1,5-diol-*1,1,5,5*-d_4, 53129-32-1; dimethyl 2,2′-oxydiacetate, 7040-23-5; 3,6,9-trioxaundecane-1,11-diol-*4,4,8,8*-d_4 di-*p*-toluenesulfonate, 53129-33-2; bis-2-chloroethyl-*2,2*-d_2 ether, 53129-34-3; 3,6,9-trioxaundecane-1,11-diol-*4,4,8,8*-d_4, 53129-35-4; phenol, 108-95-2; 1,8-dichloro-3,6-dioxaoctane, 112-26-5; 1,11-dichloro-3,6,9-trioxaundecane, 638-56-2.

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(12) The mass spectrum of **1** has been reported previously.[10a]
(13) Trivial names as suggested by Pedersen[2a] are employed for this and other cyclic polyethers. Systematic names are given in Experimental Section.
(14) The reasonable assumption is made that elemental compositions of fragment ions of **4** are identical with those of isobaric fragment ions of **5**.
(15) Structural identities of the C_2H_4O species lost are uncertain. They could be open chain species as indicated, or ring closure concomitant with bond cleavage would yield ethylene oxide.
(16) A mechanism initiated by cleavage of the bond between O-4(1) and C-5(15) of **a** with charge retention by carbon cannot be distinguished from that given. It is also possible but unlikely that initial cleavage in **a** involves the bond between O-4(1) and C-3(2).
(17) However, the mass spectrum (70 eV) of catechol methylene diether displays a molecular ion (*m/e* 122) with relative intensity ~75; the base peak is at *m/e* 121.[10a]
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Electrochemical and Electron Spin Resonance Studies of the Dibenzonorcaradiene Anion Radical

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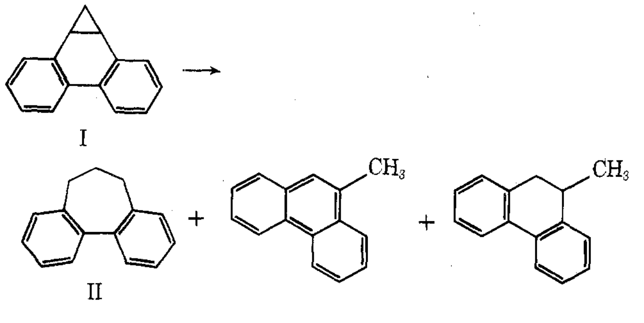
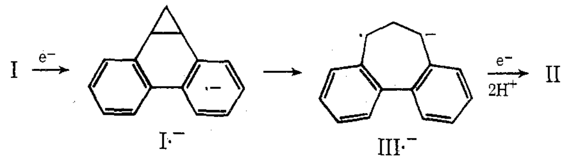
Electrochemical and esr studies of dibenzonorcaradiene have been carried out. Cyclic voltammetry data and esr hyperfine coupling constants are consistent with the reversible formation of a stable radical anion which does not undergo rapid isomerization to the anion radical of dibenzo[*a,c*]cycloheptatriene. Possible mechanisms for the cyclopropane ring opening in the parent radical anion are discussed in terms of correlation diagrams.

Isomerization reactions of ion radicals have received limited attention but are of some theoretical interest. In particular, a model to handle the influence of orbital symmetry on reactions of these open-shell species has not been well defined. With this in mind, the electron-transfer reduction of dibenzonorcaradiene (DBNC) had been investigated previously.[1] The reduction products from I and sodium in glyme include dibenzo[*a,c*]cycloheptadiene, II.



This product might arise from the concerted reaction



As described earlier[1] the bond cleavage is sterically constrained to occur in a disrotatory fashion and thus the presence or absence of this mechanism provides a test of the influence orbital symmetry considerations on the paths of ion radical isomerizations.

A correlation diagram for the $\mathrm{I}\cdot^{-} \rightarrow \mathrm{III}\cdot^{-}$ reaction (*vide infra*) predicts the product of the allowed thermally initiated reaction will be electronically excited $\mathrm{III}\cdot^{-}$ while the forbidden photochemical product will be ground-state $\mathrm{III}\cdot^{-}$. Using a combination of cyclic voltammetry and electron spin resonance spectroscopy, we will show below that neither of these processes actually occurs.

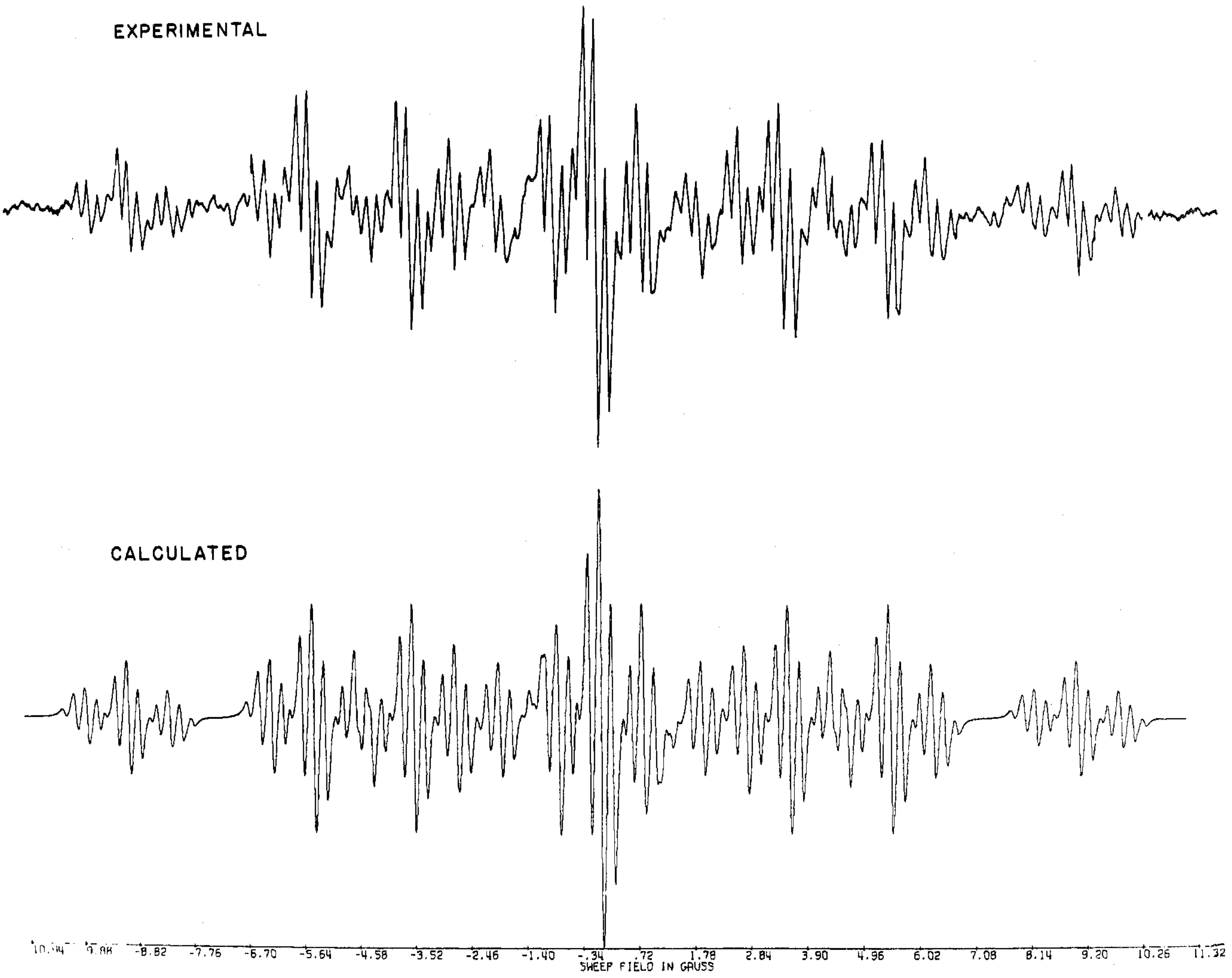


Figure 1. Top: esr spectrum of the anion radical generated by the reduction of dibenzonorcaradiene with potassium in THF at −85°. Bottom: computer-simulated spectrum using the hyperfine splitting constants given in text. The fit is not perfect because of the presence of a small amount of the impurity radical.

Results

Electrochemical studies on the reduction of DBNC were performed in DMF–tetrabutylammonium perchlorate (TBAP) at a mercury electrode. Polarograms run on 10^{-3} M DBNC in dry DMF gave $E_{1/2} = -2.55$ V *vs.* sce. A plot of $E_{1/2}$ *vs.* $I/(I_d - I)$ was linear with a slope of 72 mV.

Cyclic voltammetry was employed in search for intermediates in the reduction. Data are compiled in Table I. In DMF–TBAP a 10^{-3} M solution of DBNC gave a reduction peak $E_p{}^c = 2.56$ V and on the return (anodic) sweep an anodic peak $E_p{}^a = 2.49$ V. The peak separation of 70 mV was independent of sweep rate and the current was diffusion controlled at all sweep rates as judged by the constancy of $I_p{}^c v^{1/2}$. The ratio I_{pa}/I_{pc} was poorly reproducible, but always near unity.

The data are consistent with the reversible formation of a radical anion with a lifetime of several seconds in DMF. It is required that the radical anion have a structure closely related to that of the neutral molecule so that electron transfer is not slowed by a large free energy of activation for a structural change. I·$^-$ is clearly acceptable and III·$^-$ could only be if the isomerization were remarkably fast.

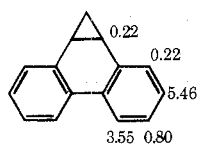
Next, we studied the radical formed by the electron spin resonance (esr) technique. Figure 1 shows the esr spectrum of the anion radical formed by the reduction of DBNC with potassium in tetrahydrofuran (THF) at −85°.[2] A similar spectrum was obtained when 1,2-dimethoxyethane was the solvent or when the reduction was carried out electrolytically using TBAP as supporting electrolyte in THF. Analysis of the spectrum yielded the hyperfine splitting constants 0.22 G (4), 0.80 G (2), 3.55 G (2), and 5.46 G (2) where the number in parentheses denotes the number of equivalent protons. The hyperfine splitting constants for two of the protons are too small to be observed. Assignment of these hyperfine splitting constants by simple molecular orbital calculations is difficult since neither I·$^-$ nor III·$^-$ is fully aromatic.

Table I
Cyclic Voltammetry Data for Dibenzonorcaradiene[a]

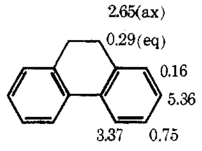
v, mV /sec	$E_p{}^c$, V	$E_p{}^a$, V	$I_p{}^c/v^{1/2}$
10	2.56	2.49	7.72
50	2.56	2.49	6.36
100	2.56	2.49	6.40
200	2.56	2.49	6.51
500	2.56	2.49	6.57

[a] 1 × 10^{-3} M DBNC in 0.1 M TBAP-DMF. Hanging Hg drop weight 3.9 mg; sce reference electrode.

If the radical formed has structure I·$^-$, the spin density distribution should resemble that of 9,10-dihydrophenanthrene, IV·$^-$.[3] The agreement for the couplings observed is very good, the only discrepancy being that one might have expected a substantial coupling from the methylene pro-



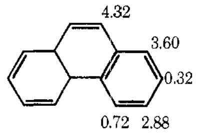
$I\cdot^-$



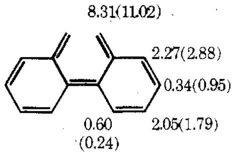
$IV\cdot^-$

tons in $I\cdot^-$ since the half-filled molecular orbital is symmetric with respect to reflection through the plane containing the methylene group and dividing the rings. Systems with similar symmetry[4,5] normally give large couplings to the methylene protons; however, the methylene group in $I\cdot^-$ is at least one bond length further removed from the π system than in the systems previously studied. Assuming one treats $I\cdot^-$ as a 1,1′-disubstituted biphenyl radical, the coupling should be substantially smaller.

If the radical formed has structure $III\cdot^-$ the predicted coupling constants depend critically on the atom 9–atom 10 distance assumed. If the distance is short (*i.e.*, ~1.4 Å), the radical will resemble the homo[*a,c*]dibenzocycloheptatriene anion radical and the spin density distribution will be similar to that of the phenanthrene anion radical ($V\cdot^-$). On the other hand, if there is no overlap between the 9 and 10 positions, the radical will resemble the 2,2′-dimethylenebiphenyl anion radical ($VI\cdot^-$). We assume the actual radical



$V\cdot^-$



$VI\cdot^-$

lies somewhere between these two extremes. The experimental couplings for $V\cdot^-$ [6] are compared below with those for $VI\cdot^-$ calculated using simple Hückel theory ($Q = -31$) and, in parentheses, including McLachlan's polarizability correction[7] ($Q = -27$, $\lambda = 1.2$). Independent of which extreme is the best approximation for $III\cdot^-$ it is clear that too many big couplings are predicted, six instead of the four observed, and too few small couplings, four instead of six, for this radical to be considered as a model for the observed stable anion radical.

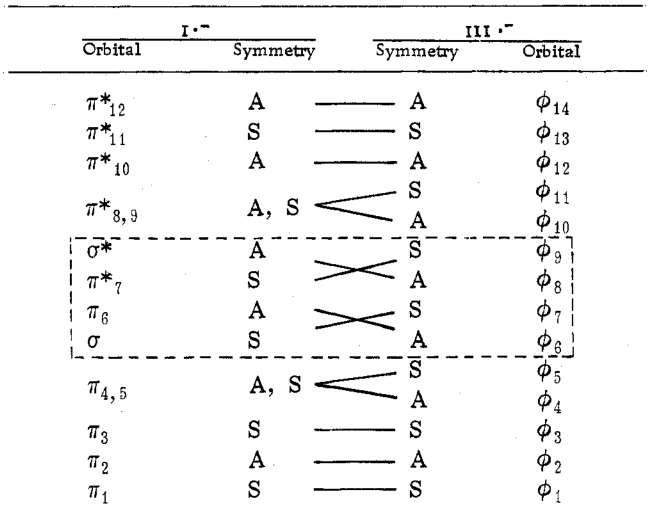
Finally, the following observations are also of interest. Except for the poorer resolution at higher temperatures (probably due to ion pairing), the spectrum is basically the same over a large temperature range (+25 to −100°). The same spectrum is obtained when the reduction was carried out in THF-d_8. Furthermore, on prolonged contact with the alkali metal, the solution yielded another radical whose esr spectrum is similar to that of the 9-methylphenanthrene anion radical. The reduction of 9-methyldihydrophenanthrene with potassium in THF gave no esr signals.

Discussion

Following the discussion in ref 1, we choose the π orbitals of biphenyl plus a σ orbital as a model for discussing the orbital symmetry of the dibenzonorcaradiene anion and 2,2′-dimethylenebiphenyl for the dibenzocycloheptatriene anion. A correlation diagram for their molecular orbitals is given in Chart I where S and A refer to symmetric and antisymmetric with respect to the mirror plane.

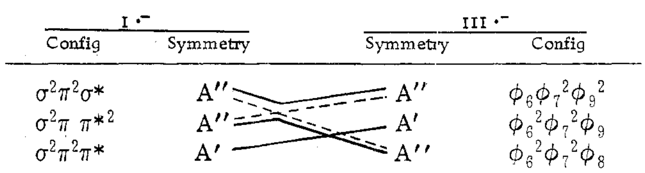
The positioning of the σ and σ^* orbitals within the biphenyl π system is arbitrary. The position chosen here allows correlation of the π orbitals of biphenyl (symmetry D_{2h}) with those of the same symmetry in III if the methylene carbons are ignored and thus presumably allows the most facile isomerization. If the σ orbital is buried deeper in the π system, the ground-state symmetry of the anion will be the same but the isomerization barrier higher. Chart II gives a correlation diagram for the ground state and photochemically accessible excited states for the orbitals in the box in Chart I.

Chart I



$I\cdot^-$		$III\cdot^-$	
Orbital	Symmetry	Symmetry	Orbital
π^*_{12}	A	A	ϕ_{14}
π^*_{11}	S	S	ϕ_{13}
π^*_{10}	A	A	ϕ_{12}
$\pi^*_{8,9}$	A, S	S	ϕ_{11}
		A	ϕ_{10}
σ^*	A	S	ϕ_9
π^*_7	S	A	ϕ_8
π_6	A	S	ϕ_7
σ	S	A	ϕ_6
$\pi_{4,5}$	A, S	S	ϕ_5
		A	ϕ_4
π_3	S	S	ϕ_3
π_2	A	A	ϕ_2
π_1	S	S	ϕ_1

Chart II



$I\cdot^-$		$III\cdot^-$	
Config	Symmetry	Symmetry	Config
$\sigma^2\pi^2\sigma^*$	A″	A″	$\phi_6\phi_7^2\phi_9^2$
$\sigma^2\pi\ \pi^{*2}$	A″	A′	$\phi_6^2\phi_7^2\phi_9$
$\sigma^2\pi^2\pi^*$	A′	A″	$\phi_6^2\phi_7^2\phi_8$

Chart II shows that if $I\cdot^-$ were to isomerize rapidly to $III\cdot^-$ by a concerted electrocyclic ring opening, $III\cdot^-$ would be created in an electronic excited state which would be expected, in solution, to decay rapidly to the ground state. This mechanism is clearly ruled out by our cyclic voltammetric results since the reoxidation of $III\cdot^-$ (ground state) to I would clearly have an activation barrier at least as great as $E\phi_9 - E\phi_8$ which we estimated[1] to be greater than 2 eV.

The $\pi \rightarrow \pi^*$ transition in the biphenyl anion occurs at 24,700 cm^{-1} [8] (blue-violet), so this first electronic excited state is populated under normal experimental conditions. Chart II shows that the photochemical reaction has an orbital symmetry barrier, so the reaction would proceed slowly by this path if at all. A slow (several hours) isomerization of this type is ruled out as a reaction mechanism if the anion radical $III\cdot^-$ is stable since only one esr spectrum is observed and we attribute it to $I\cdot^-$.

In conclusion, both the electrochemical and esr results are consistent with a stable $I\cdot^-$ radical which does not isomerize rapidly to $III\cdot^-$. Thus the primary mechanism for the observed formation of II is most probably according to the general scheme

$$I \xrightarrow{e^-} I\cdot^- \xrightarrow[\text{solvent}]{H^+} IH\cdot \xrightarrow{e^-} IH^- \xrightarrow[\text{solvent}]{H^+} IH_2 \equiv II$$

This work, however, gives no new information about the possible structures of IH· and $IH\cdot^-$, several of which were proposed in ref 1. We have not observed any effects of visible light on the reaction rate or products, but the photochemical mechanism in which $I\cdot^-$ slowly isomerizes to an unstable $III\cdot^-$ is not ruled out by the present work though it is deemed unlikely through orbital symmetry considerations. A referee has suggested the ring-opening step may involve dianions, *i.e.*, $I^{2-} \rightarrow III^{2-}$, which would be allowed photochemically. The dianion I^{2-} is not accessible electrochemically so we have no way of estimating the disproportionation equilibrium constant in order to calculate the I^{2-} concentration, nor do we have any information on the frequency of the $\pi^* \rightarrow \sigma^*$ transition involved so this mechanism cannot be ruled out. The difficulty in producing dianions of the biphenyl-like systems, however, makes it unlikely that appreciable concentrations of I^{2-} are present.

Experimental Section

Materials. Dibenzonorcaradiene was prepared as previously indicated. DMF was dried by distillation from calcium hydride. Tetrahydrofuran and 1,2-dimethoxyethane were purified by first refluxing and then distilling from calcium hydride. These solvents were then stored over Na–K alloy before use.

Equipment. Esr spectra were recorded on a Varian E-3 spectrometer equipped for variable-temperature experiments.

Cyclic voltammograms were run on a Princeton Applied Research Model 170 instrument. The cell was purged of air with argon.

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Registry No.—I, 949-41-7; I·⁻, 34468-58-1; III·⁻, 53166-03-3.

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A New Synthesis of Cyclohexadienes

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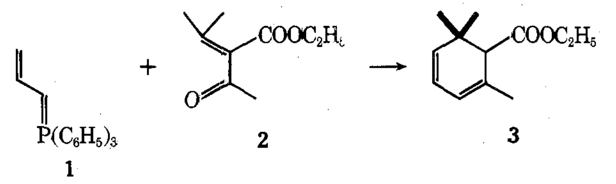
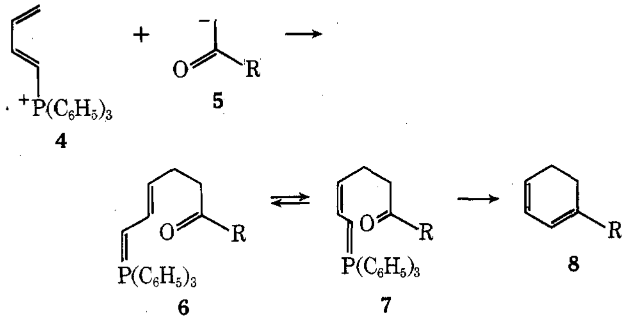
The two bicyclic cyclohexadienes 13 and 17–18 were synthesized by condensation of the two ketones 12 and 16 with 1-butadienyltriphenylphosphonium bromide prepared *in situ* from 2-butenylenetriphenylphosphonium bromide (9) or 4-bromo-2-butenyltriphenylphosphonium bromide (10) and potassium *tert*-butoxide in ether. Efforts to combine ketone 16 with the butadienylphosphonate 25 failed. Phosphonate 25 was prepared by a new method. Alkylation of diethyl ethylphosphonate (23) with propargyl bromide afforded the acetylene 24 which was isomerized to the more stable diene 25 with potassium *tert*-butoxide.

In conjunction with work on the synthesis of damascenones it was found that allyltriphenylphosphorane (1) combines with the highly electron deficient α,β-unsaturated ketone 2 to produce the cyclohexadiene 3.[1] Subsequent work demonstrated the method to be useful with simple α,β-unsaturated ketones[2,3] lacking an electron-withdrawing substituent and with more highly substituted phosphoranes.[4] It served also in strikingly simple preparations of cyclohexadienes containing bridgehead double bonds.[5] In this synthesis the cyclohexadiene is constructed from two structural units each containing three carbon atoms.



Cyclohexadienes in principle should also be available from starting materials supplying two and four carbon atoms, respectively. More specifically, an enolate 5 should add to the terminal double bond of a butadienylphosphonium salt 4 to produce stereoisomeric ylides 6 and 7. If these are in equilibrium the *Z* isomer 7 should undergo an intramolecular olefin synthesis to afford cyclohexadiene 8. A search of the literature produced little on the chemistry of butadienylphosphonium salts but nucleophilic additions to vinylphosphonium salts, their lower vinylogs, have been explored thoroughly.[6,7]



Slurries of the diphosphonium salt 9[8] or the bromophosphonium salt 10,[9] both of undefined stereochemistry, in ether on treatment with potassium *tert*-butoxide yielded brown solutions presumably containing 1-butadienyltriphenylphosphonium bromide. Addition of dihydrocarvone (12) or hydroxytetrahydrocarvone (16) in *tert*-butyl alcohol solutions produced the anticipated cyclohexadienes 13 and 17–18. The former appeared to be a single diastereomer and in analogy to the products formed in Robinson-annelations[10] structure 13 was assigned. Addition of the most stable enolate 11 to the phosphonium salt 4 should give a ketone in the chair conformation containing the new substituent in axial orientation. Annelation to hydroxytetrahydrocarvone (16) led to a 4:1 mixture of products assumed to be epimers 17 and 18, respectively. Hydrolysis of the reaction mixtures shortly after the addition of the ketones 12 and 16 led to substitution products 14 and 19 with