CONCLUSIONS

1. N-Halomethyl-N-nitrourethanes react with potassium thiophenolate and silver thiophenolate as acylating, nitroamidomethylating, and nitroaminomethylating agents.

2. The first examples of previously unknown α-thio, α-sulfo, and α-sulfoxy derivatives of alkylnitroamides were described as well as α-thio derivatives of primary nitroamines.

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EPOXIDATION OF 4β-CHLORO-3(10)CARENE

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The chemical behavior and conformation of six-membered cyclic systems having an exocyclic double bond and electronegative substituent in the adjacent position are often unique [1, 2], perhaps as a consequence of the orbital and steric interactions of the functional groups. Derivatives of 3(10)-carene hold interest in this regard since these compounds have analogous substituents as neighboring atoms. The stereochemistry of electrophilic addition to such systems is a function both of the screening of the syn side of the six-membered ring by one of the gem methyl groups and the steric and polar effect of the substituent. Thus, the predominant formation of the trans isomer of the epoxide (70%) upon the epoxidation of unsubstituted 3(10)-carene [3] is related to the former factor, while the inversion of steric selectivity in the epoxidation of 4α-chloro-3(10)-carene to give (I) was explained by the steric and polar effects of the substituent [4]. In the present work, we studied the behavior of 4β-chloro-3(10)-carene (II) with a cis-oriented C^4—Cl bond relative to the cyclopropane ring (CPR) upon epoxidation.

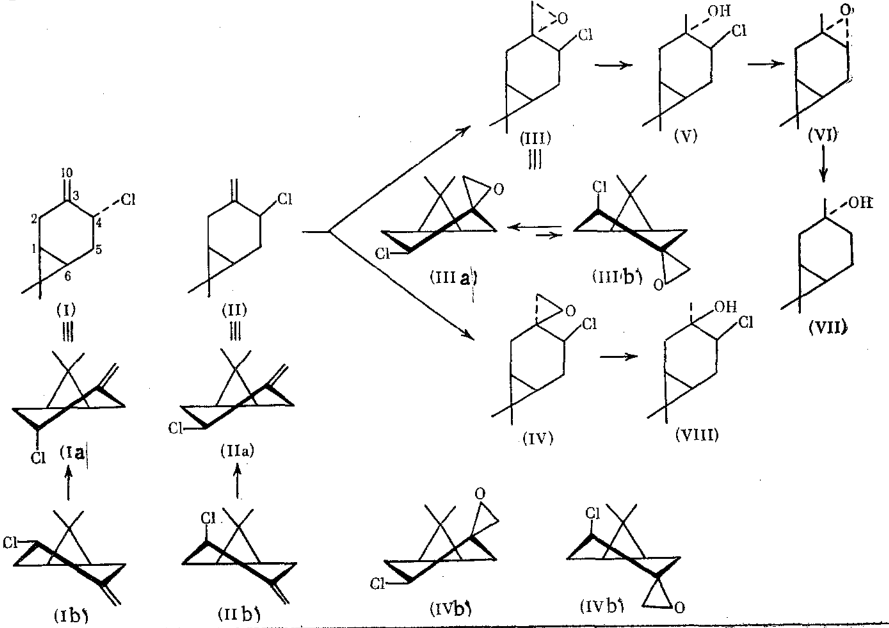

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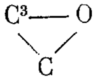
TABLE 1. Dipole Moments of Epoxychlorocarenes

Conformation	μ_{calc}	μ_{exp}	Conformation	μ_{calc}	μ_{exp}
	D			D	
(IIIa)	3,30	2,83	(IVa)	3,32	2,91
(IIIb)	0,29		(IVb)	3,58	

The action of peracetic acid (PAA) on (II) under analogous conditions gives a 3.5:1 mixture of stereoisomeric epoxides which correspond in their spectral characteristics to 4β-chloro-3α, 10α-epoxycarene (III) and 4β-chloro-3β, 10β-epoxycarene (IV), respectively. This is in accord with the transformations upon $LiAlH_4$ hydrogenolysis. The major epoxide gives α-3,4-epoxycarene (VI) and cis-3-caranol (VII). 3-Carene chlorohydrin (V), which is expected as the primary hydrogenolysis product, is formed only in the initial phase of the reaction, as indicated by thin-layer chromatography. This intermediate has preferred conformation with axial C^3—OH and C^4—Cl bond [5] and readily loses HCl to form epoxide (VI), which is readily reduced to cis-3-caranol (VII) [6, 7]. The other epoxide from (II) should thus have the structure (IV) with a cis arrangement of the CPR and epoxide ring. This epoxide reacts with $LiAlH_4$ to give cis-chlorohydrin (VIII). The carene structure is assigned on the basis of its PMR spectrum with signals at 0.65 ppm (m, 2H, HC^1, and HC^6) and 3.8 ppm (m, 1H, HC^4). The IR spectrum of a dilute solution of (VIII) in CCl_4 has a band at 3578 cm^{-1} assigned to the OH group participating in intramolecular hydrogen bonding (the analogous IR band for trans-3-caranol is found at 3610 cm^{-1}).

Thus, the epoxidation of (II) proceeds with less than trans steric selectivity than the epoxidation of 3(10)-carene and α-isomer (I). The concurrent effect of steric factors related to 8-CH_3 and C^4—Cl in (II) should lead to the exclusive formation of trans isomer (III), which is also facilitated by the polar effect of the C^4—Cl bond. The reason for this discrepancy lies apparently in the different spatial orientation of the C^4—Cl bond (equatorial and axial) in the stereoisomeric carenyl chlorides (I) and (II). For this purpose, we compared the conformational behavior of (I) and (II). Kerr effect measurements were used to establish the half-chair conformation for (I) with approximation of the unsaturated fragments (CH_2=C and CPR) and axial orientation of the chlorine atom in (Ia) [8]. Comparison of the experimental molar Kerr constant for (II) ($_mK = 124 \cdot 10^{-12}$) with the theoretically calculated values for half-chairs (IIa) and (IIb) as in our previous work [8] showed that the experimental value corresponds to the value for (IIa) [$121 \cdot 10^{-12}$, the value for (IIb) is only $42 \cdot 10^{-12}$], i.e., the same conformation for the six-membered ring with an equatorial chlorine atom located approximately in the plane of the double bond (deviation of ∿2-3°) is present virtually exclusively. In this case, the steric and polar effects of the equatorial C^4—Cl bond in (II) has no directing effect on the attack of the double bond from the syn or anti side. Thus, the observed direction of epoxidation of (II) and unsubstituted 3(10)-carene [3] is the same, i.e., the major factor in both cases which determines the stereochemistry of epoxidation is apparently the steric effect of one of the gem methyl groups at the CPR. The C^4—Cl axial bond in (I) hinders the approach of the epoxidizing agent from the side of the chlorine atom, which may account for the predominance of the cis isomer in the product mixture.

The structures of epoxychlorides (III) and (IV) were established using dipole moment measurements. Since, according to literature data [9], the half-chair conformation is characteristic for substituted bicycloheptane systems, the theoretical dipole moments (μ) were calculated for (III) and (IV) for two half-chair forms with equatorial (a) and axial (b) orientation of the chlorine atom. In the calculation, we used experimentally determined geometrical parameters for carene and its derivatives as well as group dipole moments of the polar substituents as in our previous work [8]. The theoretical and experimental values of μ are given in Table 1. In the case of (III), of the two conformations differing strongly in polarity, (IIIa) with equatorial orientation of the chlorine atom and a pseudoequatorial C—O bond is readily selected. The calculation of the molar Kerr constant using the bond and group polarizability ellipsoids taken from our previous work [10] for (IIIa) and (IIIb) supports this selection; $K_{calc} = 317 \cdot 10^{-12}$ for (IIIa) and only $3 \cdot 10^{-12}$ for (IIIb), while $K_{exp} = 282 \cdot 10^{-12}$). In this case, the somewhat overestimated values for μ and $_mK$ for (IIIa) relative to the experimental data are apparently a consequence not of traces of unfavorable conformation (IIIb) but rather failure to take account of the distortion of the bond angles in the actual molecule. The experimental dipole moments of (III) and (IV) are similar, indicating identical orientation of the C^4—Cl and  C^3—O—C group moments in both cases. Thus, the half-chair conformation established for carenyl chloride (II) is retained for its epoxidation products (III) and (IV).

EXPERIMENTAL

The IR spectra were taken neat on a UR-10 spectrometer. The PMR spectra were taken in CCl_4 solution on a Varian T-60 spectrometer relative to TMS. The n_D^{20} and $[\alpha_D^{20}]$ values were measured on a Polamat A instrument. Chromatography was carried out on Chemapol A (110/160 mμ using 10:1 petroleum ether—ether as eluent. The composition of the reaction mixtures and of the individual fractions upon column chromatography were monitored by thin-layer chromatography. The ratio of (III) and (IV) was determined using the weight ratio of the column chromatography fractions. The dipole moments and Kerr constants were measured in CCl_4 at 25°C.

Epoxidation of 4β-Chloro-3(10)-carene (II). A sample of 1.25 g (II) and a solution of 0.8 peracetic acid in 10 ml $CHCl_3$ [11] was maintained for 3 days at about 20°C. The mixture was poured into water. The chloroform layer was separated, and the aqueous layer was extracted with ether. The combined ether—chloroform extract was washed with 5% aq. $NaHCO_3$ and then with water and dried over $MgSO_4$. The solvent was evaporated to give 1.3 g residue which was subjected to chromatography. The following products were obtained: 1) 0.12 g (IV), n_D^{20} 1.4915, $[\alpha_D^{20}]$ −8°. IR spectrum (ν, cm^{-1}): 670, 860, 3005. PMR spectrum (δ, ppm): 0.7 m (2H, HC^1, HC^6), 1.02, 1.02 s, and 1.12 s (6H, 8- and 9-CH_3), 2.37 d (1H, H_AC^{10}, ^2J = 6 Hz), 2.98 d (1H, H_BC^{10}, ^2J = 6 Hz), 3.97 m (1H, HC^4). Found: C 63.86; H 8.01%. Calculated for $C_{10}H_{15}OCl$: C 64.34; H 8.04%. 2) 0.58 g (III), bp 54°C (2 mm), n_D^{20} 1.4985, $[\alpha_D^{20}]$ +59°. IR spectrum (ν, cm^{-1}): 660, 840, 3010. PMR spectrum (δ, ppm): 0.83 m (2H, HC^1 and HC^6), 1.05 s (6H, 8- and 9-CH_3), 2.42 d (1H, H_AC^{10}, ^2J = 6 Hz), 2.90 d (1H, H_BC^{10}, ^2J = 6 Hz), 3.25 m (1H, HC^4). Found: C 64.16; H 8.00%. Calculated for $C_{10}H_{15}OCl$: C 64.36; H 8.04.

Hydrogenolysis of 4β-Chloro-3α,10α-epoxycarene (III). A solution of $LiAlH_4$ in ether was added to a solution of 0.47 g (III) in 5 ml of ether until (III) disappeared. The mixture was poured into water and extracted with ether. The extract was washed with saturated aq. NH_4Cl and water and dried over Na_2SO_4. Ether was removed, and chromatography of the residue gave 0.16 g (VI), n_D^{20} 1.4670 $[\alpha_D^{20}]$ +21.9° (benzene, C 8.04), and 0.1 g (VII) identified by comparison of their PMR spectra with those of authentic samples obtained according to Mikhailov [12] and Isaeva [13], respectively.

Hydrogenolysis of 4β-Chloro-3β,10β-epoxycarene (IV). The reaction was carried out as in the case of (III). A sample of 0.48 g (IV) gave 0.31 g product which was subjected to chromatography using 25:1 petroleum ether—ether as eluent to give 0.2 g (VIII), $[\alpha_D^{20}]$ −3.2° (benzene, C 14.02). IR spectrum (δ, cm^{-1}): 660, 1110, 3485. PMR spectrum (δ, ppm): 0.65 m (2H, HC^1 and HC^6), 1.00 s, 1.11 s (6H, 8- and 9-CH_3), 1.27 s (3H 1 CH) 3.80 m (1H, HC^4). Found: C 63.36; H 8.61%. Calculated for $C_{10}H_{15}OCl$: C 63.66; H 9.02%.

CONCLUSIONS

1. The epoxidation of 4β-chloro-3(10)-carene proceeds without steric specificity to give two stereoisomeric epoxides with predominance of the trans isomer.

2. 4β-Chloro-3(10)-carene and its isomeric epoxides have half-chair conformation with equatorial C—Cl bonds.

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MECHANISM FOR THE CHEMILUMINESCENT PHOTOOXIDATION OF PHTHALHYDRAZIDES

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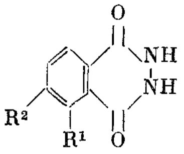
The photosensitized oxidation of some phthalhydrazides is accompanied by bright chemiluminescence (CL) [1-3]. Attempts to study the chemiluminescent oxidation of phthalhydrazides sensitized by methylene blue (MB) upon continuous photoexcitation proved unsuccessful [1-3] since information on the initiation step and reactions of the primary active species was lacking. The formation of a CL inhibitor upon the prolonged irradiation of the solution [3] creates additional difficulties for interpreting the kinetic data.

In the present work, we studied the rection mechanism upon flash photoexcitation. In this case, the inhibitor is formed in only slight amounts and its effect may be neglected.

EXPERIMENTAL

We studied phthalhydrazides (Ia-e)



(Ia—c)

$R^1 = NH_2$, $R^2 = H$ (luminol (a), $R^1 = H$, $R^2 = NH_2$ (b), $R^1 = H$, $R^2 = NMe_2$ (c), $R^1 = NMe_2$, $R^2 = H$ (d), $R^1 = h$, $R^2 = H$ (e)). The measurements were carried out in phosphate buffer at pH 10-12. Under such conditions, (I) and radicals derived from (I) are in anionic form [4-6], MB and triplet MB are in cationic form [7], and the MB radical is neutral [8].

The activity of superoxide dismutase (SOD) was $3 \cdot 10^5$ Fridovich activity units/mg [9]. The inactivation of SOD was carried out by maintaining the sample at constant 75°C for 10 min.

The absorption of short-lived intermediate species was recorded on a flash photolysis system. For the quenching of triplet MB by (I), the kinetics of triplet annihilation was observed at 820 nm ($\varepsilon_{820} = 2 \cdot 10^4$ liters/mole·cm [7]). The radical yield was found by the procedure of Steiner et al. [10] and the radical concentration was calculated relative to the decrease in the optical density at the MB absorption band immediately after the photolysis flash. Regeneration of the dye in deoxygenated solution was incomplete. The same solution,

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