

The reaction of triethyl phosphite with *o*-nitrobenzaldehyde,⁷ with benzaldehyde,⁸ and with aromatic ketones⁹ has been reported. Epoxides and 1:1 adducts (analogous to VII) have been isolated from the reaction of a phosphorus triamide with aldehydes.¹⁰

Acknowledgment.—We are grateful to Prof. P. C. Lauterbur of this department for advice on P³¹ n.m.r. spectroscopy and to Dr. E. M. Banas (American Oil Co.) and Prof. E. Eliel (University of Notre Dame) for some of the earlier H n.m.r. spectra.

(7) (a) V. A. Kukhtin and K. M. Kirillova, *J. Gen. Chem. USSR*, **31**, 2078 (1961); (b) *Zh. Obshch. Khim.*, **31**, 2226 (1961).

(8) A. Arbuzov and V. M. Zoroastrova, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 1030 (1960).

(9) A. C. Poshkus and J. E. Herweh, Abstracts, Division of Organic Chemistry 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 17-0.

(10) V. Mark, *J. Am. Chem. Soc.*, **85**, 1884 (1963).

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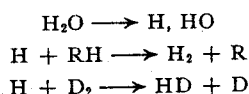
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Radical and Molecular Yields in the γ -Radiolysis of D₂O and H₂O Vapor

Sir:

Recent work^{1,2} on the γ -radiolysis of water vapor in the presence of scavengers for H and OH has led to estimates of the 100-e.v. yield $G(H)$ which are different when D₂ is used¹ from those obtained using organic scavengers.² The reactions involved are



and it is assumed that $G(\text{H}_2)$ or $G(\text{HD})$ are measures of $G(H)$. The observations² also showed the formation of H₂ with a yield of 0.5, even in the presence of benzene which should remove all H without forming H₂, and suggested that, as with liquid water, there is a yield of molecular as well as atomic hydrogen. This we have now confirmed by observations on D₂O radiolysis, and we also confirm that higher $G(D)$ are found using H₂ than using organic scavengers.

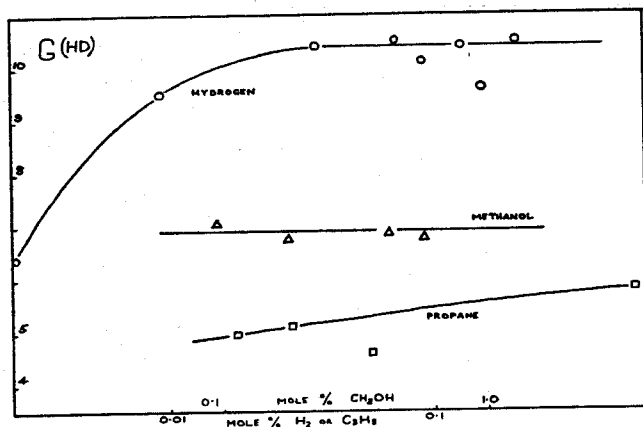


Figure 1.

The experiments were carried out as described previously² using doses of $1.5\text{--}5.5 \times 10^{19}$ e.v. delivered to the vapor at 116° and about 60-cm. pressure in a 5-l. vessel.

The values of $G(\text{HD})$ obtained with various amounts of H₂, CH₃OH, and C₃H₈ present are shown in Fig. 1.

(1) R. Firestone, *J. Am. Chem. Soc.*, **79**, 5593 (1957).

(2) J. H. Baxendale and G. P. Gilbert, *Discussions Faraday Soc.*, in press.

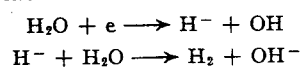
They attain limiting values of 10.5 with H₂ but appear to approach only about 7.0 with CH₃OH or C₃H₈.

Furthermore, we have observed the formation of D₂ which in the presence of the high concentrations of H₂ or C₃H₈ can only originate as molecules from D₂O. For the six experiments with H₂ present, where $G(\text{HD})$ has reached the maximum, we find $G(\text{D}_2) = 0.56 \pm 0.07$, and for the four experiments with C₃H₈ present, we observe $G(\text{D}_2) = 0.48 \pm 0.05$. Higher values, *viz.*, $G(\text{D}_2) = 0.80 \pm 0.02$, are found in the methanol experiments, but we believe the increase over 0.5 can be attributed to the reaction



occurring to a small extent.

The molecular hydrogen may be formed by an excitation process or perhaps from the ion H⁻, as proposed by Platzman³



but if this is the only source, the yield of H⁻ would need to be about twice the value he suggested.

(3) R. L. Platzman, Abstracts of the Second International Congress of Radiation Research, Harrogate, 1962, p. 128.

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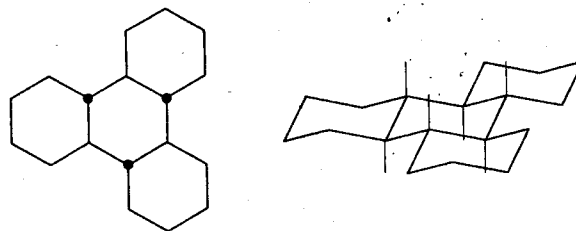
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Inclusion Compounds Containing Macromolecules

Sir:

Although several inclusion compounds have been extensively studied recently,¹ little is known about inclusion compounds containing macromolecules. Brown and White² succeeded in polymerizing 1,3-butadiene and other monomers when included in urea or thiourea; nevertheless, no direct experimental evidence as to the formation of inclusion compounds with the polymers produced has been given. Recently, Parrod and others³ verified the formation of an inclusion compound of urea with polyoxyethylene glycol, but attempts to include polyethylene and 1,4-polybutadiene into the same host structure were unsuccessful.

We have now found that several kinds of linear macromolecules such as polyethylene, *cis*-1,4 polybutadiene, *trans*-1,4 polybutadiene, and polyoxyethylene glycol give rise to very stable inclusion compounds with a host molecule of a new kind, the *trans-anti-trans-anti-trans*-perhydrotriphenylene (PHTP) (I). This com-



I a

I b

ound, recently synthesized in our Institute,⁴ has shown a very strong tendency to include, in the crys-

(1) S. M. Hagan, "Clathrate Inclusion Compounds," Reinhold Publishing Co., New York, N. Y., 1962; for detailed studies on Channel-like structures: W. Schlenk, Jr., *Fortschr. Chem. Forsch.*, **2**, 92 (1951); D. Lawton and H. M. Powell, *J. Chem. Soc.*, 2339 (1958).

(2) J. F. Brown and D. M. White, *J. Am. Chem. Soc.*, **82**, 5671 (1960); D. M. White, *ibid.*, **82**, 5678 (1960).

(3) J. Parrod and A. Kohler, *Compt. Rend.*, **246**, 1046 (1958); *J. Polymer Sci.*, **48**, 457 (1960); A. Kohler, G. Hild, and J. Parrod, *Compt. Rend.*, **265**, 2763 (1962).

(4) M. Farina, *Tetrahedron Letters*, in press.

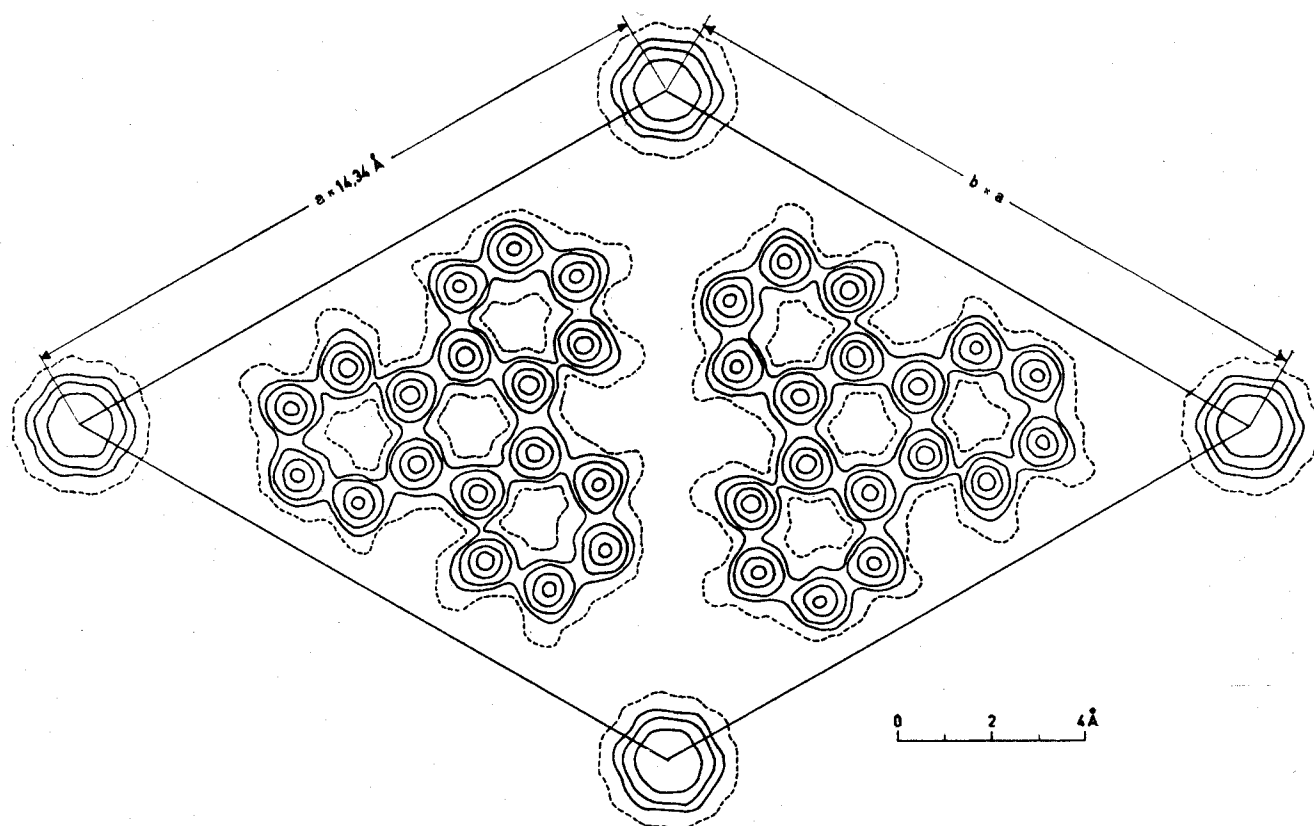


Fig. 1.—Fourier projection on (001) of the PHTP-*n*-heptane inclusion compound. Electron density levels are drawn at 1 (dashed line), 2, 3, 5, 7 $e/\text{Å}^2$.

talline state, a wide variety of compounds. Besides the above macromolecular compounds, linear nonpolymeric compounds, aliphatic hydrocarbons and halogenated hydrocarbons (*e.g.*, *n*-heptane and 1-chloropentane), mono- and dicarboxylic acids (*e.g.*, palmitic, stearic, undecilenic, adipic, and azelaic acids), alcohols (*e.g.*, cetilic alcohol), molecules with two prevailing dimensions, such as chloroform, cyclohexane, dioxane, benzene, tetralin, and decalin, and molecules with approximately spherical Van der Waals' shape, such as carbon tetrachloride, have also been found to serve as guest molecules.

The inclusion compounds have been obtained either by crystallization from a supersaturated solution, or by melting together both components, then cooling the melt.

The inclusion compounds with polyethylene and with the linear compounds of low molecular weight listed above have been found to be strictly isomorphous among themselves. The unit cell constants have practically the same values; these are $a = b = 14.34 \pm 0.07 \text{ Å}$; $c = 4.78 \pm 0.03 \text{ Å}$; $\gamma = 120^\circ$; space group (not yet unambiguously defined): $P6_3$ or $P6_3/m$; number of PHTP molecules per unit cell = 2.

The electron density projection on (001) is shown in Fig. 1 for the inclusion compound with *n*-heptane. Around the sixfold symmetry axes the electron density corresponding to the heptane molecules is clearly recognizable; their longest dimension must be parallel to the symmetry axes, and the orientation of the zig-zag planes must be statistically distributed to be in agreement with the observed hexagonal symmetry. At present, the value of the agreement factor between observed and calculated ($hk0$) structure factors is $R = 0.18$.

From the rotating crystal spectrum around the c axis obtained on the PHTP-*n*-heptane inclusion compound, in addition to the crystallographic layers with $c^* = n/c'$ a diffuse layer may be observed, which is

characterized by $c^* = 1/11.5 \text{ Å}^{-1}$. It has been attributed to the diffraction effect due to the *n*-heptane rows, 11.5 Å. being the repeat distance between two consecutive molecules in planar conformation, with faced ends at Van der Waals' contact distance; analogous conclusions may be drawn for the other inclusion compounds with linear molecules and also in some cases, as in the case of carbon tetrachloride, with nonlinear molecules. It is therefore possible to evaluate, on crystallographic grounds, the percentage weight of the included compounds; evaluated and experimental data (determined by titration or weight loss on heating at reduced pressure) have been obtained for *n*-heptane, undecilenic acid, stearic acid, chloroform, and carbon tetrachloride, and the agreement between them is within $\pm 5\%$.

A very interesting feature of these inclusion compounds is that their melting points are generally higher than the melting points of pure PHTP and of the pure included compound (see Table I); this seems to indicate a greater thermodynamic stability in the crystal state for the inclusion compound with respect to the separate compounds. An apparent exception is given by the inclusion compounds with low boiling substances; they melt at about 127° (near the melting point of pure PHTP), probably because of previous evaporation of the included molecules.

Thermal analysis of the binary system PHTP-high molecular weight polyethylene shows the existence of two eutectic points at intermediate compositions between the pure components and the inclusion compound.

The ability of PHTP to give rise to inclusion compounds with polymeric components opens a new research field in macromolecular chemistry, both on theoretical and on technological grounds. The unexpectedly high melting temperature, and the selectivity with respect to the side dimensions of the chains, sug-

TABLE I
MELTING POINTS^a OF SOME LINEAR COMPOUNDS AND OF THE
CORRESPONDING INCLUSION COMPOUNDS WITH PHTP
M.p. pure PHTP = 128°

Included compound	M.p. of guest compound, °C.	M.p. of inclusion compound, °C.
Low-molecular weight polyethylene (mol. wt. 2000)	85	165
High-molecular weight polyethylene	135	181
<i>cis</i> -1,4-Polybutadiene	<0	158
<i>trans</i> -1,4-Polybutadiene	127	183
Polyoxyethylene glycol (Carbowax 1500)	40	139
<i>n</i> -Heptane	-91	127
Palmitic acid	64	157
Stearic acid	69	158
Undecilic acid	24	148
Adipic acid	151	165
Azelaic acid	106	154
Cetyl alcohol	49	148

^a Determined by a polarizing microscope.

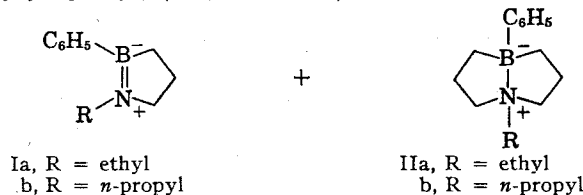
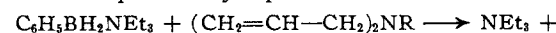
gest applications in analytical as well as in separation methods. Moreover, we think that the PHTP-polymer crystalline systems will provide new information on the conformational structure of polymers by X-ray or by infrared studies; in particular, we emphasize that any chain-chain interaction will disappear in the presence of PHTP.

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A Novel Reduction of an Allylic Carbon-Nitrogen Bond

We wish to report a novel reduction of the carbon-nitrogen bond which was discovered during investigation of the reactions between triethylaminephenylborane and diallyl alkylamines. The amineborane complexes have been recently used as hydroborating agents for reaction with allyl amines to produce new boron-nitrogen heterocyclic systems.¹⁻³ In our attempt to use this procedure to prepare bicyclic systems, it was found that refluxing a dilute toluene solution of triethylaminephenylborane with a diallyl alkylamine resulted in two products, an air-sensitive liquid and a stable solid, to which we have assigned structures I and II, respectively. Bicyclic structures such as II have not been previously reported.



Thus use of diallylethylamine resulted in a colorless liquid (Ia), b.p. 72.5–74° (1.2 mm.), in 22% yield and a solid (IIa), m.p. 72.5–73.5° (from acetone), in 7% yield. *Anal.* (Ia) Calcd. for C₁₁H₁₆BN: C, 76.33; H, 9.32; N, 8.09; B, 6.25. Found: C, 76.27; H, 9.23; N, 8.06; B, 6.30. *Anal.* (IIa) Calcd. for C₁₄H₂₂BN: C, 78.16; H, 10.31; N, 6.51; B, 5.03. Found: C, 77.87; H, 10.38; N, 6.76; B, 4.87.

- (1) R. M. Adams and F. D. Poholsky, *Inorg. Chem.*, **2**, 640 (1963).
- (2) D. C. White, *J. Am. Chem. Soc.*, **85**, 3634 (1963).
- (3) N. N. Greenwood, *et al.*, European Scientific Notes, Office of Naval Research, No. 16-3, March 23, 1962, p. 47.

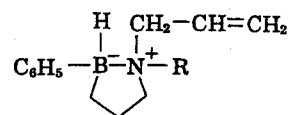
Use of diallyl-*n*-propylamine resulted in a colorless liquid (Ib), b.p. 87.5–90° (2.0 mm.), and a solid (IIb), m.p. 61–62° (from acetone), in 31 and 8% yields. *Anal.* (Ib) Calcd. for C₁₂H₁₈BN: C, 77.04; H, 9.69; N, 7.48; B, 5.78; mol. wt., 187. Found: C, 77.73; H, 9.35; N, 7.40; B, 5.62; mol. wt., 187 (mass spectrum). *Anal.* (IIb) Calcd. for C₁₆H₂₄BN: C, 78.61; H, 10.56; N, 6.11; B, 4.78; mol. wt., 229. Found: C, 78.49; H, 10.66; N, 6.27; B, 4.48; mol. wt., 239 (cryoscopic).

The mass spectrum of 1-*n*-propyl-2-phenyl-1,2-azaborolidine gave a parent ion peak at 187 mass units (m.u.). The most intense peak was at 158 m.u. corresponding to a loss of an ethyl group and consistent with the most probable mode of rupture of amines, the C–C bond β to the nitrogen atom. The intensities of the other peaks were considerably weaker, and they were found at 116 m.u. due to loss of the C₃H₇N–CH₂– group, 89 m. u., due to loss of C₃H₇NC₃H₆– group, 79, 63, 51, and 41 m. u. The last four peaks were very weak.

The infrared spectra of the products showed the absence of any olefinic or B–H units. The two 1,2-azaborolidines (Ia,b) showed strong peaks at 1512 cm.⁻¹ which have been attributed to –B=N⁺ bonds.^{2,4} The 1-aza-5-borabicyclo[3.3.0]octanes (IIa,b) showed strong bands at 1266 cm.⁻¹ which we are tentatively assigning to the –B–N⁺ coordinate bond. The boron-nitrogen bonds in diethanolamine esters of arylboronic acids and the boron-nitrogen bonds in complexes of boron halides with amine bases have been assigned to this region.^{5,6}

The boron resonance in the n.m.r. spectrum of 1-ethyl-2-phenyl-1,2-azaborolidine (Ia) was recorded at –23 and +8.9 p.p.m. for the 1-ethyl-5-phenyl-1-aza-5-borabicyclo[3.3.0]octane (IIa) relative to trimethyl borate. The p.m.r. spectrum of the former was also in accord with the structural assignment.

The bicyclic compounds are the result of intramolecular hydroboration of the two olefinic bonds by phenylborane. The 1,2-azaborolidines appear to be formed by the reduction of the allylic carbon-nitrogen bond and may be the result of the following intermediate, which apparently either does not undergo a



second hydroboration, or the rate of the second hydroboration is slow enough at the temperature of reflux (110°) so that the reduction is the predominant reaction. This reduction is somewhat analogous to hydrogenation of the benzyloxy bond in the Bergmann synthesis of polypeptides⁷ in that the groups which form relatively stable carbonium ions are easily reduced.

Acknowledgments.—We are grateful to Dr. Wallace S. Brey, Jr., of this department, for determination and interpretation of the n.m.r. spectra, to Dr. George L. K. Hunter, Citrus Experiment Station, U. S. Department of Agriculture, Winter Haven, Florida, for the mass spectral data, and to the National Lead Foundation for support of this research in the form of a fellowship.

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- (5) W. J. Dale and J. E. Rush, *J. Org. Chem.*, **27**, 2598 (1962).
- (6) N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1130 (1960).
- (7) M. Bergmann and L. Zervas, *Ber.*, **65**, 1192 (1932).

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