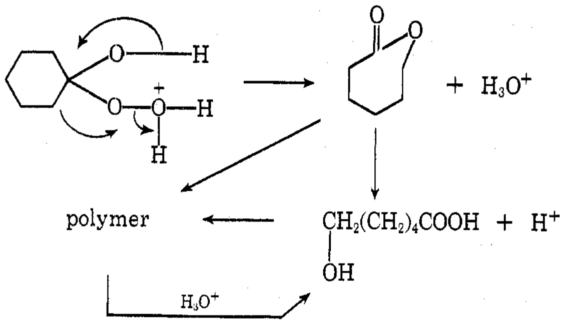
Scheme III



were chosen and an attempt was made to synthesize the diperoxides under essentially the same conditions. The results are shown in Table I. No attempt was made to maximize the yields of any but the first entry in Table I.

In conclusion and summary, the procedure given in this paper is useful for the preparation of high-purity cyclohexanone diperoxide in high yield. Furthermore, there is an indication that the diperoxide I is formed from the triperoxide IV, although one cannot discard the possibility that some of I is formed from the "open" peroxide II. The procedure is also useful for the preparation of peroxides derived from noncyclic ketones as well as cyclic ketones.

Experimental Section

Preparation of Diperoxide. Typical Procedure. Acetonitrile (25 ml) and methylene chloride (25 ml) were placed in a 300-ml round-bottom flask equipped with a stirrer and thermometer. Cyclohexanone (9.8 g, 0.1 mol) was placed in the flask. The mixture was cooled to about 5° and 8 ml of anhydrous methanesulfonic acid was added slowly (small exotherm). Hydrogen peroxide (90%, 3 ml, 0.11 mol) was then added dropwise over about a 10-min period (exothermic). The temperature was maintained at 5° during the addition and during the hold period. At the end of the hold time, 100 ml of water and 100 ml of methylene chloride were added to the reaction mixture. The contents of the flask were transferred to a separatory funnel and the organic and water layers were separated. The water layer was washed with 25 ml of methylene chloride. The methylene chloride was then separated and combined with the first cut. The methylene chloride solution was washed once more with an equal volume of water, dried over anhydrous sodium sulfate, and analyzed for percent cyclohexanone diperoxide and triperoxide by VPC using an internal standard. In some cases an aliquot of the methylene chloride was removed from the sample before it was submitted for VPC analysis and a crude yield of peroxide was obtained. In most cases the crude yield was within a few percent of the yields determined by VPC. The solid peroxide was isolated by removing most of the methylene chloride on a rotary evaporator, adding methanol, and collecting the solid by filtration.

Material Balance Experiment. Methylene chloride (250 ml) was placed in a 1-l. flask along with 250 ml of acetonitrile and cooled to about 5° in a methanol–water–ice bath. Anhydrous methanesulfonic acid (80 ml) was then added slowly (mild exotherm) such that the temperature did not rise above 10°. Hydrogen peroxide (90%, 30 ml, 1.1 mol) and cyclohexanone (98.1 ml, 1.0 mol) were then added simultaneously (slowly) to the stirred mixture by means of two addition funnels. The temperature was maintained within ±2° of 5°. Addition of cyclohexanone required about 45 min. Addition of hydrogen peroxide required about 25 min. The mixture was kept at about 5° and checked for "open" peroxide by TLC. Only a trace of "open" peroxide remained after 2 hr.

Methylene chloride (300 ml) was then added along with 200 ml of water. The mixture was transferred to a separatory funnel and shaken, and the organic and water layers were separated. The water layer was washed with 50 ml of methylene chloride and this was combined with the first cut. The methylene chloride was washed with 300 ml of saturated bicarbonate solution and dried over magnesium sulfate. An aliquot was withdrawn for VPC analysis. The crude yield of isolated dimer was 84%. By VPC the yield was 87.1% dimer and 0.1% trimer.

After filtration of the dimer, an oil was isolated (16 g, 14 wt %) which still contained some dimer–trimer (TLC). By ir, this oil appeared to be mainly a polymer of hexanolactone. (Some 6-hydroxyhexanoic acid was also present). VPC indicated that there was less than 1% cyclohexanone remaining.

VPC Assay for Dicyclohexylidene Diperoxide and Tricyclohexylidene Triperoxide. Although the peroxides are thermally unstable, they can be successfully chromatographed at temperatures below 150° using on-column injection into glass columns that have been silynized. The yields for dicyclohexylidene diperoxide and tricyclohexylidene triperoxide reported in this paper were determined on a 10 ft × 0.375 in. glass column packed with 0.1% OV-17 on glass beads 60–80 mesh. Methyl stearate was used as an internal standard.

Acknowledgment. We would like to thank Story Chemical Corp. for permission to publish this work.

Registry No.—Cyclohexanone, 108-94-1; 4-heptanone, 123-19-3; 3,3-dimethyl-2-butanone, 75-97-3; 3,3,5,5-tetramethylcyclohexanone, 14376-79-5; cyclooctanone, 502-49-8; hydrogen peroxide, 7722-84-1; acetonitrile, 75-05-8; methylene chloride, 75-09-2; methanesulfonic acid, 75-75-2.

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Synthesis and Identification by Shift Reagents of Isomeric 2-Methyl-2-*n*-propylcyclopentane-1,3-diols

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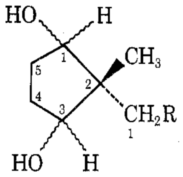
During research aimed at pinpointing the relationships between configuration and activity in meprobamate-type substances, it was necessary to obtain, as starting products, the three 2-methyl-2-*n*-propylcyclopentane-1,3-diol isomers (**4–6**). Their synthesis and structure determined by NMR spectra in the presence of Eu(DPM)$_3$ are reported here.

Chemistry. Sodium borohydride reduction of 2-methyl-2-allylcyclopentane-1,3-dione[1] gave the expected mixture of three isomeric diols, **1**, **2**, and **3**, that were separated by column chromatography. Further catalytic reduction with hydrogen afforded, in nearly quantitative yield, **4**, **5**, and **6** (Scheme I). This method was preferred to the one involving a previous reduction of the allyl group as it gave better yields and easier chromatographic separations.

To obtain the corresponding 4,5-unsaturated compounds, 2-methyl-2-*n*-propyl-4-cyclopentene-1,3-dione (**8**) was synthesized. Yet reduction of **8** with sodium borohydride or lithium aluminum hydride afforded the known mixture of saturated diols **4–6** because of the prevalence of 1,4 over 1,2 addition (Scheme I).

Structure Determination. No compound of the **1–3** and **4–6** series gives the characteristic reactions of the cis diols, probably owing to the considerable steric hindrance

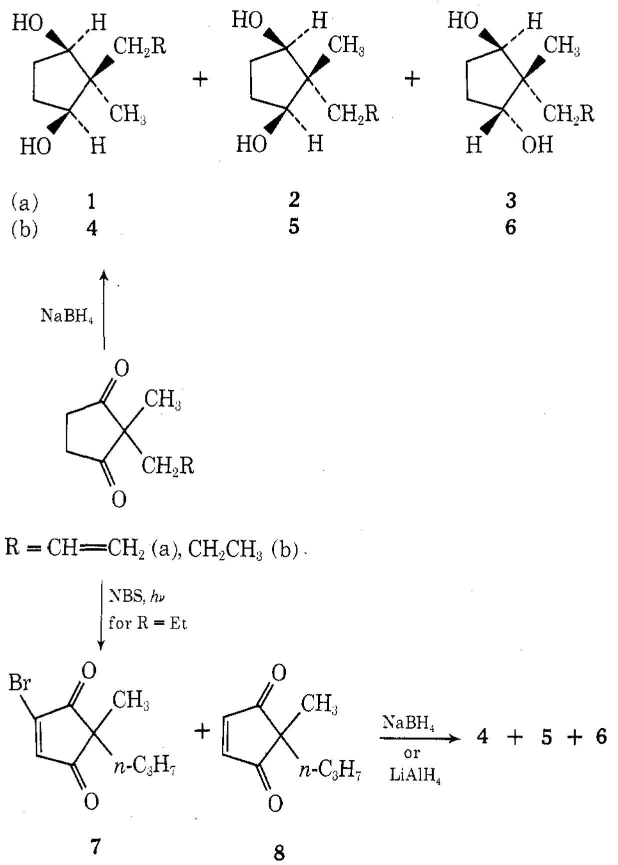
Table I
Paramagnetic Induced Shift (ΔEu)[a]



Compd	R	2-CH_3	$H_{1,3}$	$OH_{1,3}$	2-(1-CH_2)	$H_{4,5}$	2-(2-CH_2)	2-(3-CH_3)
1	$CH{=}CH_2$	−7.94	−15.51	−44.45	−14.36	−8.94 −13.29		
2	$CH{=}CH_2$	−12.66	−15.51	−46.05	−8.43	−9.06 −13.38		
3	$CH{=}CH_2$	−10.20	−16.59 −19.99	−44.63 −52.54	−10.46	*b*		
4	CH_2CH_3	−8.96	−16.12	−38.17	−10.21	−14.66	−6.93	−0.03
5	CH_2CH_3	−12.27	−15.27	−44.99	−7.09	−10.75 −13.12	−5.37	−2.51
6	CH_2CH_3	−13.61	−22.41 −26.86	−59.89 −68.37	−15.11	*b*	−8.33	−2.59

[a] $\Delta Eu = \delta_{CDCl_3} - \delta_{Eu}$ ($n = 1$). Extrapolated from least-squares lines for each protons. [b] Could not be determined.

Scheme I



of the molecule. On the other hand, NMR spectra, which are in good agreement with the general structure of compounds **1–6**, cannot be reliably used for detailed stereostructural assignments because of the impossibility of evaluating the contribution of the inductive and anisotropic effects of the hydroxyl group to the chemical shift of 2-CH_3 and 2-(1-CH_2).[2] The ir spectra in solution suggest a trans structure for the hydroxyls of compounds **3** and **6** but **2** and **5**, being solids, seem to contradict such an attribution, indicating for these last two a greater disposition to the intermolecular hydrogen bonding.

Therefore it was impossible, on these bases, to assign the structures with confidence.

Definitive evidence for the structural assignments was obtained by studying the pseudocontact shift in the NMR spectra of both series of compounds **1–3** and **4–6** by addition of $Eu(DPM)_3$. The induced paramagnetic shifts (ΔEu values), obtained from the slopes of the linear relations of the induced shift vs. $Eu(DPM)_3$/ligand molar ratios, are reported in Table I. ΔEu values were obtained according to Demarco[3] by simple extrapolation of the least-squares lines to $n = 1$ and $n = 0$. As a slight deviation[3] from linearity occurs at low $Eu(DPM)_3$ concentration, there are some differences between observed and extrapolated δ_{CDCl_3}.

As expected, the 2-methyl groups of compounds **2** and **5** are more strongly affected by the complex than the corresponding groups of compounds **1** and **4** and the reverse is true for 2-(1-CH_2) groups of the same compounds. As to products **3** and **6**, both groups are simultaneously influenced by europium action with consequential high ΔEu for both. Characteristic of these last two isomers and further confirmation of their structure is the differentiation of the 1,3 hydroxyls and 1,3 proton signals as the europium concentration increases.

It is interesting to note, in light of the results obtained with the shift reagents, that the 2-CH_3 [and that of 2-(1-CH_2) equivalently] appears at lower fields when the two hydroxyls are on the same side (δ_{CH_3} 1.06 and 1.05 for **2** and **5**, respectively), rather than on the opposite side (δ_{CH_3} 0.78 and 0.75 for **1** and **4** respectively). With trans hydroxyls, the situation is intermediate (δ_{CH_3} 0.88 and 0.83 for **3** and **6**, respectively). The values obtained show that the inductive effect of the hydroxyl groups[2,4–7] is dominated by the anisotropy effect of the C–OH bonding,[8] possibly because such molecules result sterically congested.[9–11]

Registry No.—**1**, 55319-49-8; **2**, 55319-50-1; **3**, 55319-51-2; **4**, 55399-41-2; **5**, 55399-42-3; **6**, 55399-43-4; **7**, 55319-52-3; **8**, 55319-53-4; NBS, 128-08-5; 2-methyl-2-*n*-propylcyclopentane-1,3-dione, 25112-79-2.

Supplementary Material Available. The Experimental Section containing preparation methods for compounds 1–8 as well as their spectroscopic characteristics will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-2241.

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Synthesis and Spectral Properties of a Series of New α,ω-Diphenylpolyenes

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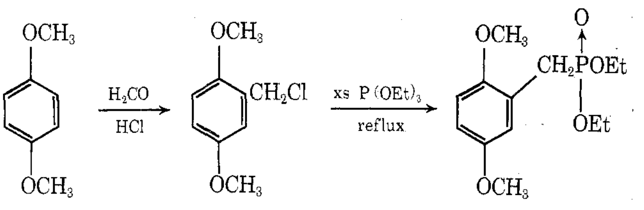
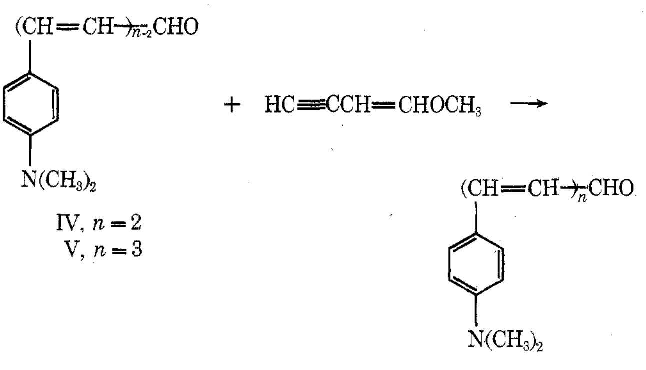
It has been determined that substituted *trans*-stilbenes act as sensitizers for the photochemical decomposition of arenesulfonyl azides.[1] A series of new α,ω-diphenylpolyenes has been synthesized which extend the spectral sensitivity of the azide-sensitizer system into the visible region of the electromagnetic spectrum. The study of energy transfer and quantum yield determination will be the topic of a forthcoming paper.

The synthesis involves formation of aromatic polyenals (IV → VII) which are subsequently converted to α,ω-diphenylpolyenes (VIII → XI) via a phosphonate carbanion reaction with 2,5-dimethoxybenzyl phosphonate (III). Several methods are available for the extension of double bond conjugation in systems containing an aldehyde function: multiple aldol condensations with paraldehyde;[2] aldol condensation with crotonaldehyde[3] or acetaldehyde;[4] reaction of 1-methylaniline penta-1,3-dienal (Zincke aldehyde) with dimethylaniline in the presence of $POCl_3$[5] and condensation of methoxybutenyne with either benzaldehyde or cinnamaldehyde followed by reduction with $LiAlH_4$.[6] The last method is a stepwise approach and was selected as being the most appropriate for the current work.

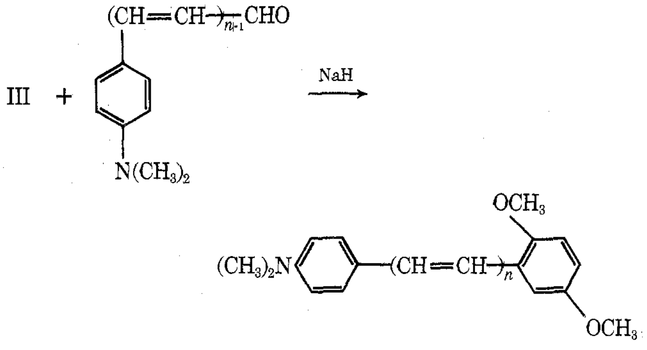


I II III



IV, $n = 2$
V, $n = 3$

VI, $n = 2$
VII, $n = 3$



VIII, $n = 1$
IX, $n = 2$
X, $n = 3$
XI, $n = 4$

It was desired to obtain the α,ω-diphenylpolyenes in the all-trans configuration to ensure the highest extinction coefficients and the longest wavelength absorption maxima. Several criteria were utilized in assigning the all-trans stereochemical configuration to the compounds synthesized: known stereochemistry of the chemical reactions involved; comparison of physical properties to those of similar compounds with known stereochemistry; analysis of the ultraviolet absorption spectra and analysis of the infrared spectra.

The reaction of the benzyl phosphonate III with an aldehyde produces an exclusively trans double bond.[9] The intermediate step in which $LiAlH_4$ is used to reduce the acetylenic bond of methoxybutenyne also results in formation of an exclusively trans double bond.[8] Finally, the *p*-dimethylaminocinnamaldehyde (V) was known to be the trans isomer. From these considerations we can assign the trans configuration to the stilbene VIII, both olefinic bonds in the butadiene IX, two of the three olefinic bonds in the hexatriene X, and three of the four olefinic bonds in the octatetraiene XI. The double bonds remaining unassigned are due to the methoxybutenyne for which the configuration of the double bond is not certain.

Table I compares some physical properties of known isomers with those of the first two members of the α,ω-diphenylpolyene series. Only the all-trans isomers are crystalline, high melting point solids.

In a review by Lewis and Calvin[7] it is reported that for a series of all-trans diphenylpolyenes the square of the ultraviolet absorbance maximum (λ^2_{max}) is related in a linear fashion to the number of olefinic bonds separating the aromatic rings (*n*). Plotting λ^2_{max} vs. *n* for the current series of diphenylpolyenes (Figure 1) gives the linear relationship expected if the members of the homologous series are in the all-trans configuration.

The 650–1050-cm^{-1} region of the infrared spectrum has been used by some researchers[6,11] to distinguish the out-of-plane vinyl C–H bonding of cis olefins (650–850 cm^{-1}) from that of trans olefins (950–1050 cm^{-1}). The presence of aromatic C–H bonding absorbances in the 700–800-cm^{-1} range[12] in the infrared spectra of the compounds under discussion, however, precludes the unambiguous assignment of any cis bond. The infrared spectrum of each α,ω-diphenylpolyene does contain a strong absorbance in the 950–1050-cm^{-1} region which could be assigned to a trans vinyl C–H bond.

In the present homologous α,ω-diphenylpolyene series each successive olefinic bond introduced into the system resulted in a bathochromic shift in the position of the ultraviolet absorbance maximum by about 17 nm and in an increase in the intensity of the absorption maximum.