Products and Rates of Decomposition of Some *t*-Butyl Perthenoates

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Information concerning the behavior of free radicals formed in the decomposition of *t*-butyl perthenoates was obtained by the preparation of six such compounds and making an examination of the rates and products of their thermal decomposition in carbon tetrachloride. Kinetic determinations were conducted in the presence and absence of a radical scavenger. With scavenger present their decomposition rates were first order. In the absence of a scavenger their rates of decomposition were of apparent orders higher than first and increased with increasing initial perester concentration. This is taken as good evidence for an induced decomposition step superimposed on the first-order, spontaneous cleavage of the oxygen–oxygen bond. Examination of the decomposition rate constants, determined in the presence of a scavenger, shows that the presence of electron-donating substituents on the thiophene ring accelerates their decomposition rates while electron-withdrawing substituents have the opposite effect. In the absence of a scavenger, the slight decrease in the decomposition rates of the alkyl-substituted perthenoates may be the result of a self-retardation process.

The rate of decomposition of benzoyl peroxide has been shown[3,4] to follow a first-order rate law in a variety of reaction media. It increases slightly with increasing initial peroxide concentration in a given solvent and varies considerably in magnitude from one solvent to another. These facts indicate that the unimolecular cleavage of the peroxide is accompanied by a higher order reaction, very probably a radical-induced attack on undecomposed peroxide. Effective separation of the induced decomposition from the primary process can be accomplished by either the use of radical traps[5,6] which inhibit the induced process, or by its kinetic analysis.[3,6]

In contrast to the mode of decomposition of diacyl peroxides, a typical dialkyl peroxide such as di-*t*-butyl peroxide decomposes, in the gas phase, by a strictly first-order process which is independent of pressure.[7] In various solvents, di-*t*-butyl peroxide decomposes at essentially the same rate as it does in the gas phase[8] indicating that the simple unimolecular cleavage of the peroxide linkage is the rate-determining step and that it is uncomplicated by any induced chain process.

Blomquist[9-11] and his collaborators investigated the decomposition of *t*-butyl perbenzoates which are, in a sense, intermediate between the diacyl and dialkyl peroxides. Their results indicated that the decomposition of these peresters are essentially of the same complex nature as that of benzoyl peroxide.

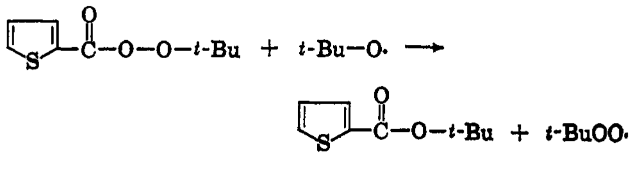
Schuetz and Teller[12] reported the initial kinetic studies on the thiophene analog of benzoyl peroxide, and found first-order rate constants for the thermal decomposition of a series of bis(2-thenoyl) peroxides in carbon tetrachloride in the presence of the radical scavenger 3,4-dichlorostyrene. The work described here reports the results of a continuing study of sulfur heterocyclic peroxides, that is, an investigation of the *t*-butyl perthenoates. These peroxides were prepared from the corresponding thenoyl chlorides and *t*-butyl hydroperoxide. Their rates of decomposition in carbon tetrachloride were studied using quantitative infrared techniques both in the absence and presence of styrene as a radical scavenger. The products of the decomposition of *t*-butyl 2-perthenoate in carbon tetrachloride and chlorobenzene were also examined.

Results and Discussion

The *t*-butyl perthenoates and several esters prepared in the course of this investigation are listed in Tables I and II. The infrared spectra of the perthenoates showed no contamination by acid or hydroperoxide.

The products isolated from the decomposition of *t*-butyl 2-perthenoate included 2-thenoic acid, acetone, carbon dioxide, and *t*-butyl 2-thenoate. A small quantity of a black, insoluble residue was also formed which was not further investigated. Quantitative determinations of the decomposition products were not experimentally feasible because of the numerous purification steps required to obtain such products in a pure form. However, the combined yields of acid and carbon dioxide accounted for approximately 75% of the total initial peroxide. The quantities of carbon dioxide evolved during the decomposition of the various peresters studied are summarized in Table III.

Acetone was an expected product of the decomposition of the *t*-butyl 2-thenoate since *t*-butoxy radicals are known to decompose into acetone and methyl radicals.[7] The formation of relatively large amounts of thenoic acid indicates that the thenoyloxy radical derived from the decomposition of the perthenoate is quite stable toward decarboxylation and reacts in the main by hydrogen abstraction. The ester, *t*-butyl 2-thenoate, which formed only in small amounts could have resulted from a direct attack of an initially formed *t*-butoxy radical on the carbonyl group of another perester molecule.



Reaction mechanisms proposed for ester formation during benzoyl peroxide decomposition cannot be im-

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[2] This work was taken in part from the Doctoral Thesis of J. L. Shea, 1963.

(3) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946).

(4) C. G. Swain, W. H. Stockmeyer, and J. T. Clark, *ibid.*, **72**, 5426 (1950).

(5) G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950).

(6) B. Barnett and W. E. Vaughan, *J. Phys. Colloid Chem.*, **51**, 926 (1947).

(7) J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 88 (1948).

(8) J. H. Raley, F. F. Rust, and W. E. Vaughan, *ibid.*, **70**, 1336 (1948).

(9) A. T. Blomquist and A. F. Ferris, *ibid.*, **73**, 3408 (1951).

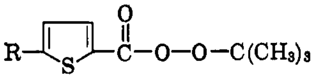
(10) A. T. Blomquist and A. F. Ferris, *ibid.*, **73**, 3412 (1951).

(11) A. T. Blomquist and I. A. Berstein, *ibid.*, **73**, 5546 (1951).

(12) R. D. Schuetz and D. M. Teller, *J. Org. Chem.*, **27**, 410 (1962).

TABLE I

ELEMENTAL ANALYSES OF THE *t*-BUTYL PERTHENOATES[a]

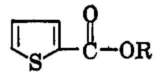


R	C, %		H, %		S, %		Halogen/nitrogen	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
H	53.98	53.95	6.04	5.85	16.01	16.12		
CH_3	55.79	56.00	6.56	6.50	14.89	14.96		
C_2H_5	57.87	57.60	7.06	6.86	14.04	14.21		
Cl	46.06	45.76	4.72	4.62			15.11	15.38
Br	38.72	39.01	3.97	4.14			28.63	28.50
NO_2	44.07	44.28	4.52	4.69			5.71	5.69

[a] Analyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich.

TABLE II

ELEMENTAL ANALYSES OF SEVERAL ESTERS[a]

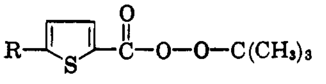


R	C, %		H, %		S, %		Halogen, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
t-Bu	58.66	58.64	6.56	6.37	17.40	17.69		
C_6H_5	64.70	64.79	3.92	4.11	15.70	15.89		
C_6H_5Cl	55.35	55.52	2.96	3.08	13.43	13.13	14.85	14.53

[a] Analyses were by Micro-Tech, Skokie, Ill.

TABLE III

AMOUNT OF CARBON DIOXIDE EVOLVED FROM THE DECOMPOSITION OF *t*-BUTYL PERTHENOATES IN CHLOROBENZENE



R	% carbon dioxide
H	15.7 ± 3
Br	28.7 ± 3
Cl	32.0 ± 3
CH_3	15.5 ± 3
C_2H^5	15.0 ± 3
NO_2	18.3 ± 3

portant in the decomposition of perthenoates, since neither the geminate recombination mechanism[13] nor the cyclic intramolecular process[14] would yield the *t*-butyl ester as a decomposition product.

The *t*-butyl 2-perthenoate was decomposed in a chlorobenzene solution with the object of being able to isolate a product or products which would elucidate the fate of the thenoyloxy radical. In addition to thenoic acid, a very small amount of what was very probably a mixture of two esters, phenyl 2-thenoate and *p*-chlorophenyl 2-thenoate was isolated. This result parallels those of Ford and Mackay[15] who decomposed bis(2-thenoyl) peroxide in chlorobenzene and isolated a mixture of these two esters.

Evolved carbon dioxide analyses were conducted by decomposing the peresters in chlorobenzene as a reaction media and absorbing the liberated gas on ascarite. The results (Table III) are somewhat difficult to rationalize. It would appear that the halogen-substituted peresters decrease the activation energy of the decarboxylation reaction probably through increased resonance stabilization of the thienyl radical. However, it would be expected that a nitro substituent should be capable of stabilizing the thienyl radical at least as well as a halogen. However, since the yields of carbon dioxide evolved depend on the relative rates of competing processes, it is very probably an oversimplification to describe the substituent effect to a single process; namely, decarboxylation. The anomaly in the result with the nitro substituent supports this view, and thus the above interpretation would be rather questionable.

Kinetic determinations were carried out in carbon tetrachloride as a reaction solvent in the presence and absence of the radical scavenger styrene using an initial perester concentration of approximately 0.03 *M*. The kinetics were determined by determining the rate of disappearance of the perester carbonyl infrared peak at approximately 5.7 μ.

The kinetic determinations obtained in the absence of any scavenger were treated by the Guggenheim[16] procedure for calculating apparent first-order rate constants. The kinetic determinations made in the presence of styrene scavenger showed good first-order rate constants for one half-life of the peresters, as shown by the linearity of a plot of the log absorbance *vs.* time. Further, the rates of decomposition remained unchanged when the initial perester concentrations were varied. Solutions of the unsubstituted perester at concentrations of 0.04 and 0.015 *M*, when decomposed at 123.5°, gave identical rate constants within experimental error.

It was not feasible experimentally to follow the reaction further than one half-life in these cases owing to the appearance of an absorption peak at approximately 5.85 μ caused by the formation of styrene esters. The rate constants and thermodynamic parameters are summarized in Tables IV and V.

Examination of the rate constants for the peresters decomposed in the presence of styrene shows that electron-donating substituents on the thiophene ring increase the rate of decomposition while electron-

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[13] G. S. Hammond, J. H. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955).

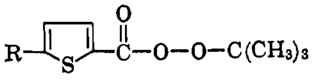
[14] D. F. Detar and C. Weis, *ibid.*, **78**, 4296 (1956).

[15] M. C. Ford and D. Mackay, *J. Chem. Soc.*, 4620 (1957).

[16] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

TABLE IV

DECOMPOSITION OF VARIOUS *t*-BUTYL PERTHENOATES IN CARBON TETRACHLORIDE



R	Temp., °C.	No inhibitor $k \times 10^3$ min.$^{-1}$	No inhibitor $t_{1/2}$, min.	0.2 *M* in styrene $k \times 10^3$, min.$^{-1}$	0.2 *M* in styrene $t_{1/2}$, min.
H	99.2	1.02	681	0.201	3448
	112.0	3.77	184	1.00	693
	124.5	16.4	42.3	4.14	165
CH_3	99.2	0.764	908	0.281	2452
	112.0	3.02	231	1.17	592
	124.5	15.0	46	4.79	145
C_2H_5	99.2			0.325	2132
	112.0	2.30	301	1.28	544
	124.5	15.0	46	4.77	145
Cl	99.2	0.924	750	0.138	5022
	112.0	2.88	240	0.576	1205
	124.5	10.4	67	2.66	260
Br	99.2	0.470	1475	0.135	5134
	112.0	1.69	410	0.714	972
	124.5	7.00	100	2.59	268

TABLE V

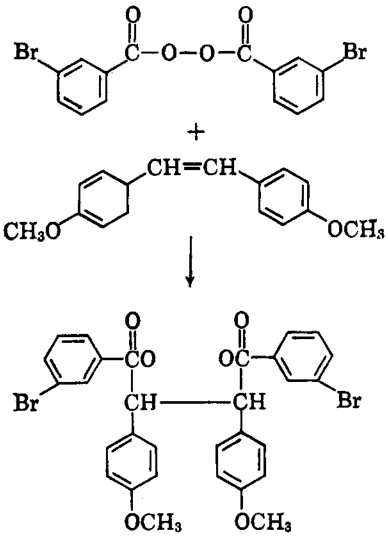
ACTIVATION PARAMETERS FOR VARIOUS *t*-BUTYL PERTHENOATES IN CARBON TETRACHLORIDE, 0.2 *M* IN STYRENE

R	E_a, kcal. mole^{-1}	S^*, e.u.
H	35.2 ± 1	16.8 ± 3
Cl	34.3 ± 1	13.8 ± 3
Br	34.3 ± 1	14.0 ± 3
CH_3	32.9 ± 1	11.4 ± 3
C_2H_5	31.2 ± 1	7.07 ± 3

withdrawing substituents have the opposite effect. These results parallel both those observed with benzoyl peroxides[4] and *t*-butyl perbenzoates.[9] As anticipated in a free-radical decomposition, substituent effects are not large.

The nitro-substituted perthenoate gave results markedly different from the other peresters. When this perester was decomposed in the presence of styrene, the reaction rate was found to be considerably faster than expected and it failed to follow a first-order rate law. These results suggests that the styrene, in this case, is not acting solely as a radical scavenger but that it is in some manner entering into a direct reaction with the perester, accelerating its decomposition. Blomquist[9] reported a similar acceleration when radical traps were added to a solution of *t*-butyl *p*-nitroperbenzoate and Swain[4] observed an acceleration on the decomposition rates of *p*-nitrobenzoyl peroxide by dichlorostyrene. Both authors have implied that the rapid, induced decomposition is a result of the electrical unsymmetry of the nitro-substituted compounds which makes them very susceptible to induced radical attack. A strongly electron-attracting group such as a nitro group could result in a rather polar oxygen–oxygen bond in the transition state which, in turn, could result in a partial ionic decomposition of the peroxide.

In an elegant investigation, Greene[17] and his collaborators reported definite evidence for a direct peroxide-olefin reaction in a benzoyl peroxide-stilbene system. Two 1:1 adducts of peroxide and olefin were isolated in good yield (84%). These products were the *meso*- and *dl*-benzoates, and they were not formed by a radical mechanism since only a very small number of radicals derived from the peroxide was observed during the reaction.



The apparent first-order rate constants obtained in the kinetic runs containing no styrene scavenger were determined by following for three or four half-lives the decomposition of the peresters. They are over-all rate constants for the perester decomposition and are the sum of at least two processes: namely, the spontaneous cleavage of the oxygen-oxygen bond and the induced cleavage caused by radical attack on the undecomposed perester. This is supported by the observation that the rate of decomposition of the unsubstituted perester increases with increasing perester concentration. At 112.0°, a solution 0.032 *M* in *t*-butyl 2-perthenoate had a half-life of 259 min. while a solution 0.038 *M* in perester had a half-life of 184 min.

When the rate of decomposition of the ethyl-substituted perester is compared with that of the unsubstituted compound, an anomaly is apparent. At 112.0°, the ethyl-substituted compound decomposed more slowly than the parent compound, suggesting that there is less induced decomposition in the first compound since the spontaneous cleavage should be faster in the case of the substituted perester. Such a proposal would

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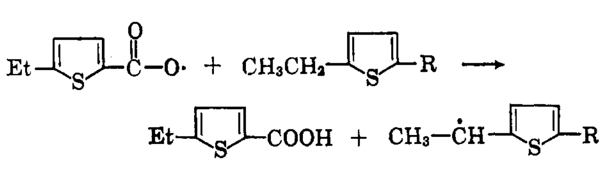
[17] F. D. Greene, W. Adam, and J. E. Cantrill, *J. Am. Chem. Soc.*, **83**, 3461 (1961).

require the removal from the reaction medium of the radical or radicals which are causing the induced decomposition. Since the thenoyloxy radical is probably responsible for most of the induced decomposition, its removal should result in a slower decomposition rate. The ethyl substituent is a ready source of easily abstractable hydrogen atoms and a thenoyloxy radical could remove a hydrogen from the methylene group of the substituent resulting in the formation of 5-ethyl-2-thenoic acid and the thiophene analog of a benzyl radical.



R = $-CO_3C(CH_3)_3$

The newly formed radical should be relatively more stable and therefore less reactive than the thenoyloxy radical due to delocalization of the electron throughout the aromatic π-electron system of the thiophene ring. The end result would be the removal of a reactive radical causing less induced decomposition and a slower rate of decomposition. This process could be termed an example of "self-retardation." Studies of the ethyl-substituted perester were carried out at varying concentrations to establish that it showed self-retardation.

The activation parameters show that the effect of the substituent on the thiophene ring has only a small effect on its decomposition rate. For the series of substituents H, Cl, and Br the activation energy and entropy values are all actually within experimental error. The methyl- and ethyl-substituted perthenoates had lower activation energies than the initial series of compounds mentioned. These results were expected since the electron-releasing alkyl groups would be expected to facilitate the decomposition of the perthenoates.

The gross mechanism of perthenoate decomposition appears to resemble the decomposition of the perbenzoates, that is, an induced decomposition step superimposed upon the spontaneous cleavage of the oxygen-oxygen bond. The induced step can be effectively eliminated by the use of a radical trap such as styrene. The nitro-substituted perthenoate reacts in an anomalous manner similar to the nitro-substituted perbenzoate.

At this juncture insufficient data has been obtained to permit postulating a tentative mechanism for the decomposition of perthenoate esters. In particular, the formation of *t*-butyl 2-thenoate from the decomposition of *t*-butyl 2-perthenoate requires further study.

Experimental

Reagents.—The carbon tetrachloride was purified following the procedure of Fieser.[18] Chlorobenzene was dried in contact with calcium chloride and distilled directly from phosphorus pentoxide. Styrene was distilled and used to prepare a 0.2 *M* solution in carbon tetrachloride, then stored as such at 0° in the dark. The perthenoate solutions were titrated with sodium thiosulfate for peroxide content according to the method of Silbert and Swern.[19]

Preparation of *t*-Butyl Perthenoate.—The peresters were prepared by the direct interaction of the appropriate thenoyl chloride with *t*-butyl hydroperoxide. The acid chlorides were prepared from the corresponding acids by their reaction with thionyl chloride.

The thiophene peroxyesters were synthesized using a modification of the experimental procedure reported by Blomquist and Berstein[11] in their synthesis of perbenzoates. In a typical preparation, 0.63 g. (0.007 mole) of *t*-butyl hydroperoxide and 0.42 g. of distilled water were mixed at 0° to obtain a 60% hydroperoxide solution. To the cold, stirred hydroperoxide solution was added simultaneously, 1.0 g. (0.0058 mole) of 2-thenoyl chloride and 1.5 g. of a 30% aqueous potassium hydroxide solution, with the aid of medicine droppers. The reaction mixture was stirred for 1 hr. at 0° and transferred to a small separatory funnel. Approximately 10 ml. of pentane was added and the aqueous layer was discarded. The pentane solution was washed five times with small portions of 5% sodium carbonate solution and then five times with small portions of water. The pentane solution was set aside overnight in contact with anhydrous magnesium sulfate. The drying agent was removed by filtration and the pentane was removed on a rotary evaporator retaining the colorless liquid residue in the evaporator for several hours. The peresters prepared by this procedure were all colorless liquids except for the nitro-substituted perester, which was a very light yellow solid, m.p. 55.5–56°. At Dry Ice temperature, the liquid peresters became glassy solids but failed to crystallize. All of the peresters gave acceptable carbon, hydrogen, and sulfur or functional group analyses (Table I). The infrared spectra of the peresters showed no contamination by hydroperoxide or acid.

Preparation of Esters.—The esters synthesized in the work were prepared in carbon tetrachloride from 2-thenoyl chloride and the required alcohol or phenol using pyridine to remove the liberated hydrogen chloride. Table II lists the analyses of these compounds.

Product Analyses.—The unsubstituted perthenoate, 2.0 g., dissolved in 40 ml. of carbon tetrachloride and sealed in a combustion tube was heated in an oven at 140° for 20 hr. After cooling, the low-boiling material was analyzed by vapor phase chromatography and showed three peaks. Two of these peaks gave identical retention times with acetone and carbon tetrachloride. The third peak was not identified. An infrared spectrum of the crude combustion mixture had no alcohol absorption peaks showing that no appreciable amount of *t*-butyl alcohol was formed as a decomposition product. Acetone was identified by preparation of its 2,4-dinitrophenylhydrazone which showed no melting point depression when mixed with an authentic sample. After removal of the major part of the carbon tetrachloride from the decomposition mixture, thenoic acid was isolated by extraction with 10% sodium hydroxide solution and acidification of the aqueous layer. A mixture melting point with an authentic sample of thenoic acid showed no depression. Following the extraction with base, the residual liquid of the decomposition mixture was washed with water and dried over magnesium sulfate. The remaining carbon tetrachloride was removed leaving a very small amount of a brown oil. After treatment with Norit and repeated, unsuccessful attempts to crystallize this oil, high vacuum distillation yielded a small quantity of a pure, colorless oil whose infrared spectrum was identical with that of an authentic sample of *t*-butyl thenoate.

t-Butyl perthenoate was also decomposed in chlorobenzene solution under the experimental conditions described above. In addition to thenoic acid, the only other material isolated was very probably a mixture of two esters, phenyl thenoate and *p*-chlorophenyl thenoate, as shown by an examination of the infrared spectrum of the material isolated and spectra of the pure esters.

Carbon Dioxide Analyses.—The peresters were dissolved in chlorobenzene and a measured aliquot of the reaction mixture was heated at its reflux temperature for a minimum period equivalent to 10 half-lives of the perester. The carbon dioxide which absorped on ascarite and determined gravimetrically. The results are given in Table III.

Kinetic Determinations.—The rates of decomposition were followed by measuring the rate of disappearance of the perester

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[18] L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, p. 283.

[19] L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

carbonyl peak at approximately 5.7 μ employing a Perkin-Elmer Model 21 recording infrared spectrophotometer. This method was chosen after repeated attempts to use the iodometric method of Silbert and Swern[18] proved unreliable with the later stages of a kinetic run.

The perester solutions in carbon tetrachloride were degassed, then sealed in thoroughly cleaned ampoules prepared from 9-mm. Pyrex tubing. The samples were immersed into an electrically heated oil bath controlled to ±0.2° by means of a Fisher-Serfass electronic relay. An equilibration time of 2 min. was allowed for the samples to reach bath temperature. At definite time intervals an ampoule was removed and immediately quenched by immersion in ice-water. The ampoules were stored at −70° until the completion of the kinetic run, then they were broken, and the sample was transferred directly to an infrared cell.

The rate constants determined are the average of at least two runs and are summarized in Table IV.

The energies of activation were calculated from a plot of the log of the rate constant *vs.* the reciprocal of the absolute temperature employing the method of least squares to determine the slope. The entropies of activation were calculated by the method of Foster, Cope, and Daniels.[20]

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(20) E. G. Foster, A. C. Cope, and F. Daniels, *J. Am. Chem. Soc.*, **69**, 1893 (1947).

The Products of Raney Nickel Desulfurization of Monothioketals[1]

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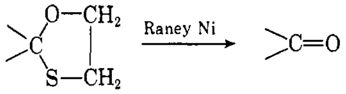
Desulfurization of the two stereoisomeric 4-*t*-butylcyclohexanone ethylene monothioketals (I) with Raney nickel in benzene at room temperature gave 4-*t*-butylcyclohexanone (53–55%), *cis*-4-*t*-butylcyclohexyl ethyl ether (12–14%), 4-*t*-butylcyclohexanone diethyl ketal (6–11%), 4-*t*-butylcyclohex-1-enyl ethyl ether (16%), and 4-*t*-butylcyclohexene (7–12%), in addition to much ethane and a little ethylene. Product composition was independent of the stereochemistry of the starting material. Similarly, the two 3-cholestanone ethylene monothioketals (II) gave 3-cholestanone (43–47%), 3α-ethoxycholestane (11–12%), 3-ethoxy-2-cholestene (20–21%), 3-cholestanone diethyl ketal (7–8%), and 2-cholestene (4–5%). The two isomers of 4-*t*-butylcyclohexanone trimethylene monothioketal (III) gave 4-*t*-butylcyclohexanone (47–48%), *cis*-4-*t*-butylcyclohexyl *n*-propyl ether (12%), 4-*t*-butylcyclohex-1-enyl *n*-propyl ether (16%), 4-*t*-butylcyclohexanone di-*n*-propyl ketal (7%), and 4-*t*-butylcyclohexene (7%). The recovery of the three-carbon fragment as propane (with traces of propylene and cyclopropane) was low in this case.

Desulfurization by Raney nickel, discovered but 25 years ago,[2] has become a reaction of considerable preparative significance.[3,4] One of its useful applications is in the removal of a protective monothioketal function to regenerate a ketone.[5] The course and mechanism of this reaction has been investigated by Djerassi and co-workers.[6,7]



These authors found[7] that in benzene solution one of the products of the Raney nickel treatment of monothioketals is the ethyl ether formed by simple hydrogenolytic removal of the sulfur atom. From the then only known 3-cholestanone ethylene monothioketal (m.p. 135–136°) they obtained, as the only ether product, 3α-ethoxycholestane (axial ethoxy group). From this finding it was inferred[7] that the starting monothioketal had the oxygen in the α- and the sulfur in the β-configuration, from which inference, in turn, conclusions were drawn regarding the mechanism of monothioketal formation. The implication that desulfurization involves retention of configuration in this case must be subject to doubt, however, since it has been shown[8] that the reaction is, in most instances, not stereospecific. Having at our disposal *both* stereoisomers of 3-cholestanone monothioketal[9a] (Figure 1: IIb,[9b] m.p. 112–113°, and IIa,[9b] 135–136°) as well as both stereoisomeric monothioketals of the simple model compound 4-*t*-butylcyclohexanone (Figure 1, Ia and Ib) of known configuration[9-11] we decided to reinvestigate the stereochemistry of thioketal hydrogenolysis.

In summary, the present results, discussed in greater detail below, indicate that *both* stereoisomeric 3-cholestanone monothioketals (Figure 1, II) give 3α-ethoxycholestane (axial ethoxyl) as the sole saturated ether product. Similarly, both 4-*t*-butylcyclohexanone ethylene monothioketals (Figure 1, I) give *cis*-4-*t*-butylcyclohexyl ethyl ether (axial ethoxyl) without any of the *trans* isomer and both 4-*t*-butylcyclohexanone trimethylene monothioketals (Figure 1, III)[11] give *cis*-4-*t*-butylcyclohexyl *n*-propyl ether uncontaminated by its stereoisomer. The reaction is therefore "stereoconvergent" (*i.e.*, both stereoisomeric starting materials give the same stereoisomeric product) rather than stereospecific (meaning that each stereoisomeric starting material gives the corresponding stereoisomeric product) as previously surmised.[7]

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(1) We gratefully acknowledge support of this work by a National Institutes of Health Grant (GM-08848) and by a grant-in-aid from Merck Sharp & Dohme, Inc. This paper is taken from the Ph.D. Dissertation of S. Krishnamurthy.

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