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

Reaction of 1 with $NaBH_4$.—A solution of 0.5 g of **1** in 30 ml of methanol was cooled to 0°. $NaBH_4$ (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^+); ir $\nu_{max}^{CHCl_3}$ 3575, 3035, and 1105 cm^{-1}; nmr $\tau_{TMS}^{CDCl_3}$ 3.98 (m, 4, vinyl), 4.75 (m, 2, vinyl), 5.62 (m, 1, α-H), 6.96 (t, 2, bridgehead), and 8.22 (m, 1, OH).

Anal. Calcd for $C_9H_{10}O$: 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[1]

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Received January 20, 1972

Benzofurazan 1-oxide (**1**) is known to react with enamines[2] and β diketones[3] to yield substituted quinoxaline 1,4-dioxides and with phenolate anions[4,5] 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 prepared 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.[6] 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.

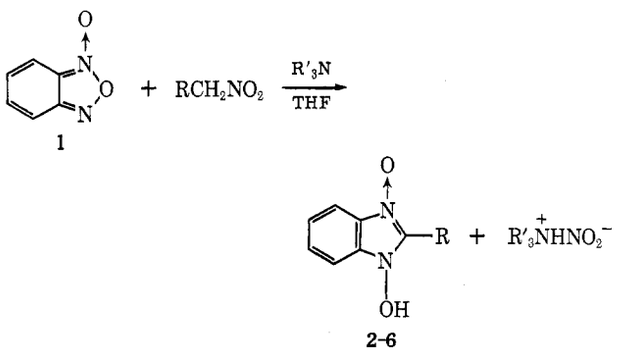


TABLE I[a]

Compd no.	R	Yield, %	Mp, °C[b]
2	–H	40	223
3	$-CH_3$	65	204–205
4	$-CH_2CH_3$	66	194–195
5	$-CH_2CH_2CONH_2$	70	220
6	$-CO_2CH_2CH_3$	35	156.5

[a] All compounds were analyzed for C, H, and N and the results were within ±0.3% of the theoretical values. Spectral data were consistent with assigned structures. [b] Compounds **2**–**5** were recrystallized from MeOH; **6** from AcOH.

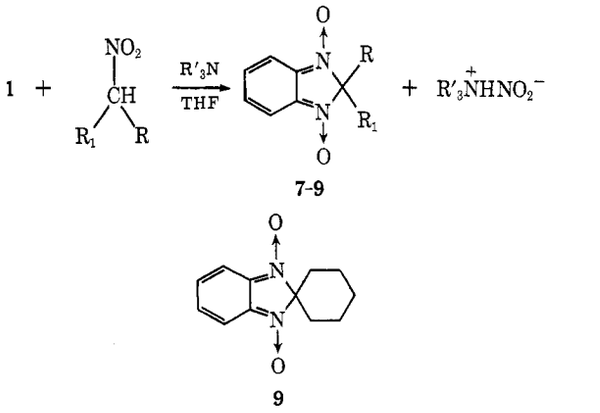
In a typical procedure, 0.1 mol of **1** and 0.12 mol of nitroethane were dissolved in 100 ml of tetrahydrofuran. To this was added at room temperature 0.12 mol of diethylamine over a period of 0.5 hr. An instantaneous exothermic reaction was observed (40°) and within 1 hr the product crystallized from 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.[7]

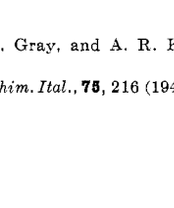
Of particular interest was the reaction of secondary nitroalkanes with **1** to afford a novel new class of compounds, 2,2-dialkyl-2*H*-benzimidazole 1,3-dioxides (Table II). These compounds are red with a green fluorescence. The procedure described above gave 2,2-dimethyl-2*H*-benzimidazole 1,3-dioxide (**7**) in 60%

TABLE II[a]

Compd no.	R	R_1	Yield, %	Mp, °C
7	$-CH_3$	$-CH_3$	60	132–134
8	$-CH_3$	$-CH_2CH_3$	52	127–129
9	$-(CH_2)_5$		75	112–115

[a] All compounds were analyzed for C, H, and N and the results were within ±0.3% of the theoretical values. Spectral data were consistent with assigned structures. Compounds were recrystallized from acetone–hexane.





(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).

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

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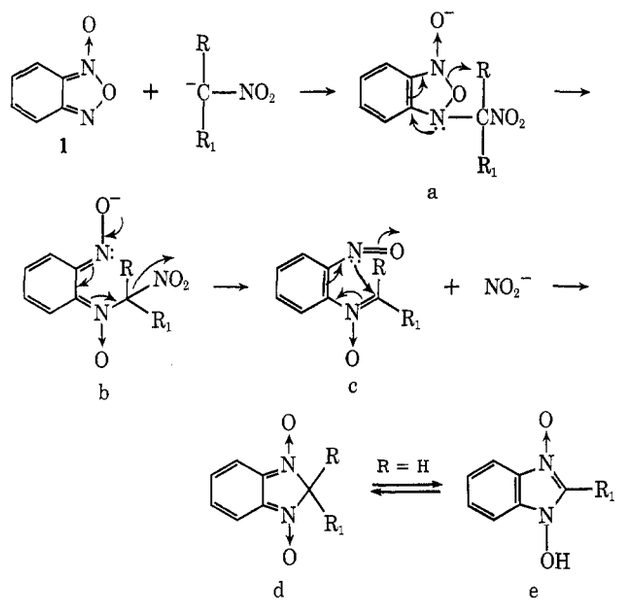
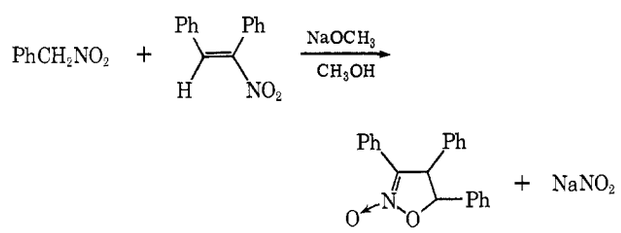
yield from 2-nitropropane. The ir spectrum (KBr) exhibited strong absorption bands for the N→O at 1399, 1361, and 1307 cm^{-1}; the uv spectrum (MeOH) exhibited maxima at 510 mμ (ε 7.25 × 10^3) and 245 (2.34 × 10^4). The nmr spectrum ($CDCl_3$) showed absorption at δ 1.7 (s, 6 H) due to the dimethyl grouping and two A_2B_2 quartets for the aromatic protons at δ 6.9 (J = 3 Hz) and 7.25 (J = 3 Hz). The spiro compound **9** was obtained by allowing **1** to react with nitrocyclohexane in the presence of DBN.

A possible mechanism for the formation of the above products from **1** and the nitroalkanes is outlined below. The nitroanion probably adds to the N-3 nitrogen to



give a, which can tautomerize to b. Elimination of NO_2^- would give c, which could rearrange to d. The latter is the final product where R and R_1 are alkyl, whereas if R = H, the product tautomerizes to form e. A similar displacement of a nitro group was reported during the formation of 3,4,5-triphenylisoxazoline 2-oxide from phenylnitromethane and *cis*-α-nitrostilbene in the presence of base, as shown below.[8]



The first observation of the displacement of a nitro group from a tertiary carbon atom (by thiophenoxide and malonate anions) was reported by Kornblum, *et al.*[9]

Another route from benzofurazan oxides to 1-hydroxy-1*H*-benzimidazole 3-oxides, using β-keto sulfoxides, has recently been reported.[10]

Registry No.—**2**, 15966-49-1; **3**, 15966-52-6; **4**, 31980-09-3; **5**, 34759-59-6; **6**, 31980-11-7; **7**, 31980-12-8; **8**, 34789-56-5; **9**, 31983-86-5.

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(10) D. P. Claypool and D. R. Sidani, *J. Org. Chem.*, in press.

The Rearrangement of 3a,7a-Dihydro-3,3a,5,6-tetraphenylinden-1-one

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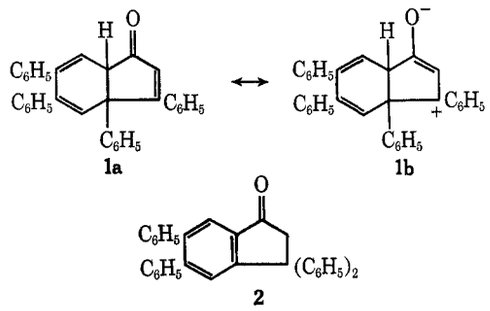
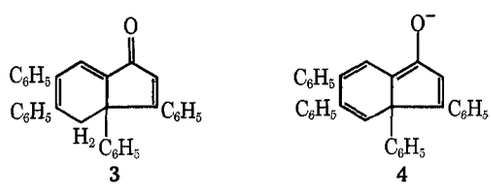
Received January 18, 1972

The thermal rearrangement of 3a,7a-dihydro-3,3a,5,6-tetraphenylinden-1-one (**1a**) to 3,3,5,6-tetraphenyl-



indan-1-one (**2**), which has been considered to proceed through the polarized form **1b**,[1] has now been found to be catalyzed by base and acid. Addition of catalytic amounts of sodium methoxide to an alcohol solution of **1a** forms a purple enolate ion which on heating for a short time gives mainly the less acidic 3a,4-dihydro-3,3a,5,6-tetraphenylinden-1-one (**3**) and a small amount



of **2**. Further heating of this solution converts **3** to **2**. These results preclude the participation of **1b** in this rearrangement and indicates that the enolate ion **4**, which can be formed from both **1a** and **3**, is involved and would allow the rearrangement to proceed by a 1,5-suprafacial sigmatropic shift of the phenyl group.

The behavior of **1a** with acid is similar. Treatment with hydrogen bromide in acetic acid at 100° for 30 min gives **3**.[2] Prolonged heating of **1a** with hydrochloric acid in ethanol gave mainly **2**. This sequence of reactions favors the enol form of **1a** as a precursor of **2**.

The uncatalyzed thermal rearrangement of **1a** may proceed through the enol form even though this form could not be detected by either infrared or nmr spectroscopy. Studies of **1a** using the first technique were carried out at temperatures varying from 25 to 175°. At the melting point **1a**, when present as a film, was found to rearrange to **2**.

Nmr studies of **1a** found no evidence for the enol form; similar peak heights were observed in polar ($DCCl_3$) and nonpolar (C_6D_6) solvents.

The uncatalyzed thermal rearrangement[2] of **3** to **2** would involve first a 1,5 shift of hydrogen and the formation of **1a**. The possibility of a 1,7 shift of

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