielded a residue which was crystallized from hexane at -5° to give 0.48 g (95%) of 8 as white needles: mp 52.0–52.5°; mass spectrum *m/e* 137 (M<sup>+</sup>);  $\nu_{\text{max}}^{\text{CHCl}_3}$  3575, 3035, and 1105 cm<sup>-1</sup>; nmr  $\tau_{\text{MS}}^{\text{CDCl}_3}$  3.98 (m, 4, vinyl), 4.75 (m, 2, vinyl), 5.62 (m, 1,  $\alpha$ -H), 6.96 (t, 2, bridgehead), and 8.22 (m, 1, OH).

*Anal.* Calcd for C<sub>9</sub>H<sub>10</sub>O: C, 80.56; H, 7.56. Found: C, 80.44; H, 7.66.

**Registry No.**—1, 34733-74-9; 2, 17339-68-3; 3, 25894-22-8; 4, 34733-77-2; 5, 34771-56-7; 8, 34712-67-9; dilithium cyclooctatetraenide, 34728-91-1; phosgene, 75-44-5.

### Novel Synthesis of

### 1-Hydroxy-1*H*-benzimidazole 3-Oxides and 2,2-Dialkyl-2*H*-benzimidazole 1,3-Dioxides<sup>1</sup>

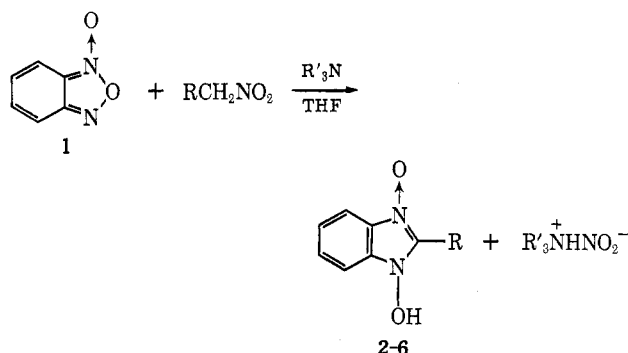
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Received January 20, 1972

Benzofurazan 1-oxide (1) is known to react with enamines<sup>2</sup> and  $\beta$  diketones<sup>3</sup> to yield substituted quinoxaline 1,4-dioxides and with phenolate anions<sup>4,5</sup> to yield substituted phenazine 5,10-dioxides and related compounds. We have recently discovered its utility for the preparation of substituted benzimidazole 1,3-dioxides. The method constitutes a highly convenient preparative procedure.

We have found that benzofurazan 1-oxide (1) reacts exothermically with primary nitroalkanes in tetrahydrofuran in the presence of organic amine bases to give good yields of 2-substituted 1-hydroxy-1*H*-benzimidazole 3-oxides (see Table I) and nitrite salts of the amines. The parent compound 2 (R = H) was pre-



(1) Presented in part at (a) IUPAC Meeting in London, July 1968, Abstract H4, 437; (b) 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Medicinal Chemistry Abstract 15.

(2) M. J. Haddadin and C. H. Issidorides, *Tetrahedron Lett.*, 3253 (1965).

(3) C. H. Issidorides and M. J. Haddadin, *J. Org. Chem.*, **31**, 4067 (1966).

(4) K. Ley, F. Seng, V. Eholzer, R. Nast, and R. Schubart, *Angew. Chem., Int. Ed. Engl.*, **8**, 596 (1969).

(5) M. J. Abu El-Haj, B. W. Dominy, J. D. Johnston, M. J. Haddadin, and C. H. Issidorides, *J. Org. Chem.*, **37**, 589 (1972).

TABLE I<sup>a</sup>

Compd no.	R	Yield, %	Mp, °C <sup>b</sup>
2	-H	40	223
3	-CH <sub>3</sub>	65	204–205
4	-CH <sub>2</sub> CH <sub>3</sub>	66	194–195
5	-CH <sub>2</sub> CH <sub>2</sub> CONH <sub>2</sub>	70	220
6	-CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	35	156.5

<sup>a</sup> All compounds were analyzed for C, H, and N and the results were within  $\pm 0.3\%$  of the theoretical values. Spectral data were consistent with assigned structures. <sup>b</sup> Compounds 2–5 were recrystallized from MeOH; 6 from AcOH.

pared in 40% yield from nitromethane in the presence of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN). This compound was identical with an authentic sample prepared by Katritsky's method.<sup>6</sup> Diethylamine was the base used for the preparation of compounds 3–6 (Table I), and in these experiments the other product was characterized as the nitrite salt of diethylamine.

In a typical procedure, 0.1 mol of 1 and 0.12 mol of nitroethane were dissolved in 100 ml of tetrahydrofuran. To this was added at room temperature 0.12 mol of diethylamine over a period of 0.5 hr. An instantaneous exothermic reaction was observed (40°) and within 1 hr the product crystallized from the solution. The solution was allowed to stand overnight at room temperature and filtered to give 9.6 g of 3. The product was recrystallized from methanol and was found to be identical with authentic material prepared by a known procedure.<sup>7</sup>

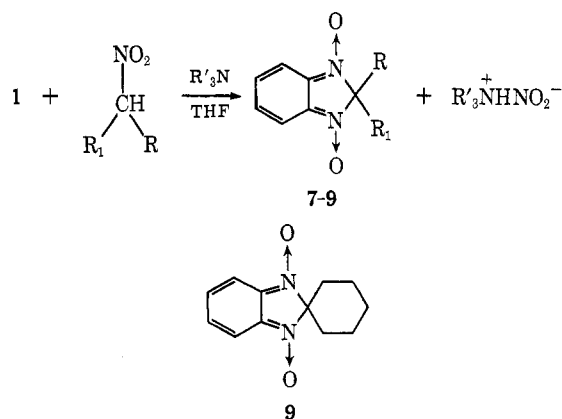
Of particular interest was the reaction of secondary nitroalkanes with 1 to afford a novel new class of compounds, 2,2-dialkyl-2*H*-benzimidazole 1,3-dioxides (Table II). These compounds are red with a green

TABLE II<sup>a</sup>

Compd no.	R	R <sub>1</sub>	Yield, %	Mp, °C
7	-CH <sub>3</sub>	-CH <sub>3</sub>	60	132–134
8	-CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>3</sub>	52	127–129
9	-(CH <sub>2</sub> ) <sub>6</sub>		75	112–115

<sup>a</sup> All compounds were analyzed for C, H, and N and the results were within  $\pm 0.3\%$  of the theoretical values. Spectral data were consistent with assigned structures. Compounds were recrystallized from acetone-hexane.

fluorescence. The procedure described above gave 2,2-dimethyl-2*H*-benzimidazole 1,3-dioxide (7) in 60%



(6) A. J. Boulton, A. C. Gray, and A. R. Katritsky, *Chem. Commun.*, 741 (1966).

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