Considering the *trans* form of I–XI, and in support of what appears to be a stereospecificity of the reaction under the conditions applied by us, it is very likely that the *trans* isomer predominates in the 35:65 mixture found for XII.

Experimental Section

Starting Materials.—A 53.5% NaH suspension in mineral oil was used after the oil was removed by repeated washing with petroleum ether (bp 30–60°) and decanting. The aldehydes were freshly purified. The solvents were dry. The diethyl ethylsulfonylmethylphosphonate was prepared by the Arbuzov, *et al.*,[8] method and had bp 121–122° (0.04 mm) [lit.[8] bp 194° (4.5 mm)].

General Procedure.—To a suspension of 0.22 mol of NaH in 250–500 cc of solvent was added slowly 0.2 mol of diethyl ethylsulfonylmethylphosphonate over a period of *ca.* 20 min while stirring at 25–35°. The reaction mixture was stirred for additional 30 min at *ca.* 25° to allow completion of the H_2 evolution. A solution of 0.22 mol of the aldehyde in 30–50 cc of solvent was added dropwise to the reaction suspension over a period of 20–50 min while stirring at 25–35°. The suspension became thinner and a new, gummy solid [$NaOP(O)(OEt)_2$] started to precipitate. After an additional 50–60 min stirring at 20–35° the reaction was complete. The liquid phase was separated by decantation or filtration. In the cases where the product was soluble in the reaction solvent (products I, V, VI, VII, IX, XI, and XII) the solution was washed with water, dried and worked up to obtain the product. The products II and III were recovered by filtration of the reaction mixture and by washing the filter cake with water. In the remaining three cases, the products (*i.e.*, IV, VIII, and X) were partially soluble in the solvent and both the filter cake and the liquid phase were worked up for recovery of the product. Purification was achieved by distillation as indicated for each product in Table I.

Following are three examples for this general procedure, *i.e.*, the preparation of I, III, and XII.

Ethyl Styryl Sulfone (I).—To a stirred suspension of 5.3 g (0.22 mol) of NaH in 250 cc of $MeOCH_2CH_2OMe$ was added a solution of 49.9 g (0.2 mol) of diethyl ethylsulfonylmethylphosphonate in 50 cc of $MeOCH_2CH_2OMe$ over a period of 15 min at 25–30°. After an additional stirring for 20 min at 20–25°, the solution of 23.3 g (0.22 mol) of freshly distilled PhCHO in 30 cc of $MeOCH_2CH_2OMe$ was added in 25 min at 25–34° using cooling with ice-water when required. The reaction mixture was stirred for additional 25 min at room temperature and the liquid phase was separated by decantation from the gummy solid. The solution was evaporated to dryness *in vacuo* to obtain 38.3 g (98%) of a solid residue, mp 62–64°. It was recrystallized from EtOEt to recover 33 g (84%) of the *trans* isomer (see Table II), mp 66–67° (lit.[7] mp 66–67°).

4-Acetamidostyryl Ethyl Sulfone (III).—To the stirred suspension of the sodium salt of diethyl ethylsulfonylmethylphosphonate in 500 cc of EtOEt, prepared (as described above for I) from 6.2 g (0.256 mol) of NaH and 61.5 g (0.25 mol) of diethyl ethylsulfonylmethylphosphonate, was added 40.8 g (0.25 mol) of *p*-acetamidobenzaldehyde in 15 min while refluxing. After an additional refluxing for 1 hr the reaction mixture was filtered; the filter cake was triturated with 2 × 500 cc of H_2O and recrystallized from acetone to obtain 60.5 g (96%) of the *trans* isomer (see Table II), mp 203–204°.

Ethyl 1-(4-Methylthio)butenyl Sulfone (XII).—To the stirred suspension of the sodium salt of diethyl ethylsulfonylmethylphosphonate in 360 cc of EtOEt, prepared from 6.0 g (0.25 mol) of NaH and 57.6 g (0.24 mol) of diethyl ethylsulfonylmethylphosphonate, was added the solution of 25.0 g (0.24 mol) of 3-methylmercaptopropionaldehyde in 30 cc of EtOEt in 35 min at 25–35° using cooling by ice-water as required. After an additional 15 min stirring at room temperature the liquid was decanted from the gummy solid, washed with water, dried, and fractionated to obtain 34.7 g (75%) of the product, bp 120–122° (0.05 mm), n^{25}_D 1.5221. Its nmr spectrum established it as a 35:65 mixture of the two stereoisomers but did not prove which isomer is predominant (see Table II).

Nmr Studies.—The nmr spectra were recorded with a Varian DP-60 spectrometer with TMS as internal standard. The compounds were studied as 20% solutions in $CDCl_3$, CCl_4, acetone, DMSO or mixtures of these, and spectra were calibrated by the side-band method. The vinyl protons gave in most cases two doublets (AB system), or singlets in cases where their chemical shifts were identical. The doublet centers reported are the observed values rather than the corrected chemical shifts.

The coupling constant J_{AB} of 14.5–15.7[11a] cycles, the doublets for –CH=CH–, the single triplet for $-CH_3$, and the single quartet[11b] for $-CH_2-$ of $EtSO_2-$ of I–VI, VIII, and XI unequivocally prove that there is only the *trans* isomer present in these products. In the case of VII, IX, and X we also have one isomer but can not ascertain that it is *trans*. The two triplets for CH_3 in $EtSO_2-$, the two singlets for CH_3 in CH_3S-, and the two singlets for $-CH_2CH_2S-$ are criteria[11b] for the 35:65 mixture of the two isomers of XII.

Registry No.—I (*trans*), 18723-83-6; II (*trans*), 18723-84-7; III (*trans*), 18723-85-8; IV (*trans*), 18723-86-9; V (*trans*), 18723-87-0; VI (*trans*), 18723-88-1; VII, 18723-89-2; VIII (*trans*), 18723-90-5; IX, 18723-91-6; X, 18723-92-7; XI (*trans*), 18723-93-8; XII (*cis*), 18723-94-9; XII (*trans*), 18723-95-0.

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[11] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Pergamon Press, New York, N. Y., 1966: (a) p 714; (b) p 739.

The Preparation and Electronic Spectra of *trans*-1,2-Vinylenebis(di-*n*-butylphosphine) and Its Monoxide

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In a previous report from this laboratory,[1] the single peak above 220 mμ in the ultraviolet spectra of vinylphosphines was assigned to an electron-transfer type of transition, in which an electron is removed from the nonbonded orbital on phosphorus and transferred to the empty π* orbital of the vinyl group. Thus the excited state contains a negatively charged vinyl group. In the present study, *trans*-1,2-vinylenebis(di-*n*-butylphosphine) (**1**) has been prepared for the first time and its ultraviolet spectrum obtained. It is observed that the single peak above 200 mμ is significantly red shifted from the peak found in the spectrum of di-*n*-butylvinylphosphine (see Table I). This lowering of the transi-

TABLE I

ULTRAVIOLET SPECTROSCOPIC DATA

No.	Compound[a]	Solvent[b]	λ_{max},[c] mμ ($\epsilon_{max} \times 10^{-3}$)
1	$(n-C_4H_9)_2PCH=CHP(n-C_4H_9)_2$	I	263 (7.52)
	$(n-C_4H_9)_2PCH=CHP(n-C_4H_9)_2$	M	263 (6.60)
2	$(n-C_4H_9)_2PCH=CHP(O)(n-C_4H_9)_2$	H	266 (6.14)
	$(n-C_4H_9)_2PCH=CHP(O)(n-C_4H_9)_2$	M	273 (5.15)
3	$(n-C_4H_9)_2P(O)CH=CHP(O)(n-C_4H_9)_2$	M	*Ca.* 200[d]
4	$(n-C_4H_9)_2P(C_2H_3)$[e]	I	246 (2.60)
	$(n-C_4H_9)_2P(C_2H_3)$[e]	M	245 (2.63)

[a] All vinylene compounds have the *trans* configuration. [b] Isooctane (I), methanol (M), hexane (H). [c] Due to the broadness of the peak near the maximum, λ_{max} is reported only to the nearest millimicron. [d] Region of inflection. [e] See ref 1.

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[1] M. A. Weiner and G. Pasternack, *J. Org. Chem.*, **32**, 3707 (1967).

tion energy, upon substitution of a second phosphino group, may be attributed to the ability of the second phosphino group to stabilize the electron-transfer excited state of the $R_2PCH{=}CH-$ chromophore by withdrawal of charge from the negatively charged vinyl group into the vacant d orbitals of phosphorus. It is thus suggested that the transition mechanism in effect involves the action of one trivalent phosphorus atom as an electron donor and the other phosphorus atom an electron acceptor. The possibility of electron withdrawal from a negatively charged vinyl group by trivalent phosphorus has been suggested by Peterson[2] to account for the Michael-type addition reactions of diphenylvinylphosphine and di-*n*-butylvinylphosphine with *n*-butyllithium. He has attributed the apparent activating effect of the phosphino group to the ability of trivalent phosphorus to stabilize the transition state by withdrawing negative charge from the α carbon into its vacant d orbitals.

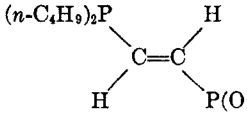
An alternative explanation is that the band observed in the spectra of vinylphosphines is actually due to an ethylenic $\pi \rightarrow \pi^*$ transition, red shifted by a conjugative interaction between the nonbonded orbital on phosphorus and the π orbitals of the vinyl group. The effect of the nonbonded orbital on the second phosphino group would then merely be to reinforce the effect of the first, leading to a further bathochromic shift. This suggestion is analogous to that proposed by Schindlbauer[3] in comparing the spectra of triphenylphosphine and 1,4-phenylenebis(diphenylphosphine). However, this explanation is inconsistent with the observation that the single transition found in the spectrum of *trans*-1,2-vinylenebis(di-*n*-butylphosphine) monoxide (**2**), in which one of the lone pairs of electrons has now been coordinated, is at an even lower energy than the transition observed for **1**. On the other hand (assuming the same transition mechanism obtains for both **1** and its monoxide) the electron-transfer mechanism would account for this observation, since the phosphinyl group $[R_2P(O)-]$ would be expected to provide a somewhat greater stabilization of the electron-transfer excited state by electron withdrawal. The greater electron-withdrawing ability of a phosphinyl group over a phosphino group has been documented.[4] Moreover the increased electron-withdrawing power of the hydrogen-bonded phosphinyl group would account for the observed red shift upon substituting ethanol for the hydrocarbon solvent.

The necessity of the lone pair of electrons to the observed transition is demonstrated by the effective disappearance of any maximum above 200 mμ in the spectrum of the dioxide of **1**. The same result was obtained upon oxidation of the vinylphosphines to the corresponding oxides.[1]

Compound **1** was prepared by the reaction between lithium di-*n*-butylphosphide in tetrahydrofuran and *trans*-1,2-dichloroethylene. The compound *trans*-1,2-vinylenebis(diphenylphosphine) had previously been prepared from lithium diphenylphosphide and *trans*-1,2-dichloroethylene.[5] However, in this study, preliminary experiments yielded a product contaminated with an impurity, presumably tetra-*n*-butylbiphosphine, which was quite difficult to remove by distillation. The reaction conditions finally employed led to a product which was isolated in only 25% yield but contained <1% tetra-*n*-butylbiphosphine (vpc analysis). The compound was identified on the basis of its elemental analysis and proton nmr spectrum and by the product of its reactions with methyl iodide and hydrogen peroxide (*vide infra*). The compound consisted of only one isomer (vpc analysis) which was assigned the *trans* configuration on the basis of its infrared spectrum and by analogy with the results obtained in the preparation of *trans*-1,2-vinylenebis(diphenylphosphine). The infrared spectrum of **1** contains a strong band at 965 cm^{-1}, diagnostic for the *trans* $-CH{=}CH-$ group,[5,6] and exhibits no band at 720 cm^{-1} (the latter band apparently is diagnostic for the *cis* $-CH{=}CH-$ structure[5,7]).

Compound **2** was prepared by the addition reaction of di-*n*-butylphosphine with di-*n*-butylethynylphosphine oxide, as well as by the reaction of di-*n*-butylphosphine oxide with di-*n*-butylethynylphosphine (eq 1 and 2).

$$(n\text{-}C_4H_9)_2P(O)C{\equiv}CH + (n\text{-}C_4H_9)_2PH \xrightarrow{\Delta}$$



2 (1)

$$(n\text{-}C_4H_9)_2PC{\equiv}CH + (n\text{-}C_4H_9)_2P(O)H \xrightarrow[\Delta]{\text{AIBN}} \mathbf{2} \qquad (2)$$

Although there have been several reports recently on the preparation of vinylene derivatives of the group IV elements[8] (as well as Sb[9]) by the hydride addition reaction, this appears to be the first report on the preparation of vinylene derivatives of phosphorus by this reaction. The fact that **2** can be prepared by either of these reactions (eq 1 and 2) suggests that the hydride addition reaction may be a general route to the preparation of various vinylene derivatives of phosphorus.

The di-*n*-butylphosphine addition (eq 1) appeared to proceed vigorously without the aid of a catalyst at 80°, the temperature at which the components of the reaction mixture formed a homogeneous phase. The di-*n*-butylphosphine oxide addition (eq 2) appeared to proceed more slowly at 80–110° in the presence of a

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(2) (a) D. J. Peterson, *ibid.*, **31**, 950 (1966); (b) D. J. Peterson and H. R. Hays, *ibid.*, **30**, 1939 (1965).

(3) (a) H. Zorn, H. Schindlbauer, and D. Hammer, *Monatsh. Chem.*, **98**, 731 (1967); (b) H. Schindlbauer and V. Hilzensauer, *ibid.*, **98**, 1196 (1967).

(4) (a) G. P. Shiemenz, *Angew. Chem.*, **78**, 145, 605, 777 (1966); (b) H. Schindlbauer, *Chem. Ber.*, **100**, 3432 (1967).

(5) A. M. Aguiar and D. J. Daigle, *J. Amer. Chem. Soc.*, **86**, 2299 (1964).

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958, pp 45–48.

(7) The reaction between lithium di-*n*-butylphosphide and *cis*-1,2-dichloroethylene gives a mixture of *cis*- and *trans*-1,2-vinylenebis(di-*n*-butylphosphine). The infrared spectrum of a distillation fraction with a *cis*:*trans* ratio of 7:3 (vpc analysis) contained a band at 720 cm^{-1}, and a band at 965 cm^{-1} the relative intensity of which was greatly reduced from the corresponding band in the spectrum of **1**. Significantly the ultraviolet spectrum of this mixture had the same λ_{max} as the spectrum of **1**.

(8) (a) A. N. Nesmeyanov and A. E. Borisov, *Proc. Acad. Sci. USSR, Chem. Sect.*, **174**, 424 (1967); (b) C. S. Kraihanzel and M. L. Losee, *J. Organometal. Chem.*, **10**, 427 (1967).

(9) (a) A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 749 (1965); (b) A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, *Proc. Acad. Sci. USSR, Chem. Sect.*, **172**, 172 (1967).

catalyst [in this study, the free-radical catalyst, azobis(isobutyronitrile), was used]. The yields from the two reactions were almost the same (*ca.* 20%). The low yields were caused by the formation of large amounts of tarry material during the reactions. Since this was true with both the vigorous and the milder addition reactions, no further attempt was made to find conditions which might improve the yield.

The products of the two reactions were shown to be the same by their identical melting points and proton nmr spectra. The mixture melting point of the two products showed no depression. Oxidation of the products of the two reactions (hydrogen peroxide in acetone) gave the same dioxide **3**.

The region of vinyl hydrogen absorption in the nmr spectrum of **2** was much more complex than the same region in the spectra of the more symmetrical molecules **1** and **3**. While the spectrum of **1** (pure liquid) exhibited a set of three peaks centered at τ 3.57 (the center peak is partially resolved into two), and the spectrum of **3** ($CDCl_3$ solution) contained a triplet centered at τ 2.95, the spectrum of **2** consisted of a complex multiplet of 15 observable peaks from τ 2.15 to 4.30. Thus an unsymmetrical structure for **2** is indicated. The presence of one trivalent phosphorus per molecule of **2** was further demonstrated by the formation of a 1:1 adduct with methyl iodide. (In contrast, the reaction of **1** with methyl iodide yielded only the 2:1 adduct.) The *trans* configuration for **2** was assigned from the observation that its oxidation product, **3**, was identical with the product formed from the oxidation of **1** (identical melting point and proton nmr spectra, undepressed mixture melting point).

Experimental Section

Ultraviolet spectra were obtained on a Cary Model 14 recording spectrophotometer. The samples were prepared as previously described.[1] Infrared spectra were obtained on a Perkin-Elmer Model 621 spectrophotometer. Proton nmr spectra were recorded on Varian A-60 and A-60A instruments, using tetramethylsilane as the internal standard. The vpc analyses were carried out using a Perkin-Elmer Model 881 instrument with a flame-ionization detector and a 3% JXR on Chromosorb Q (100–120 mesh) column. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. All melting points are uncorrected.

All reactions were carried out under an atmosphere of argon or prepurified nitrogen. Ethereal solvents were freshly distilled over lithium aluminum hydride.

Di-*n*-butylphosphine was prepared, according to the procedure of Issleib,[10] by the lithium aluminum hydride reduction of tetra-*n*-butylbiphosphine disulfide.[10] Di-*n*-butylphosphine oxide was prepared, according to the procedure of Williams,[11] from diethyl phosphite and *n*-butylmagnesium bromide. Di-*n*-butylethynylphosphine[12] was prepared from ethynylmagnesium bromide and di-*n*-butylchlorophosphine. A sample of di-*n*-butylethynylphosphine was oxidized with 30% H_2O_2 in acetone to produce di-*n*-butylethynylphosphine oxide.[13]

Preparation of *trans*-1,2-Vinylenebis(di-*n*-butylphosphine) (1).—An ethereal solution of lithium di-*n*-butylphosphide was prepared, according to a procedure previously described for the preparation of lithium diethylphosphide,[14] from 59.0 g (0.40 mol) of di-*n*-butylphosphine and 390 ml of 0.97 *M* ethereal phenyllithium (0.38 mol). The ether was replaced with 100 ml of tetrahydrofuran, and the resulting solution was added dropwise to 18.6 g (0.19 mol) of *trans*-1,2-dichloroethylene in 200 ml of tetrahydrofuran. The reaction flask was cooled to −78° throughout the addition. The yellow color of the lithium reagent was immediately discharged upon addition, and a white solid separated from the solution. After the addition was complete, the contents of the flask were allowed to warm to 0°. Water was then added, the organic layer was separated from the aqueous layer and the organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent from the filtered solution, the residue was distilled using a 300 × 13 mm distilling column packed with $^3/_{16}$-in. glass helices. After a forecut of 20.0 g was collected,[15] bp 60–104° (0.05 mm), 19.2 g of a liquid was obtained, bp 104–130° (0.05 mm). This liquid was redistilled twice to yield finally 15.0 g (25%) of **1**, bp 123–125° (0.05 mm). Analysis by vpc showed the absence of any *cis* isomer and <1% of tetra-*n*-butylbiphosphine. The essential features of the proton nmr spectrum of **1** were described above. The ratio of alkyl to vinyl hydrogens was 18:1.

Anal. Calcd for $C_{18}H_{38}P_2$: C, 68.31; H, 12.10. Found: C, 68.49; H, 12.20.

Treatment of **1** with methyl iodide yielded the 2:1 adduct, mp 130–132°.

Anal. Calcd for $C_{20}H_{44}P_2I_2$: C, 40.01; H, 7.38; I, 42.28. Found: C, 39.62; H, 7.72; I, 42.43.

Oxidation of **1** with 30% H_2O_2 in acetone yielded dioxide **3**, mp 266–267°. The essential features of the proton nmr spectrum of **3** were described above. The ratio of alkyl to vinyl hydrogens was 18:1.

Anal. Calcd for $C_{18}H_{38}P_2O_2$: C, 62.04; H, 10.99; P, 17.77. Found: C, 61.82; H, 10.84; P, 17.58.

Preparation of *trans*-1,2-Vinylenebis(di-*n*-butylphosphine) Monoxide (2). A. From the Reaction of Di-*n*-butylphosphine with Di-*n*-butylethynylphosphine Oxide.—Di-*n*-butylphosphine (3.65 g, 0.025 mol) and solid di-*n*-butylethynylphosphine oxide (4.65 g, 0.025 mol) were placed in a 240 × 25 mm reaction tube and slowly heated to 80° by means of an oil bath. After *ca.* 5 min at this temperature, the components of the reaction mixture formed a clear solution, whereupon a vigorous reaction appeared to take place. The oil bath was quickly removed and the reaction mixture allowed to cool to room temperature. The contents of the reaction tube were then heated *in vacuo* at 160°, and, after 24 hr, 4.1 g of crude, solid material was collected from the wall of the tube, leaving a tarry residue at the bottom of the tube. The crude solid was placed in a sublimation apparatus and heated at 90–100° (0.02 mm) until the small amount of liquid which formed on the walls of the apparatus had disappeared. The solid was sublimed at 140° (0.02 mm), crystallized from hexane and resublimed to yield 1.8 g (22%) of **2**, mp 107–109°. The essential features of the proton nmr spectrum were described above. The ratio of alkyl to vinyl hydrogens was 18:1.

Anal. Calcd for $C_{18}H_{38}P_2O$: C, 65.03; H, 11.52; P, 18.63. Found: C, 65.32; H, 11.51; P, 18.40.

Treatment of **2** with a fourfold excess of methyl iodide yielded only the 1:1 adduct, mp 82–83°.

Anal. Calcd for $C_{19}H_{41}P_2OI$: C, 48.10; H, 8.71; I, 26.75. Found: C, 47.94; H, 8.75; I, 26.71.

Oxidation of **2** with 30% H_2O_2 in acetone yielded dioxide **3**, mp 266–267°. A mixture melting point with a sample from the oxidation of **1** was not depressed. The nmr spectrum was identical with the spectrum of **3** formed from the oxidation of **1**.

Anal. Calcd for $C_{18}H_{38}P_2O_2$: C, 62.04; H, 10.99; P, 17.77. Found: C, 61.76; H, 11.24; P, 17.99.

B. From the Reaction of Di-*n*-butylphosphine Oxide with Di-*n*-butylethynylphosphine.—Di-*n*-butylphosphine oxide (1.63 g, 0.010 mol) and di-*n*-butylethynylphosphine (1.46 g, 0.0086 mol) were placed in a reaction tube together with 0.16 g (0.010 mol) of azobis(isobutyronitrile). The contents of the tube were warmed slowly to 80° by means of an oil bath, whereupon the resulting solution began to darken. Heating was continued until the temperature of the oil bath reached 110°, and at this point the reaction mixture was allowed to cool to room temperature. The resulting product was isolated, following the procedure

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[10] K. Issleib and A. Tzschach, *Chem. Ber.*, **92**, 704 (1959).

[11] R. H. Williams and L. A. Hamilton, *J. Amer. Chem. Soc.*, **74**, 5418 (1950).

[12] W. Voskuil and J. F. Arens, *Rec. Trav. Chim. Pays-Bas*, **81**, 993 (1962).

[13] W. Voskuil, Ph.D. Thesis, Rijhsuniversiteit Utrecht, 1963. We are indebted to Dr. W. Hagens of the Rijhsuniversiteit Utrecht for sending us a copy of this procedure.

[14] K. Issleib and A. Tzschach, *Chem. Ber.*, **92**, 1118 (1959).

[15] The forecut was a mixture which appeared difficult to separate into its components by distillation. However, 7.0 g of di-*n*-butylphosphine was isolated from this mixture.

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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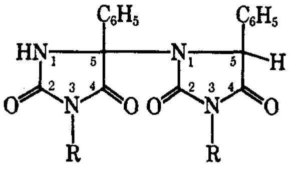
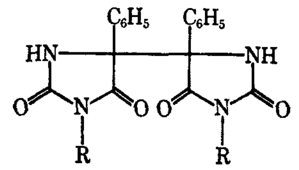
The "diphenylhydantils" are dimeric oxidation products which may be formed by either bromine oxidation of a 5-phenylhydantoin or by exposure of an alkaline solution of a 5-phenylhydantoin to air.[2-6] Gabriel's investigation[2] on 5-phenylhydantoin's dimer, $C_{18}H_{14}N_4O_4$ (**1a**, which he named "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]

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

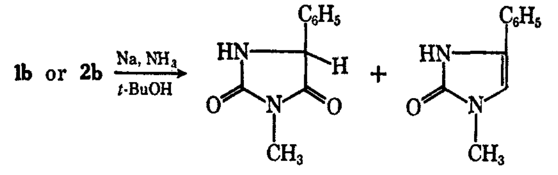


1a, R = H
b, R = CH_3
c, R = C_2H_5



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]



3 **4**

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

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[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).

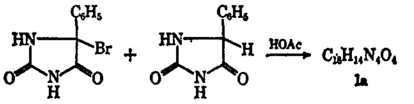
[3] A. Kjaer, *Acta Chem., Scand.*, **4**, 892 (1950).

[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).

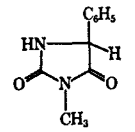
[7] In brief summary, Gabriel[2] showed that 5-bromo-5-phenylhydantoin (i) would react with 5-phenylhydantoin (ii) to give **1a**; the reaction could be



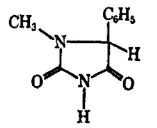
i ii **1a**

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**.

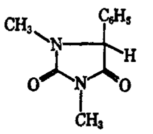
Gabriel considered structure **2a** for diphenylhydantil, but rejected this possibility in favor of one having a N_1–C_5 linkage (*i.e.*, **1a**). While iii formed dimethyldiphenylhydantil (**2b**), analogous hydantils could not be produced (Br_2, HOAc) from either iv or v; furthermore, neither iv nor 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



iii

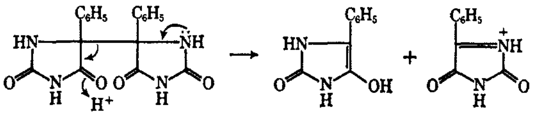


iv



v

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 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



2a

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).