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SINGLET OXYGENATION OF 7-ARYL AND 7-ALKYL-1,3,5-CYCLOHEPTATRIENES: SUBSTITUENT EFFECTS ON THE PRODUCT DISTRIBUTION OF TROPILIDENE- AND NORCARADIENE-DERIVED ENDOPEROXIDES

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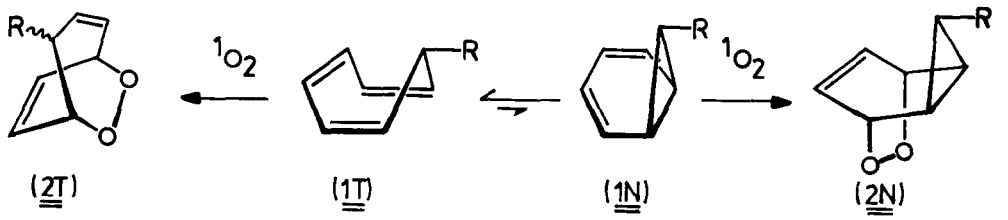
SUMMARY The N/T ratio, i. e. the proportion of norcaradiene (N) versus tropilidene (T) endoperoxides in the cycloaddition of singlet oxygen with 7-substituted 1,3,5-cycloheptatrienes, decreases in the order p-ClC_6H_4 > C_6H_5 >p-$MeOC_6H_4$ and t-Bu > i-Pr > Et > Me, presumably reflecting the ability of these substituents in promoting the tropilidene to norcaradiene valence isomerization.

A long standing problem of mechanistic interest concerns the influence of substituents on the valence isomerization of cycloheptatrienes. Recent work has dealt with the elucidation of the electronic and steric nature of the substituents by examining the equilibrium distribution of the tropilidene (1T) and norcaradiene (1N) valence isomers (Eq.1) with the help of dynamic ^1H-



(1)

and ^{13}C-NMR techniques.[1]

On the other hand, in the singlet oxygenation of cycloheptatrienes (1) both endoperoxides (2T) and (2N) were formed[2], representing cycloadditon to the tropilidene (1T) and norcaradiene (1N) isomers, respectively The ratio of norcaradiene versus tropilidene endoperoxides, i. e. the N/T ratio, was a sensitive function of the electronic demand of the 7-substituent, affording exclusively (2T)-endoperoxide for the methoxy group (π-donor) and exclusively (2N)-endoperoxide for the cyano group (π-acceptor). In contrast, with 1,2,4-triazoline-3,5-diones (TAD) as dienophile, irrespective of the electronic nature of the substituent, only the (2N)-urazole was formed. This unusual and dramatic substituent effect in cycloaddition reactions with cycloheptatrienes was rationalized in terms of the relative energy barriers of the cycloaddition versus valence isomerization.[2a] For singlet oxygen (an excited state dienophile) the cycloaddition is competitive with the valence isomerization and the nature of the "through-bond" interaction[3] of

the 7-substituent dictates the N/T ratio of endoperoxides (2). In contrast, for triazolinedione (a ground state dienophile), cycloaddition is significantly slower than valence isomerization, so that the more reactive norcaradiene valence isomer reacts exclusively Provided physical quenching[4] of the electronically excited dienophile is of no concern, a greater reactivity and thus a lower selectivity is expected for singlet oxygen compared to triazolinedione.

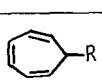
One difficulty with the series of the 7-substituents that has been chosen in the above study [2a], concerns their varying steric demand The influence of the electronic nature of these substituents could, therefore, be obscured by their steric effects. Consequently, it was of interest to probe electronic effects by employing the series of 7-aryl-1,3,5-cycloheptatrienes, where 7-aryl is p-ClC_6H_4 (1a), C_6H_5 (1b) and p-$MeOC_6H_4$ (1c), and steric effects by means of the series of 7-alkyl-1,3,5-cycloheptatrienes, where 7-alkyl is Me (1d), Et (1e), i-Pr (1f) and t-Bu (1g). The preliminary results of the characterization of the (2T) and (2N) endoperoxides and their chemical transformations have been previously communicated for the 7-alkylcycloheptatrienes.[2b,5] Presently we report on the quantitative product distribution, i. e. N/T ratios of endoperoxides (1), and the mechanistic interpretation of the substituent effects on the cycloheptatriene valence isomerization

The photooxygenations of cycloheptatrienes (1a-1g) were carried out in methylene chloride at -20°C using tetraphenylporphine as sensitizer and a 150-W sodium street lamp as light source. The methylene chloride was evaporated, deuterochloroform was added and the crude endoperoxide mixture heated at 65°C for 3 h, converting the endoperoxide (2N) quantitatively into its bisepoxide.[2a] Control experiments confirmed that under these thermolysis conditions the (2T) endoperoxide was perfectly stable. Quantitative ^{1}H-NMR analysis at 90 MHz, using p-chloronitrobenzene as internal standard and calibration charts of the authentic products, gave the relative product yields of (2T) and (2N) endoperoxides shown in Table I.

The data for the 7-arylcycloheptatrienes (Table I) reveal that the N/T ratio of endoperoxides decreases in the order p-ClC_6H_4 > C_6H_5 > p-$MeOC_6H_4$. Although in every case the N/T ratio is greater than unity, i. e. norcaradiene endoperoxide (2N) is formed preferentially, the relative order clearly reflects the electron withdrawing ability of the substituents, i. e. p-Cl > H > p-MeO. In fact, a Hammett plot of $\log_{10}$ (N/T) versus σ affords a good linear correlation with a slope $\rho = 0.78 \pm 0.05$. In the 7-aryl series steric factors are kept constant, so that only the electronic nature of these substituents is being sensed.[1c] Since triazolinedione affords only norcaradiene cycloadducts with these 7-arylcycloheptatrienes, our present results confirm our previous conclusions[2a] that i) singlet oxygen is a sufficiently reactive dienophile to compete with the tropilidene-norcaradiene valence isomerization by yielding both (2T) and (2N) endoperoxides and ii) the N/T endoperoxide ratio reflects the π-acceptor nature of the 7-aryl substituents by promoting the tropilidene-norcaradiene valence isomerization as the electron-withdrawing power of the substituent increases.

A similar trend is also observed for the 7-alkylcycloheptatrienes (Table I), i. e. the N/T ratio decreases in the order t-Bu > i-Pr > Et > Me, however, with the important difference that for t-Bu and i-Pr the N/T ratio is greater than unity (norcaradiene endoperoxides predominate), while for Et and Me the N/T ratio is less than unity (tropilidene endoperoxides predominate). Obviously, the 7-alkyl substituents exert a much more dramatic influence on the N/T ratio of endoperoxide products. Again it is important to stress that with triazolinedione only norcaradiene

TABLE I. Absolute and Relative Product Composition and Product Ratios in the Photooxygenation of 7-Aryl and 7-Alkyl-1,3,5-cycloheptatrienes (1).[a]

	Absolute Yields (%)[b]			Relative Yields (%)[c]		N/T
	(2N)	(2T)	(ArCHO)	(2N)	(2T)	Ratio
(1a) p-ClC_6H_4	79.8±1.5	7.5±0.4	d	91.2±0.4	8.8±0.4	10.4±0.4
(1b) C_6H_5	81 3±1 0	13.4±0.4	d	86.4±0.7	13.6±0.7	6.4±0.2
(1c) p-$MeOC_6H_4$	79.3±1.6	18.6±1.2	d	80.9±0.7	19.1±0.7	4.2±0.3
(1d) Me	10.1±0.2	27.0±0.5	43.1±0 7	26.8±0.6	73 2±0.6	0.37±0.09
(1e) Et	19.3±1.2	46.4±2.5	38.1±2 9	29 4±0.2	70.6±0.2	0.42±0.05
(1f) i-Pr	40.5±0.6	50.9±0.6	8.0±1.0	55.7±0.5	44.3±0.5	1.26±0.11
(1g) t-Bu	69.4±0.9	27.3±0.4	4.0±0.5	72.7±0 3	27.3±0.3	2.66±0.20

a. In CH_2Cl_2 at -20°C, [1] ca. 1.3 M.

b. Determined by ^{1}H-NMR integrations using p-chloronitrobenzene as internal standard, a minimum of 4-6 independent determinations.

c. Normalized the sum of endoperoxides (2N) and (2T) to 100%.

d. No aldehydes detected, for the characterization of the endoperoxide products (2N) and (2T) derived from the 7-arylcycloheptatrienes (1a-c) cf. G. Pollak, Diplomarbeit, University of Wurzburg, July 1981.

cycloadduct is produced. Clearly, also for the 7-alkyl substituents singlet oxygen cycloaddition is competitive with the valence isomerization and the N/T ratios apparently reflect the influence of these alkyl substituents on the ease of valence isomerization. The question is, what factors, i.e. steric or electronic, of the alkyl group dictate the observed N/T ratios?

Alkyl substituents operate either as electron donors via induction (Taft's σ^* scale[6]) in the order t-Bu > i-Pr > Et > Me, via hyperconjugation (Baker-Nathan effect[7]) in the order t-Bu < i-Pr < Et < Me, or as electron acceptors via polarizability (gas phase acidities[8]) in the order t-Bu > i-Pr > Et > Me. Clearly, only the two latter electronic effects can account for the observed trend in the N/T ratio. Thus, from the point of view of electronic effects, the t-butyl group could promote formation of (2N) endoperoxide either by less efficient electron donation via hyperconjugation or more efficient electron withdrawal via its polarizability, thereby explaining the observed t-Bu > i-Pr > Et > Me order in the N/T ratios. However, polarizability effects are gas phase phenomena and unlikely in condensed media, while hyperconjugative effects, which engages π-type interaction, are significant in cationic intermediates and excited states. These electronic factors can only play a minor role, if discernible at all, in the 1T $\rightleftharpoons$ 1N isomerization. Presumably steric factors must dominate the equilibrium to rationalize the observed order in the N/T ratio of endoperoxides.

Unquestionably, steric factors are operating in valence isomerization equilibria of substituted cycloheptatrienes.[1b,d,e] On one hand, unfavorable nonbonding interaction between the C_3-C_4 double bond and the alkyl substituent in the 1T isomer, obliges preferential population of the exo-7-alkyl ring invertomers (Eq. 1) Furthermore, in the two exo-forms 1T and 1N, steric compression between the 7-alkyl substituent and the hydrogens at $C_{1,6}$ is best relieved (cf. Dreiding models) in the norcaradiene valence isomer and follows the order t-Bu > i-Pr > Et > Me. Thus, on the basis of these steric effects, the 1T ⇄ 1N equilibrium should be progressively displaced in that order towards the 1N isomer. Consequently, the N/T ratio of endoperoxides should increase in the order t-Bu > i-Pr > Et > Me, as indeed observed (Table I). We conclude the singlet oxygenation of cycloheptatrienes is a valuable but qualitative tool to diagnose substituent effects on the 1T ⇄ 1N valence isomerization.

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