described above, and 0.50 g (17%) of **2**, mp 107–108°, was obtained.

Anal. Calcd for $C_{18}H_{38}P_2O$: C, 65.03; H, 11.52; P, 18.63. Found: C, 64.92; H, 11.73; P, 18.46.

Registry No.—**1**, 18723-96-1; **1** dimethiodide, 18723-97-2; **2**, 18723-98-3; **2** methiodide, 18723-99-4; **3**, 18724-00-0.

Diphenylhydantil[1]

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The "diphenylhydantils" are dimeric oxidation products which may be formed by either bromine oxidation of a 5-phenylhydantoin or by exposure of an alkaline solution of a 5-phenylhydantoin to air.[2–6] Gabriel's investigation[2] on 5-phenylhydantoin's dimer, $C_{18}H_{14}N_4O_4$ (**1a**, which he named "diphenylhydantil"), ended with assignment of a structure characterized by a C_5–N_1 linkage (*e.g.*, as in **1**). After an encounter with these compounds, we wish to propose revision of structure to that of the symmetrical dimer shown by **2**.[7]

(1) This investigation was supported by Public Health Service Research Grant GM 13606 (Dr. Thomas C. Butler, Principal Investigator) from the National Institute of General Medical Sciences.

(2) S. Gabriel, *Ann.*, **350**, 118 (1906).

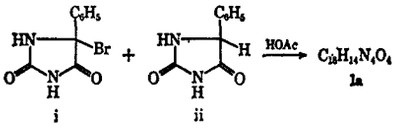
(3) A. Kjaer, *Acta Chem., Scand.*, **4**, 892 (1950).

(4) Gust.-Ad Holmberg, *ibid.*, **4**, 821 (1950).

(5) J. Klosa, *Arch. Pharm.*, **285**, 31, 274 (1952).

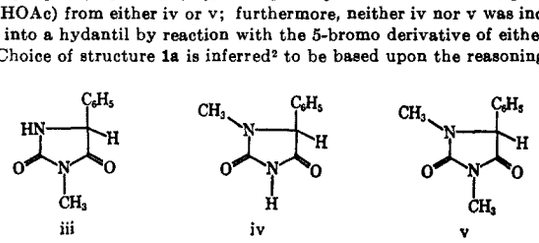
(6) J. T. Edward and S. Nielsen, *J. Chem. Soc.*, 2327 (1959).

(7) In brief summary, Gabriel[2] showed that 5-bromo-5-phenylhydantoin (i) would react with 5-phenylhydantoin (ii) to give **1a**; the reaction could be



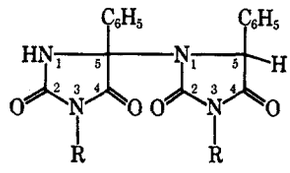
conducted by reacting equimolar quantities of i and ii in acetic acid or, more conveniently, by generating *in situ* the required proportion of i through addition of the calculated quantity of bromine. It was similarly shown that equimolar proportions of 5-hydroxy-5-phenylhydantoin and ii in HOAc would provide **1a**.

Gabriel considered structure **2a** for diphenylhydantil, but rejected this possibility in favor of one having a N_1–C_5 linkage (*i.e.*, **1a**). While iii formed dimethyldiphenylhydantil (**2b**), analogous hydantils could not be produced (Br_2, HOAc) from either iv or v; furthermore, neither iv nor v was incorporated into a hydantil by reaction with the 5-bromo derivative of either ii or iii. Choice of structure **1a** is inferred[2] to be based upon the reasoning that

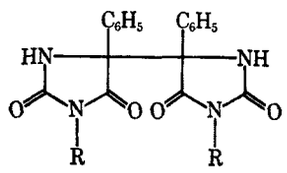


N_1 alkylation blocks a function required for product formation. Regarding the proposed revision (*i.e.*, **2a–c**), the failure of iv and v to form, or to be incorporated into, a hydantil is apparently due to increased hindrance at C_5; whatever the actual mechanism for dimerization may be, molecular models (CPK Atomic Models, Ealing Corp.) suggest that N_1 alkylation would probably suppress C_5–C_4 enolization as well as retard dimerizations mediated by

Infrared spectra (KBr disks) of dimethyldiphenylhydantil (**2b**) and diethyldiphenylhydantil (**2c**) were similar in the 3600–3200- and 1800–1500-cm^{-1} regions.

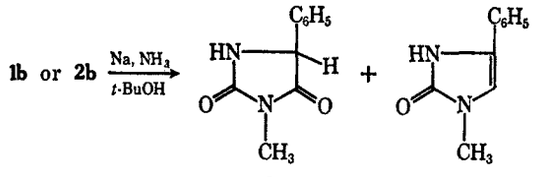


1a, R = H
b, R = CH_3
c, R = C_2H_5



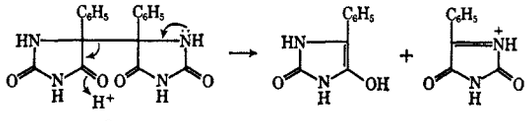
2a, R = H
b, R = CH_3
c, R = C_2H_5

Each spectrum contained a sharp intense band at 3300 cm^{-1} (assignable to an amide –NH–[8a]) and only two bands at 1780 and 1720 cm^{-1} in the carbonyl region (assignable to the 4-oxo and 2-oxo groups, respectively, of a hydantoin system[8b]). Amide II bands were not observed in the spectra, thus indicating that –NH– moieties were retained in cyclic lactam structures.[8c] Total preservation of the hydantoin system upon conversion into a hydantil was indicated by sodium–ammonia–*t*-butyl alcohol cleavage of **2b**; approximately 80% of **2b** was accounted for in terms of 3-methyl-5-phenylhydantoin (Nuvarone, **3**) and 1-methyl-4-phenylimidazol-2-one (**4**) (~2.5:1 ratio, respectively). The appearance of imidazol-2-one **4** as a cleavage product is probably due to an overreduction of **3**.[9]



Mass spectra of the diphenylhydantils, though supporting dimeric oxidation products (*i.e.*, weak molecular ions), did not show any fragments of mass greater

C_5 radicals. Structure **1a** was supported[2] by cleavage (fuming HCl, 165°, 3 hr) into phenylglyoxylic acid and α-aminophenylacetic acid; milder conditions (refluxing aqueous HBr, 2 hr) gave 25% cleavage. It would seem that under these strenuous conditions that products could be rationalized equally well by assuming the following initial cleavage of **2a**. Proposal **1a** may be



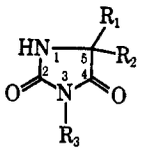
viewed as a "bisamide," *i.e.*, $RCH(HNCOR')_2$. The strenuous conditions required for cleavage of **1a** do not parallel examples mentioned in the literature; labilities of bisamides have been indicated to be similar to those of an acetal, *i.e.*, unstable in warm dilute acid, stable in dilute alkali. For examples and discussion, see E. Roth, *Ann.*, **154**, 72 (1870); A. Schuster, *ibid.*, **154**, 80 (1870); G. Stefanovic' and J. Bojanovic', *J. Org. Chem.*, **17**, 816 (1952); S. L. Vail, C. M. Moran, and R. H. Barker, *ibid.*, **30**, 1195 (1965), and references therein.

(8) (a) A. R. Katritzky and A. P. Ambler in "Physical Methods in Heterocyclic Chemistry," Vol. II, A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1963, p 193; (b) p 228; (c) *cf.* ref 8a and L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1962, p 217.

(9) Imidazol-2-one **4** may be prepared by sodium–ammonia–*t*-BuOH reduction of **3** (note Experimental Section). The compound may be prepared also by $LiAlH_4$ reduction of **3** [I. J. Wilk and W. J. Close, *J. Org. Chem.*, **15**, 1020 (1950)], and **4** is one of three products encountered in the sodium borohydride reduction of **3** (unpublished results).

TABLE I

CHEMICAL SHIFTS (δ, PARTS PER MILLION) OF THE NH RESONANCES OF SOME HYDANTOINS IN TFA AND DMSO-d_6 SOLUTION



			TFA		DMSO-d_6	
R_1	R_2	R_3	δ_{N_1H}	δ_{N_3H}	δ_{N_1H}	δ_{N_3H}
C_6H_5	H	H[a]		9.41	8.38	10.8
C_6H_5	H	CH_3[b]			8.63	
C_6H_5	H	C_2H_5[c]			8.62	
C_6H_5	C_2H_5	H[d]	7.75	9.36	8.64	10.8
C_6H_5	C_2H_5	CH_3[d]	7.56		8.95	
C_6H_5	C_6H_5	H[e]	7.96	9.54	9.32	11.1
C_6H_5	C_6H_5	CH_3[f]	7.78		9.63	
C_6H_5	$C_6H_5CH_2$	H[g]	7.70	9.05	8.70	10.5
C_6H_5	$C_6H_5CH_2$	CH_3[g]	7.63		8.96	

[a] Columbia Chemical Co. [b] Abbott Laboratories, and as described in ref 3. [c] Abbott Laboratories, and by reaction of ethyl isocyanate and α-amino-α-phenylacetic acid as described for related examples by E. Ware, *Chem. Rev.*, **46**, 403 (1950). [d] Sandoz Pharmaceutical Co. [e] Eastman Organic Chemicals Co. [f] C. Hoffman, *Bull. Soc. Chim. Fr.*, **45** (1950). [g] Note Experimental Section.

than that in the order of a monomer ion. Ultraviolet spectra of the diphenylhydantils were similar to spectra of model hydantoins; in addition, acid–base spectra of the dialkyldiphenylhydantils indicated no dissociable protons.

To accord with expression **1**, nuclear magnetic resonance spectra of the diphenylhydantils ought to contain a one-proton singlet for an amide (–NH–) proton, as well as a one-proton singlet for a C_5 hydrogen in a region at which this latter proton would be displayed by appropriate model compounds. Furthermore, it was anticipated that supportive evidence for either expression, **1** or **2**, would be revealed by the resonances exhibited by the di-N,N′-alkyl groups in the dialkyldiphenylhydantils; *i.e.*, it was anticipated that resonances for the di-N,N′-alkyl groups would be nonequivalent in the unsymmetrical case (*e.g.*, **1b** and **1c**) and equivalent in the symmetrical case (*e.g.*, **2b** and **2c**).

5-Phenylhydantoin and its 3-alkyl derivatives, Nuvarone (**3**) and Peganone (**5**), showed one-proton singlets for the C_5 hydrogen in the region 5.0–5.5 ppm (δ) when their nmr spectra were examined in either trifluoroacetic acid (TFA) or dimethyl-d_6 sulfoxide (DMSO-d_6) solution. The TFA or DMSO-d_6 spectrum of dimethyldiphenylhydantil (**2b**) contained three groups of signals. In TFA a single sharp NCH_3 resonance occurred at δ 2.72, two distinct aromatic multiplets appeared at 7.40–7.48 and 7.68–7.78, and a rather sharp –NH– singlet was seen at 8.81; relative intensities were 3 ($-CH_3$), 3 (aromatic H), 2 (aromatic H), 1 (–NH–), respectively. Spectra of diethyldiphenylhydantil (**2c**) in TFA and DMSO-d_6 followed a similar pattern, in that a single, rather sharp singlet was observed for –NH– protons and equivalencies for the NCH_2CH_3 groups were indicated by well-defined multiplets; the integrated ratios of the signals were 3 ($-CH_3$), 2 ($-CH_2-$), 3 (aromatic H), 2 (aromatic H), 1 (–NH–). It would thus seem that the absence of any signal attributable to a C_5 hydrogen and the equivalencies indicated for N-alkyl and amide (–NH–) groupings would be more compatible with a symmetrical dimer (*i.e.*, **2a–c**) than with the presently accepted unsymmetrical expression (*i.e.*, **1a–c**).

Contrasting to the TFA spectra of the dialkyldiphenylhydantils (*i.e.*, **2b** and **2c**) which contained signals attributable to N_1H resonances, the spectra of TFA solutions of 5-phenylhydantoin, Nuvarone (**3**), and Peganone (**5**) indicated that N_1H resonances were averaged out by exchange with solvent. Examination of a series of model hydantoins in TFA solution (note Table I) showed, however, that the pattern of substitution in the 5 position of the hydantoin ring apparently determines the disposition of the N_1-amide proton resonance. Of the 5,5-disubstituted hydantoins here examined (TFA), each showed a signal attributable to a N_1-amide proton, an occurrance which is consistent with the assignment of the low field proton found in each of the TFA spectra of the dialkyldiphenylhydantils, **2b** and **2c**.

Experimental Section[10]

Diphenylhydantil (2a) and Its Dimethyl and Diethyl Derivatives 2b and 2c. Method A (Br_2, HOAc).—Diphenylhydantil (**2a**) and dimethyldiphenylhydantil (**2b**) were prepared by bromine oxidation[2] of 5-phenylhydantoin and Nuvarone (**3**), respectively. The infrared spectrum of diphenylhydantil (**2a**) contained bands at 3210 (m), 1790 (m), 1715 (s), 1500 (w), 1450 (m), and 1400 cm^{-1} (m); **2a** was insoluble in the solvents (TFA and DMSO-d_6, etc.) used for measurement of nmr spectra.

Diethyldiphenylhydantil (**2c**) was similarly prepared (~30%) by bromine oxidation of Peganone (**5**). Thus 1.2 g (5.9 mmol) of **5** and 0.5 g (3.0 mmol) of bromine in 1.2 ml of acetic acid were heated on a water bath for 1 hr (45 min required for decolorization of bromine). The precipitate was filtered off and was washed successively with acetic acid, ethanol, and ether: yield 400 mg; mp 328–330°. Recrystallization by solution in 100 ml of boiling acetic acid followed by addition of 25 ml of warm water gave 300 mg of analytically pure **2c**, mp 325–327°.

(10) Thin layer chromatograms were prepared by coating microscope slides with silica gel H; solvent systems were benzene–ethyl acetate–acetic acid (90:10:1 or 9:1:1); nonfluorescing compounds were developed with 5% phosphomolybdic acid in ethanol (PMA). Micromelting points were taken on a Kofler hot stage microscope supplied with a calibrated thermometer and are otherwise uncorrected. Ultraviolet spectra were recorded on a Cary Model 15 spectrophotometer. Nmr spectra were recorded on Varian HA-100 (North Carolina State University) and Varian A-60 (Research Triangle Institute) instruments, using tetramethylsilane as an internal standard. Infrared spectra were measured with a Perkin-Elmer Model 257 instrument; samples were prepared in the form of pressed KBr disks. Mass spectra (70 eV) were measured on a AEI-MS-902 spectrometer at the Research Triangle Institute Center for Mass Spectrometry (Dr. D. Rosenthal). Microanalyses were carried out by Micro-Tech Laboratories, Skokie, Ill.

Method B (Alkylation of 2a). Dimethyldiphenylhydantil (2b).—To a vigorously stirred suspension of 4.0 g of diphenylhydantil (**2a**)[2] and 12.0 g of anhydrous potassium carbonate (powder) in 80 ml of DMF at 47–50° (oil bath) was added over 15 min a solution of 12 ml of dimethyl sulfate in 40 ml of DMF. After addition was complete, the mixture (milky suspension) was stirred vigorously for 25 min, then diluted with 400 ml of water (final pH was 10–12), and stirring was continued for another 10 min. The white precipitate was filtered off, washed with two 40-ml portions of 0.2% sodium hydroxide and then successively with water, methanol, and ether: yield 4.1 g. The sample was recrystallized by solution in 800 ml of boiling acetic acid and addition of an equal volume of water: yield 3.5 g; mp 340°; ir 3300 (m), 1785 (s), 1710 (s), 1465 (m) and 1450 (m) (doublet), and 1400 cm^{-1} (m); uv $\lambda^{MeOH}_{inflection}$ 215 mμ (ε 16,700); mass spectrum, *m/e* (relative intensity) 378 (0.56), 190 (56), 189 (100), 105 (15), 104 (94), 103 (20), and 77 (24); nmr, A-60 [TFA, TMS (see text)], HA-100 [DMSO-d_6, TMS δ 2.54 (s, three protons, NCH_3), 7.16–7.32 (m, three protons, aromatic H, 7.36–7.52 (m, two protons, aromatic H), 9.38 (s, one proton, NH)].

Diethyldiphenylhydantil (2c).—Alkylation of **2a** (2.0 g) in potassium carbonate–DMF mixture (6.0 g in 40 ml) by ethyl iodide (2.3 g in 20 ml of DMF) as described for **2b** gave 1.8 g of crude **2c**, which was recrystallized from acetic acid–water (by addition of equal volume of water to 375 ml of acetic acid) to give pure **2c**: yield 1.6 g; mp 326–328°; ir 3310 (s), 1780 (s), 1710–1700 (s), 1460 and 1450 (m) (doublet) and 1430 cm^{-1} (m); uv $\lambda^{MeOH}_{inflection}$ 215 mμ (ε 16,700); mass spectrum, *m/e* (relative intensity) 406 (0.11), 204 (56), 203 (100), 105 (14), 104 (100), and 77 (20); nmr, A-60 [TFA, TMS δ 0.75 (t, J = 7.5, three protons, CH_3), 3.38 (q, J = 7.5, two protons, CH_2, 7.35–7.63 (m, three protons, aromatic H), 7.71–7.97 (m, two protons, aromatic H), 8.86 (s, one proton, NH)], HA-100 [DMSO-d_6, TMS (sample was only slightly soluble; TMS side band and DMSO water peak interfered with integration of the resonances of the $-NCH_2CH_3$ group) δ 0.58 (t, J = 8, CH_3), 3.02 (q, J = 8, CH_2), 7.18–7.32 (m, three protons, aromatic H), 7.50–7.64 (m, two protons, aromatic H), 9.34 (s, one proton, NH)].

Anal. Calcd for $C_{22}H_{22}N_4O_4$ (406.4): C, 65.01; H, 5.46; N, 13.79. Found: C, 64.84; H, 5.42; N, 13.79.

Method C (Autoxidation in Alkaline Solution).—A solution of 0.5 g of Nuvarone (**3**) in 10 ml of absolute methanol was treated with 200 mg of sodium borohydride, and the resulting solution was stirred at ~25° for 65 hr. The precipitate was filtered off and was washed with absolute methanol, then ether, giving **2b** (266 mg). A similar reaction of Peganone (**5**, 0.5 g) using the same quantities of reagents (by weight) gave **2c** (160 mg).

Cleavage of Dimethyldiphenylhydantil (2b) by Sodium–Ammonia–*t*-BuOH.—To a stirred suspension of 378 mg (1.0 mmol) of **2b** in ~35 ml of ammonia and 5 ml of *t*-butyl alcohol was added 92 mg (4.0 g-atoms) of sodium in small pieces over a period of 2 min. The blue color was rapidly discharged, fading a few seconds after the last addition of metal to a canary yellow. The yellow color was immediately discharged with solid ammonium chloride, and the ammonia was evaporated under a stream of nitrogen. Remaining liquid was stripped *in vacuo;* the residue was suspended in ~25 ml of water; and the pH was lowered to ~2. After 1–2 hr, the solid (294 mg) was filtered off; tlc (9:1:1, PMA)[10] indicated one zone (note: **3** and **4** have same R_f in this solvent system); ir and nmr confirmed the presence of **3** and **4**; relative intensities (nmr) indicated the ratio of **3**:**4** to be about 2.5:1.

In a separate experiment, a sample of the cleavage products (299 mg, mixture of **3** and **4** as confirmed by ir) was rubbed under small portions of ether. Ether-insoluble material (208 mg) was recrystallized from ~8 ml of ethanol to give **4** (72 mg, mp 257–261.5°), which was identical with authentic **4** as regards mixture melting point and ir. The combined, filtered ether extract was evaporated and the residue was recrystallized from 2 ml of ethanol (4°) to give 32 mg of pure **3**, mp 163–166°, identical with authentic **3**, mp 164–166°, as regards mixture melting point and ir.

In the absence of alcohol donor, the crude product (236 mg) was indicated by ir and tlc to be a mixture of **3** and **4**; fractionation gave **4** (68 mg, mp 238–252°) and **3** (87 mg, mp 159–166°), each of which was confirmed by ir spectra.

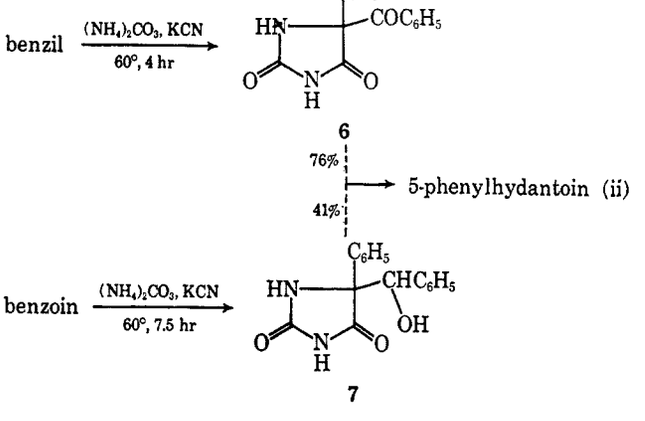
When a reduction was conducted using 1.0 mmol of **2b** in 35 ml of ammonia containing 8.0 mmol of ammonium chloride as donor, approximately 8.0 g-atoms of sodium metal was rapidly consumed before hydrogen evolution ceased and before **2b** commenced to dissolve; a total of about 10 mmol of sodium was added. The crude product (240 mg) was freed from **2b** by solution in hot ethanol; the filtered alcohol solution was stripped; and the residue was fractionated to give 66 mg of **4** and 20 mg of **3**.

3-Methyl-4-phenylimidazol-2-one (4).—To a magnetically stirred solution of Nuvarone (**3**, 570 mg, 3.0 mmol) in 35 ml of ammonia and 5 ml of *t*-butyl alcohol was added sodium metal (138 mg, 6.0 g-atoms) over *ca.* 6 min; the blue color faded (~5 min after last addition) to canary yellow. The yellow color was discharged with solid ammonium chloride, the ammonia was evaporated under a stream of nitrogen, and the residual alcoholic suspension (ammonia free) was diluted with 25 ml of water. The pH was lowered to 2, the suspension was chilled, and the solid (389 mg) was filtered off and recrystallized from about 35 ml of ethanol giving **4** (240 mg), mp 267.5–269° uncor (lit.[9] mp 275–278°). The sample was identical with **4** (our mp 266.5–268° uncor) prepared by $LiAlH_4$ reduction[9] as regards mixture melting point and ir spectra: ir 1697 and 1682 cm^{-1} (doublet); mass spectrum 174 (M^+); uv $\lambda^{pH\,7}_{max}$ 281 mμ (ε 14,700); $\lambda^{pH\,7}_{inflection}$ 213 (12,100); nmr (TFA) δ 3.58 (s, three protons, NCH_3), 6.72 (s, one proton, vinyl H), 7.42 (s, five proton, aromatic H).

3-Methyl-5-benzyl-5-phenylhydantoin.—A mixture of 0.5 g (1.9 mmol) of 5-benzyl-5-phenylhydantoin[11] and 1.1 g (8.0 mmol) of powdered, anhydrous potassium carbonate in 10 ml of DMF was treated with 280 mg (2.0 mmol) of methyl iodide; the suspension was stirred vigorously (magnetically) for 30 min, and diluted with 50 ml of water (final pH 10–11); and stirring was continued for 10 min. Filtration of the precipitate and washing with 20 ml of 5% sodium hydroxide and then water gave 487 mg of solid (one zone, tlc), which was recrystallized from absolute ethanol to give 3-methyl-5-benzyl-5-phenylhydantoin (382 mg): mp 208–209°; ir KBr disk 3250 (m), 1785 and 1770 (m) (doublet), 1725 and 1705 cm^{-1} (s) (doublet); ir $CHCl_3$ (5%) 3450 (w), 3250 (w), 1780 (m), and 1720 cm^{-1} (s).

Anal. Calcd for $C_{17}H_{16}N_2O_2$ (280.3): C, 72.84; H, 5.75; N, 9.99. Found: C, 72.74; H, 5.82; N, 9.94.

Attempted Synthesis of Diphenylhydantil (2a).—An attempt at unambiguous synthesis of **2a** was thwarted by the labilities shown by benzil and benzoin (or by the lability of **6** and/or **7**) under mild Bucherer–Berg conditions. Attempted synthesis of intermediates **6** and **7** led, in both cases, to 5-phenylhydantoin (ii).[12] Small quantities of **2a** were formed in these reactions when more forcing conditions were employed; however, production of **2a** in these cases is probably due to autoxidative dimerization of 5-phenylhydantoin (ii) in the alkaline medium. A related example, where **2a** and 5-phenylhydantoin (ii) are formed, is during the Bucherer–Berg reaction of α-(4-morpholinyl)propiophenone.[13]



A. Bucherer–Berg Reaction of Benzil.—By employing the Goodson procedure (method A)[11] and by adjusting the ratios according to the suggestion of Makoto,[14] reaction of benzil

(11) L. H. Goodson, I. L. Honigberg, J. J. Lehman, and W. H. Burton, *J. Org. Chem.*, **25** 1920 (1960), and references therein.

(12) The isolation of ii corroborates earlier work by R. A. Jesus [*Quimica* (Mex.), **2**, 8 (1944); *Chem. Abstr.*, **38**, 5214 (1944)], whose reaction conditions were not described in the *Chemical Abstracts* article.

(13) (a) H. R. Henze and W. C. Craig, *J. Org. Chem.*, **10**, 2 (1945); (b) W. C. Craig and H. R. Henze, *ibid*, **10**, 10 (1945).

(14) A. Makoto, *Chem. Abstr.*, **69**, 282 (1968).

(2.1 g), ammonium carbonate (2.0 g), potassium cyanide (0.72 g in 5 ml of water), and 60% aqueous ethanol (35 ml) (reaction conditions—4 hr at 60°, 0.5 hr at 85°) gave at the expected point in the procedure 1.33 g (mp 181–187.5°, one zone on tlc) of crude 5-phenylhydantoin, whose ir accorded with pure material (our melting point of pure material was 186–187.5°).

B. Bucherer–Berg Reaction of Benzoin.—Employing benzoin (2.0 g) and prorated quantities of reactants as described above for benzil, there was obtained after 7.5 hr at 60° (then 0.5 hr at 85°) 1.72 g of crude solid (tlc two zones), which was separated by partitioning between ether and 2% alkali into benzoin (793 mg) and 5-phenylhydantoin (676 mg, mp 185–187.5°).

Registry No.—2a, 18749-95-6; 2b, 18744-13-3; 2c, 18749-96-7; 3-methyl-5-benzyl-5-phenylhydantoin, 4927-56-4.

Acknowledgments.—We wish to thank Dr. Thomas C. Butler, who supported this work and kindly provided several of the samples for the nmr study. We are indebted to Dr. C. G. Moreland (North Carolina State University) and to Mr. C. Fenske and J. Younger (Research Triangle Institute), who kindly measured nmr spectra.

Additions of Sulfenes to 1-Diethylaminopropyne

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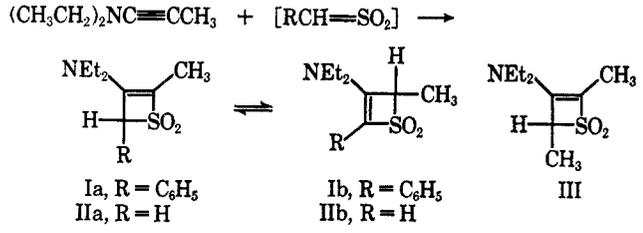
Received August 26, 1968

We wish to report the syntheses of three derivatives of 3-diethylaminothiete 1,1-dioxide from the addition of *in situ* generated sulfenes[1] to an ynamine. 3-Dialkylaminothiete 1,1-dioxides have been previously synthesized by sulfene cycloaddition to ketene O,N- and N,N-acetals.[2] Recently there have been three reports of thiete 1,1-dioxide syntheses by sulfene additions to a triple bond.[3]



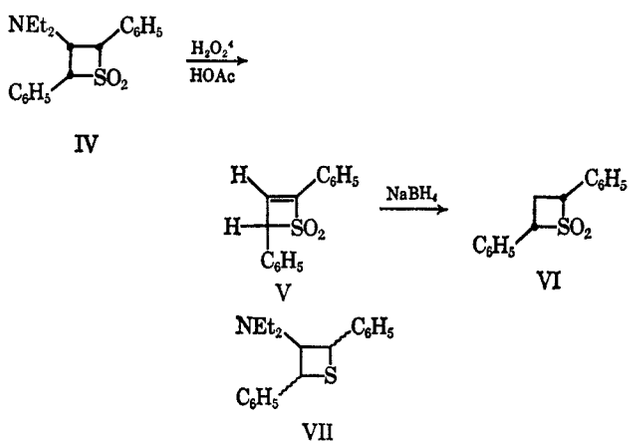
Ia, R = C_6H_5 Ib, R = C_6H_5 III
IIa, R = H IIb, R = H

Tautomeric mixtures of 2(4)-methyl-4(2)-phenyl-3-diethylaminothiete 1, 1-dioxides (Ia and Ib) and 2(4)-methyl-3-diethylaminothiete 1,1-dioxides (IIa and IIb), as well as 2,4-dimethyl-3-diethylaminothiete 1,1-dioxide (III) were obtained from the reactions of 1-diethylaminopropyne with the sulfenes generated *in situ* from toluene-α-sulfonyl chloride, methanesulfonyl chloride, and ethanesulfonyl chloride, respectively. Only the mixture of Ia and Ib has been successfully crystallized and separated into its tautomers; II and III are dark oils which have resisted all attempted methods of purification but whose spectral properties allow them to be easily characterized.

Attempted reductions of the carbon–carbon double bond in I, II and III with sodium borohydride were unsuccessful; only the starting materials could be recovered. Since it has been shown that a sodium borohydride reduction works on the thiete 1,1-dioxide ring system,[4] we assumed that the diethylamino group was in some way hindering the attempted reductions.

In an effort to test our hypothesis, 2,4-diphenylthiete 1,1-dioxide (V) was produced by oxidative deamination[5] of 2,4-diphenyl-3-diethylaminothietane 1,1-dioxide (IV) synthesized by the addition of *in situ* generated phenylsulfene to 1-diethylamino-2-phenylethene.[6] Indeed, sodium borohydride reduction of V proceeded smoothly to afford *cis*-2,4-diphenylthietane 1,1-dioxide (VI).[7]

Lithium aluminum hydride reduction of IV was attempted in an effort to produce the corresponding thietane (VII).[8] The reduction afforded a complex mixture from which only diethylamine has been identified. This is in accord with the implied assumption of Wells and Abbott[9] that the α proton on 2-phenyl-substituted thietane 1,1-dioxides is too acidic for hydride reduction of the sulfone. The failure of lithium aluminum hy-



(1) For a review of sulfenes, see G. Optiz, *Angew. Chem. Intern. Ed. Engl.*, **6**, 107 (1967).

(2) (a) R. H. Hasek, P. G. Gott, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **30**, 1495 (1965); (b) G. Opitz and H. Schempp, *Ann*, **684**, 103 (1965).

(3) Shortly after we submitted this Note we became aware of reports of three other groups who had independently performed additions of sulfenes to ynamines: A. M. Hamid and S. Trippet [*J. Chem. Soc., C*, 1612 (1968)] reported the addition of phenylsulfene to diethylphenylethynylamine. M. E. Kuehne and P. J. Sheeran [paper 0–74, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968] reported the formation of a four-membered ring from the condensation of a sulfene with an ynamine. W. E. Truce, R. H. Bavry, and P. S. Bailey, Jr. [*Tetrahedron Lett.*, 5651 (1968)] reported the addition of phenylsulfene to 1-diethylaminopropyne.

(4) D. C. Dittmer and M. E. Christy, *J. Amer. Chem. Soc.*, **84**, 399 (1962).

(5). Method of L. A. Paquette and M. Rosen, *J. Org. Chem.*, **33**, 2130 (1968).

(6) Synthesized from the method of C. Mannich and H. Davidson, *Ber.*, **69**, 2106 (1936).

(7) Previously synthesized *via* another route by R. M. Dodson and G. Klose, *Chem. Ind.* (London), 450 (1963).

(8) (a) F. G. Bordwell and W. H. McKellin [*J. Amer. Chem. Soc.*, **73**, 2251 (1951)] reported the reduction of thietane 1,1-dioxide to thietane with lithium aluminum hydride. (b) G. Opitz, H. Schempp, and H. Adolph [*Ann.*, **684**, 92 (1965)] reported the lithium aluminum hydride reduction of 2-propyl-3-morpholino-1,1-dioxide to the corresponding thietane in 51% yield.

(9) J. N. Wells and F. S. Abbott [*J. Med. Chem.*, **9**, 489 (1966)] have suggested only that the 2-phenyls seem to hinder the hydride reduction.