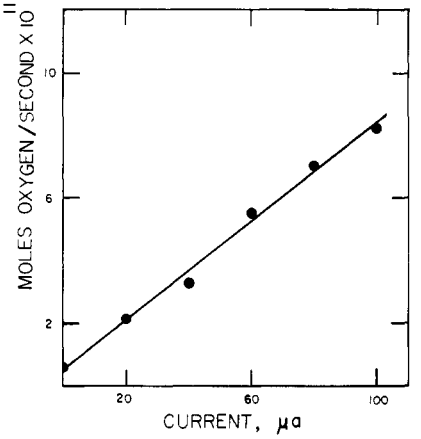

Figure 3. Oxygen flux to mass spectrometer as a function of generation current.

ganic species will have a sufficiently high volatility to be detected as they are produced during an electrochemical or a heterogeneous chemical reaction.

A detailed study of the properties of our porous electrode is given elsewhere.[2] The principal results of that study are as follows. (1) The collection efficiency of a volatile intermediate is only a weak function of the solution diffusion coefficient of the gas. (2) The electrode behaves as if about 50% of the available electrode surface exists below the visible electrode solution interface. (3) Gas transport through the electrode is principally by molecular, rather than viscous flow.

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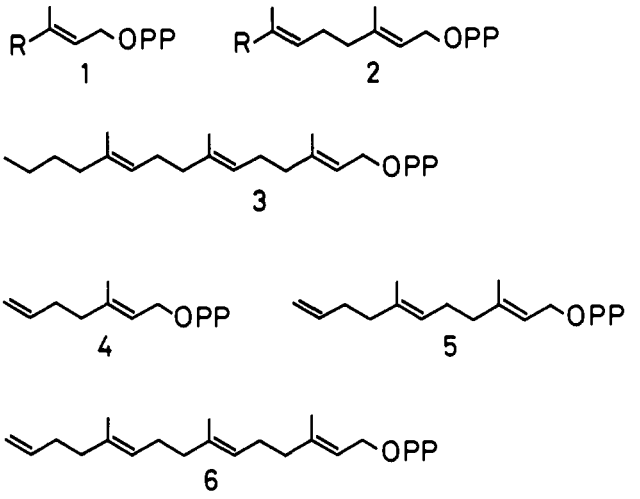
Stanley Bruckenstein,* R. Rao Gadde
Department of Chemistry, State University of New York at Buffalo Buffalo, New York 14214
Received November 4, 1970

Formation of 16,16′-Bisnorgeranylgeranyl Pyrophosphate by Farnesyl Pyrophosphate Synthetase

Sir:

During the study of substrate specificity of farnesyl pyrophosphate synthetase of pumpkin, we found that the enzymic reaction of *trans*-3-methyl-2-heptenyl pyrophosphate (**1a**, R = *n*-C_4H_9) with isopentenyl pyrophosphate proceeded to the formation of a C_{18} compound, trishomofarnesyl pyrophosphate (**3**), *via* **2a** (R = *n*-C_4H_9), and that the reaction of the higher homologs (for example, **1b**, R = *n*-C_5H_{11} and **1c**, R = *n*-C_6H_{13}) stopped at the diprenyl homolog stage to give the corresponding derivatives of type **2**.[1] Popják, *et al.*, showed that the product derived from 6,7-dihydrogeranyl pyrophosphate by the liver enzyme was 10,11-dihydrofarnesyl pyrophosphate.[2] These findings suggested that the termination of the chain elongation by the prenyltransferase was determined by the size of the alkyl group of the product. However, it is not known whether this enzyme can afford a product possessing four double bonds of the tetraprenyl type. Therefore, we examined the effect of double bonds by comparison of C_8 compound **1a** and its dehydro derivative **4**, the former capable of reacting with isopentenyl pyrophosphate to afford the C_{18} compound **3** as well as the C_{13} compound **2a**. It was expected that the introduction of the $\Delta^{6,7}$ double bond into **1a** might cause "full stop" at the stage of a C_{13} compound, **5** (which is a farnesyl analog with respect to the double bonds), if the enzyme were "coded" by the number and position of the double bonds (see Chart I).

Chart I



-OPP = $-OP_2O_6^{3-}$

A mixture of methyl *cis*- and *trans*-3-methyl-2,6-heptadienoates, obtained by the Wittig reaction of 5-hexen-2-one with diethyl methoxycarbonylmethyl phosphonate, was hydrolyzed to the free acid, from which the trans isomer was isolated by recrystallization from petroleum ether (bp 50–60°). The trans structure was supported by the nmr spectrum in which a signal for the 3-methyl group appeared at δ 2.18 ppm in carbon tetrachloride.[1] The acid, mp 16–17°, was reduced with $LiAlH_4$ to *trans*-3-methyl-2,6-heptadienol,[3] which was then phosphorylated by a previously described method.[1] The pyrophosphate ester **4** was obtained as the lithium salt and characterized by the ir absorptions at 1120, 940, and 725 cm^{-1}.[4] Farnesyl pyrophosphate synthetase purified from pig liver according to the literature[5] was used for the present study, and the enzymic reaction of the artificial substrates with [^{14}C]isopentenyl pyrophosphate was examined in the usual way.[1] The incubation mixture contained, in a final volume of 2 ml, 40 μmol of phosphate buffer, pH 7.0, 10 μmol of $MgCl_2$, 0.1 μmol of [^{14}C]isopentenyl pyrophosphate (1.2 μCi/μmol), 0.05 μmol of **1a** or **4**, and *ca.* 50 μg of the enzyme. After the incubation at 37° for 1 hr, the mixture was treated with dilute acid to hydrolyze the allylic pyrophosphates. The amounts of [^{14}C]isopentenyl pyrophosphate converted into the acid-labile allylic pyrophosphates by the condensation with **1a** and **4** were 30,900 and 34,400 dpm, respectively. The control incubations of [^{14}C]isopentenyl pyrophosphate with and without geranyl pyrophosphate were carried out, and

(1) K. Ogura, T. Nishino, T. Koyama, and S. Seto, *J. Amer. Chem. Soc.*, 92, 6036 (1970).
(2) G. Popják, P. W. Holloway, and J. M. Baron, *Biochem. J.*, 111, 325 (1969).
(3) R. Helg, F. Zobrist, A. Lauchenauer, K. Brack, A. Caliezi, D. Stauffacher, E. Zweifel, and H. Schinz, *Helv. Chim. Acta*, 39, 1269 (1956).
(4) The absorption at 725 cm^{-1} can also be taken as a characteristic band for pyrophosphate esters (T. Nishino, unpublished results).
(5) P. W. Holloway and G. Popják, *Biochem. J.*, 104, 57 (1967).

the conversions were 48,400 and 500 dpm, respectively. For the analysis of the products the reaction mixture was treated with alkaline phosphatase and the radioactive alcohols were extracted with light petroleum. Reference terpene alcohols were added to the extract, and it was subjected to radiogas chromatography. The gas chromatography[6] was carried out at a linear programmed temperature at a rate of 4°/min from 140 to 245° on a 1-m PEG 20M column. Helium gas was used as a carrier at a rate of 30 ml/min. In this condition linalool, dihydrogeraniol, geraniol, dihydronerolidol, nerolidol, *trans,trans*-dihydrofarnesol, *trans,trans*-farnesol, *all-trans*-geranyllinalool, and *all-trans*-geranylgeraniol had retention times of 3.3, 5.4, 7.0, 8.8, 10.4, 14.2, 16.2, 20.4, and 26.0 min, respectively. Radioactive peaks due to trishomogeraniol and trishomofarnesol derived from **1a** appeared at retention times of 11.5 and 21.0 min, respectively, the ratio of the intensities being 4:5. The analysis of the products from **4** also showed two components with retention times of 12.3 and 22.0 min in a ratio of 1:2. Comparison of these retention times with those for the reference prenols and their analogs indicates that these two components correspond to the C_{13} and C_{18} compounds. The radiogas chromatography on the sample obtained from the acid-treated mixture gave two major radioactive peaks at 7.1 and 16.1 min and two minor peaks at 12.3 and 22.0 min, the former two being attributable to the tertiary alcohols formed by the allylic rearrangement during the hydrolysis. The ratio of the two peaks at 7.1 and 16.1 min was also *ca.* 1:2. These results indicate that the introduction of the $\Delta^{6(7)}$ double bond has no effect on the termination of the chain elongation, but in the products derived from **4** the C_{18} compound was predominant over the C_{13} compound, suggesting that the C_{13} compound is highly reactive.

The products thus formed by the condensation of **4** with isopentenyl pyrophosphate are nor derivatives **5** and **6** of farnesyl and geranylgeranyl pyrophosphate in regard to the number and position of the double bonds. Liver farnesyl pyrophosphate synthetase, which can synthesize from its natural substrates only farnesyl pyrophosphate,[2] might have also been able to produce geranylgeranyl pyrophosphate if its binding site had been larger than it apparently is, by a space sufficient to accommodate a further *gem*-dimethyl group. Comparison of farnesyl pyrophosphate synthetase and geranylgeranyl pyrophosphate synthetase in this respect would be interesting.

Acknowledgment. We are grateful to Hoffman-La Roche, and to Takasago Perfumary Co. for their kind gifts of the terpene alcohols. A part of the expense for this research was supported by Grant-in-Aid 40702 from the Ministry of Education.

(6) A Shimadzu Radiogas chromatograph RID 2E was used.

Tokuzo Nishino, Kyozo Ogura, Shuichi Seto*
Chemical Research Institute of Non-Aqueous Solutions
Tohoku University, Sendai, Japan
Received December 2, 1970

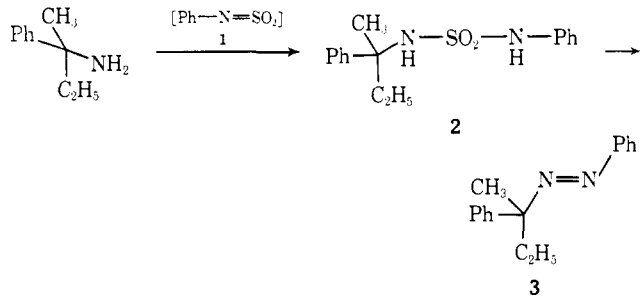
The Photolysis of Unsymmetric Azo Compounds

Sir:

Although symmetric azo compounds apparently decompose thermally by simultaneous scission of both C–N bonds,[1] recent evidence indicates that some unsymmetric azo compounds undergo thermolysis by one-bond cleavage leading to a nitrogen-containing radical.[2,3]

We present here evidence concerning the mechanism of the photoinduced decomposition of a new unsymmetric azo compound, **3**. Our observations suggest that **3** undergoes photolysis by an initial one-bond scission. We present new evidence supporting the existence of a nitrogen-containing radical intermediate.

The azo compound **3** was synthesized by the route outlined below.



The unsymmetric sulfamide **2** was prepared by trapping sulfurylaniline **1** (prepared *in situ* from the triethylammonium salt of *N*-*p*-nitrobenzenesulfonoxysulfonamide) with 2-phenyl-2-butylamine.[4] **2** was converted to **3** with NaOH and NaOCl at 45°.[5] The structure of **3** is supported by elemental analysis (*Anal.* Calcd: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.59; H, 7.69; N, 11.89) and uv (λ_{max} 416 nm (ϵ121)), ir, and nmr spectral data. Optically active **3** was obtained if the starting amine had been previously resolved with l-malic acid.[6] Thus, (−)-2-phenyl-2-butylamine ($[\alpha]_D$ −12.2° (*c* 8.78, methanol))[7] gave **3** with $[\alpha]_{589}$ +82°, $[\alpha]_{452}$ +336°, $[\alpha]_{380}$ −153° (*c* 0.14, octane); CD $\lambda([\theta]_{max})$ 416 nm, $\Delta\epsilon$ +0.34 (*c* 0.14, octane).

The following observations are important for a discussion of the mechanism of the photolysis of **3**: (1) racemization of optically active **3** accompanies photodecomposition; (2) quantum yields for disappearance of **3** are dependent on solvent viscosity; (3) *cis*-**3** can be isolated after low-temperature photolysis of *trans*-**3**.

Thus, 0.01 *M* (+)-**3** ($[\alpha]_{452}$ +336°, $[\alpha]_D$ +82°; $\Delta\epsilon$ +0.34) in hexadecane was photolyzed at 25° to 40% completion and the remaining azo compound was recovered and purified by chromatography on alumina.[8] Recovered **3** had $[\alpha]_{452}$ +253°, $[\alpha]_D$ +61°, $\Delta\epsilon$ +0.25, indicating optical activity about 74% that of the starting azo compound.[9]

Quantum yields for disappearance of **3** in four solvents are presented in Table I. Samples were irradiated simultaneously on a merry-go-round apparatus

(1) (a) S. Seltzer, *J. Amer. Chem. Soc.*, **83**, 2625 (1961); (b) S. Seltzer, *ibid.*, **85**, 14 (1963).
(2) (a) W. A. Pryor and K. Smith, *ibid.*, **92**, 5403 (1970); (b) W. A. Pryor and K. Smith, *ibid.*, **89**, 1741 (1967).
(3) S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965).
(4) W. Lwowski and E. Scheiffle, *ibid.*, **87**, 4359 (1965).
(5) R. Ohme and E. Schmitz, *Angew. Chem., Int. Ed. Engl.*, **4**, 433 (1965).
(6) D. J. Severn and E. M. Kosower, *J. Amer. Chem. Soc.*, **91**, 1710 (1969).
(7) Amine used for all experiments reported was 67% optically pure.
(8) Thin-layer, ir, uv, and nmr data showed that the recovered **3** was uncontaminated. Control experiments show that the work-up does not lead to any racemization of **3**.
(9) Identical results were obtained with more dilute solutions of **3**.