Discussion

Examples of reactions which reach equilibrium are rare in organic chemistry, and kinetic considerations are usually more useful than thermodynamics in predicting reaction products, particularly at the temperatures at which most carbon chemistry is studied (−100 to +200°). Notable exceptions are the rearrangements of various groups on the benzene nucleus[11] and scrambling of atoms other than carbon on carbon atoms.[12] Equilibrium considerations also sometimes outweigh kinetic ones in cases of structural isomerism (*e.g.*, *cis–trans* isomerization about double bonds or in aliphatic rings). However, the study presented here is one of the very few reported instances in which the distribution and structure of nonisomeric products is governed by stability considerations.

From the data presented herein, it is impossible to decide whether the observed equilibrium represents a reversible metastable situation or truly corresponds to an infinite equilibration time. This problem will be solved when accurate thermodynamic information is obtained on the chlorocarbons. Although little pertinent data are available to permit comparison of the chlorocarbon system with other branches of carbon chemistry, some recent investigations of the aromatization of hydrocarbons[13] strongly suggest that a metastable equilibrium analogous to eq. 2 may have been approached in the hydrocarbon system; *i.e.*

$$9C_2H_6 \rightleftarrows 12CH_4 + C_6H_6 \tag{8}$$

In pyrolyses conducted at 10 atm. and 700° for 7 sec., both pentane–hydrogen and heptane–hydrogen mixtures yielded products containing methane, ethane, ethylene, benzene, and toluene (C_3 and higher aliphatics are formed, but they are shown to decrease as the reaction time increases). Furthermore, the data show that the heptane mixture produces a higher proportion of aromatics than does the pentane mixture; the authors interpreted this in kinetic terms, noting that the C_7 backbone gives rise initially to larger concentrations of olefins, which are presumably intermediates in the aromatization. We have shown, however, that these temperature–time conditions[14] are adequate for equilibrium reshuffling of the carbon skeleton, and we think that the higher proportion of aromatics in the heptane mixture may be attributed to the lower H/C ratio in that mixture (*i.e.*, 2.8 for the heptane–hydrogen mixture *vs.* 3.2 for the pentane–hydrogen mixture).

No carbonization was observed below 750° in the hydrocarbon experiments referred to above, although this is somewhat unexpected in view of the free-energy changes of the two reactions at 700°.

$$9C_2H_6 \rightleftarrows 12CH_4 + C_6H_6 \quad \Delta F = -86 \text{ kcal.} \tag{9}$$

$$9C_2H_6 \rightleftarrows 13.5CH_4 + 4.5C \quad \Delta F = -139 \text{ kcal.} \tag{10}$$

As one of us has discussed in detail elsewhere,[15] complete thermodynamic equilibrium in the hydrocarbons should lead only to methane and char. That this is not observed except at very high temperatures or long reaction times is due to there being no low-energy route for converting benzene to carbon. It is interesting to note that the free-energy change for reaction 1 is −36 kcal. as calculated from the average equilibrium constant at 400° (3×10^{11} from Table I) as compared to −54 kcal. for reaction 8 at the same temperature.

Acknowledgment.—We wish to thank Dr. Harold Weingarten for helpful discussions concerning the reaction mechanism.

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[11] *E.g.*, D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **79**, 5953 (1957); H. Weingarten, *J. Org. Chem.*, **27**, 2024 (1962).

[12] *E.g.*, G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, **66**, 931 (1944), describe equilibration of CCl_4 with CBr_4 to give all the mixed species. Exchange of parts between molecules having broken sequences of carbon atoms in their backbone (*e.g.*, C–O–C, C–N–C, etc.) occurs rather readily through scission of C–O or C–N bonds. This is exemplified by the well-known interchange reactions in condensation polymers; *e.g.*, P. J. Flory, "High-Molecular-Weight Organic Compounds," R. E. Burke and O. Grummitt, Ed., Interscience Publishers, Inc., New York, N. Y., 1949, p. 246.

[13] A. C. Reeve and R. Long, *J. Appl. Chem.* (London), **13**, 176 (1963).

[14] Assuming an activation energy of 70 kcal. (approximately the C–C bond energy), for the reactions involved in these equilibrations, a reaction at 700° should be about 10^7 times faster than it would be at 400°. Equilibration of the chlorocarbons in this work was shown to be essentially complete in 10^7 sec. at 405°, thus placing it on roughly the same time scale as the hydrocarbon work of ref. 13.

[15] D. W. Matula, L. C. D. Groenweghe, and J. R. Van Wazer, *J. Chem. Phys.*, in press; also see J. R. Van Wazer, *Am. Scientist*, **50**, 450 (1962).

[Contribution from the Department of Chemistry, The Upjohn Co., Kalamazoo, Michigan]

α-Halosulfones. IV. A Facile Conversion of Mercaptans to Homologous Terminal Olefins[1]

By Leo A. Paquette[2]

Received May 9, 1964

A procedure is described by which mercaptans which have at least one α-hydrogen atom can be readily converted in good yields to terminal olefins containing one additional carbon atom. Application of the described principle to *p*-chloromethanesulfonylphenol did not result in an Ar_1-3 assisted solvolytic rearrangement.

The ready conversion of carbonyl compounds to olefins by the action of suitable alkylidene and arylidene triphenylphosphoranes, now commonly known as the Wittig reaction,[3] has met with a large degree of success. The frequent use of this reaction by numerous groups of workers demonstrates not only the versatility of the method, but also the need for olefins in a large array of synthetic organic chemical problems.

During the course of our studies of the Ramberg–Bäcklund rearrangement of α-halosulfones[4] we have

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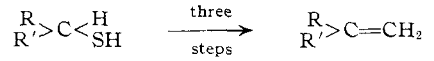
[1] Part III: L. A. Paquette, *J. Org. Chem.*, **29**, 2854 (1964).

[2] Correspondence should be addressed to the Department of Chemistry, The Ohio State University, Columbus 10, Ohio.

[3] For recent reviews on this subject see (a) S. Trippett, "Advances in Organic Chemistry," Vol. I, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 83; (b) U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959); (c) J. Levisailles, *Bull. soc. chim France*, 1021 (1958).

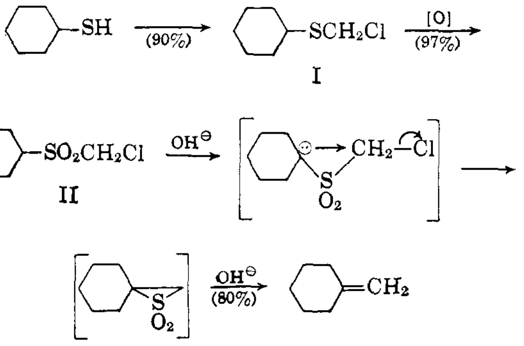
[4] L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4089 (1964).

discovered a reaction sequence which readily converts mercaptans possessing at least one α-hydrogen to homologous terminal olefins according to the equation



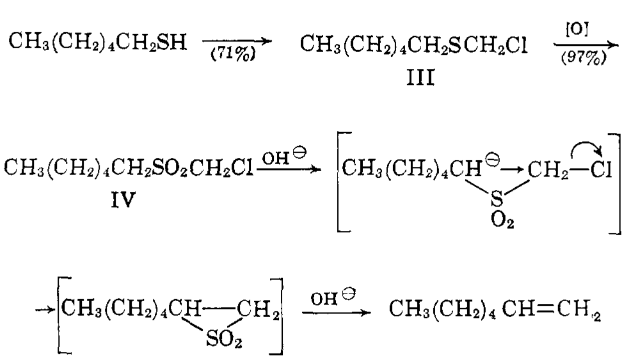
$$\begin{matrix}R\\R'\end{matrix}\!>C<\!\begin{matrix}H\\SH\end{matrix} \xrightarrow[\text{steps}]{\text{three}} \begin{matrix}R\\R'\end{matrix}\!>C{=}CH_2$$

Cyclohexylmercaptan and 1-hexanethiol were chosen as examples of this facile conversion because of their commercial availability. Treatment of cyclohexylmercaptan with paraformaldehyde and hydrogen chloride according to the procedure of Walter, Goodson, and Fosbinder[5a] afforded a 90% yield of chloromethyl cyclohexyl sulfide (I). *m*-Chloroperbenzoic acid oxidation of I in chloroform gave the related sulfone II in near quantitative yield. When II was refluxed in 25% aqueous sodium hydroxide for 24 hr. and the product extracted with ether and carefully distilled, methylenecyclohexane was obtained in 80% yield. Assignment of structure to this solvolytic rearrangement product was achieved by a comparison of its infrared spectrum and vapor phase chromatography (v.p.c.) retention time with that of an authentic sample. Careful v.p.c. examination of the isolated olefin indicated it to be of 98+% purity. This important observation demonstrates that the position of the resulting double bond formed in this reaction remains terminal despite the fact that it occupies an energetically unfavorable position.[6,7] Thus, cyclohexylmercaptan was converted in three synthetic manipulations to methylenecyclohexane in 70% over-all yield.



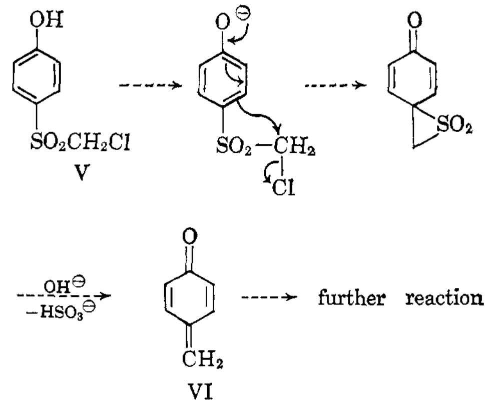
In similar fashion, *n*-hexylmercaptan could be converted *via* its corresponding chloromethyl sulfide III and chloromethyl sulfone IV to heptene-1 in 54% over-all yield. That the reaction product was indeed the desired one was again proved by correlation of infrared spectrum and v.p.c. retention time with that of pure heptene-1. The purity of the solvolysis product was greater than 97%.

In summary, it may be stated that mercaptans can be satisfactorily converted to terminal olefins containing one additional carbon atom by a relatively simple three-step procedure. The limitation of the method resides in the necessity that the moiety bearing the sulfhydryl group be stable to strong acid (step 1) and strong alkali (step 3).



The ease with which mercaptans condense with hydrogen chloride and aldehydes of greater molecular weight than formaldehyde[5b,8] may allow the conversion of mercaptans to internal olefins of any desired length through the use of the same procedure.

The Inability of the Chloromethylsulfonyl Group to Undergo Ar$_1$-3 Assisted Solvolysis.—The success of the procedure described above prompted us to explore the possibility of utilizing the chloromethylsulfonyl group in an Ar$_1$-3 participation reaction.[9] More specifically, it appeared highly probable that *p*-chloromethanesulfonylphenol (V)[10] with suitable ionization could lead to *p*-quinonemethide (VI)[11] *via* an Ar$_1$-3 solvolytic rearrangement process similar to the intramolecular process discussed above. Prolonged (3–7 days) heating (100–160°) of V with excess (3.5 molar equivalents) potassium hydroxide in water or aqueous diglyme mixtures afforded, in each case, a 75–95% recovery of V, identified by mixture melting determination, comparison of infrared spectra and, in some cases, reanalysis of the sulfur content of the recovered material. When excess potassium *t*-butoxide in *t*-butyl alcohol was employed as the source of base, a 72% recovery of V was obtained.



The surprising stability of V under these forcing conditions suggests that the negative charge in the phenoxide moiety is strongly delocalized; the net result is to render the *p*-carbon atom considerably less nucleophilic than in the more favorable cases of Ar$_1$-participation observed to date.[12] In their study of the effect

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(5) (a) L. A. Walter, L. H. Goodson, and R. J. Fosbinder, *J. Am. Chem. Soc.*, **67**, 655 (1945); (b) *ibid.*, **67**, 657 (1945).

(6) For a discussion of the relative stabilities of endocyclic and exocyclic double bonds in cyclic systems see H. C. Brown, J. H. Brewster, and H. Shechter, *ibid.*, **76**, 467 (1954).

(7) The lack of isomerization of the terminal olefins under the conditions of the Ramberg–Bäcklund reaction is undoubtedly attributable to the fact that they form part of a heterogeneous system. For recent work on base-catalyzed isomerizations of *exo*- to *endo*-olefins in a homogeneous medium, see A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *ibid.*, **84**, 3164 (1962).

(8) H. Böhme, L. Tils, and B. Unterhalt, *Chem. Ber.*, **97**, 179 (1964), and leading references contained therein.

(9) For an explanation of this terminology see S. Winstein and R. Baird, *J. Am. Chem. Soc.*, **79**, 756 (1957), and references cited therein.

(10) B. C. Jain, B. H. Iyer, and P. C. Guha, *J. Indian Chem. Soc.*, **24**, 220 (1947).

(11) For an excellent summary of the present state of *p*-quinonemethide chemistry see J. D. McClure, *J. Org. Chem.*, **27**, 2365 (1962).

(12) Many examples of Ar$_1$-participation are summarized by R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **84**, 788 (1962).

of the p-CH_3SO_2 group on the acid dissociation constants of benzoic acid, phenol, and the anilinium ion, Bordwell and Copper[13] have likewise observed evidence indicating appreciable conjugative effects for the p-sulfone group even in the ground state. Therefore, the inability of V to undergo an Ar_1-3 assisted solvolysis can be rationalized by considerable charge delocalization in the phenoxide moiety.

Experimental[14]

Chloromethyl Cyclohexyl Sulfide (I).—Cyclohexylmercaptan was treated with paraformaldehyde and anhydrous hydrogen chloride according to the method of Walter, Goodson, and Fosbinder[5] to give I as a colorless, foul-smelling liquid, b.p. 99–102° (14 mm.).

Chloromethyl Cyclohexyl Sulfone (II).—To a stirred solution of 34.5 g. (0.20 mole) of m-chloroperbenzoic acid in 400 ml. of chloroform cooled to -5 to $-10°$ was added dropwise over 15 min. 16.5 g. (0.10 mole) of chloromethyl cyclohexyl sulfide. When the addition was completed, the contents were allowed to warm to room temperature and kept overnight in this condition. The insoluble m-chlorobenzoic acid was removed by filtration and washed with chloroform. The combined filtrate and washings were shaken with 10% sodium carbonate solution, dried, filtered, and evaporated to give 19.0 g. (97.0%) of a colorless oil which crystallized on scratching, m.p. 35–39°. Pure II was obtained as shiny white plates from ether–hexane; m.p. 51°, ν^{Nujol} 1300 and 1135 cm.$^{-1}$ (SO_2).

Anal. Calcd. for $C_7H_{13}ClO_2S$: C, 42.74; H, 6.66; S, 16.30; Cl, 18.03. Found: C, 43.01; H, 6.90; S, 16.38; Cl, 17.93.

Methylenecyclohexane—A mixture of 5.9 g. (0.03 mole) of II and 50 ml. of 25% aqueous sodium hydroxide solution was refluxed with stirring for 24 hr. The flask was cooled and the liberated oil was extracted with ether and the combined ethereal layers were washed with water and dried. The dried ethereal solution was carefully distilled at atmospheric pressure through a 2-ft. Vigreux column to remove the major portion of the ether. The residual colorless liquid was subsequently carefully distilled through a 1-ft. Vigreux column to give 2.3 g. (80%) of methylenecyclohexane, b.p. 97–99°.

Chloromethyl n-Hexyl Sulfide (III).—1-Hexanethiol (Eastman White Label) was treated with paraformaldehyde and anhydrous hydrogen chloride according to the method of Walter, Goodson, and Fosbinder[5] to give III as a colorless, foul-smelling liquid, b.p. 90–93° (13 mm.).

Chloromethyl n-Hexyl Sulfone (IV).—A 0.10-mole sample (16.7 g.) of II was oxidized as described above for II to give 19.2 g. (97.0%) of white solid, m.p. 47–50°. Pure IV was obtained as a white solid from ether–hexane; m.p. 50.5–51.5°, ν^{Nujol} 1300 and 1135 cm.$^{-1}$ (SO_2).

Anal. Calcd. for $C_7H_{15}ClO_2S$: C, 42.31; H, 7.61; S, 16.14. Found: C, 42.36; H, 7.72; S, 16.60.

Hexene-1.—A mixture of 9.9 g. (0.05 mole) of IV and 75 ml. of 25% aqueous sodium hydroxide solution was refluxed overnight with stirring. The resulting heptene-1 was isolated as described above for methylenecyclohexane to give 3.8 g. (77.6%) of colorless liquid, b.p. 88–92°.

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[13] F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **74**, 1058 (1952).

[14] Melting points and boiling points are uncorrected. An F and M Model 500 gas chromatograph equipped with a 20% Carbowax-packed column (0.25 in. × 4 ft.) was employed for the v.p.c. analyses. The author is indebted to the Physical and Analytical Chemistry Department of The Upjohn Co. for the microanalytical and spectral determinations.

[CONTRIBUTION FROM SHELL DEVELOPMENT CO., EMERYVILLE, CALIF.]

Inhibition Reactions of Hindered Phenols[1]

BY G. M. COPPINGER

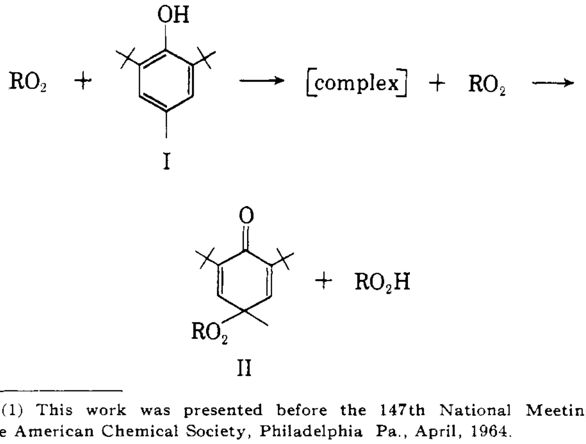
RECEIVED JUNE 1, 1964

The principal alternative descriptions of oxidative chain inhibition by hindered phenols have been examined with reference to products found in model peroxy radical hindered phenol systems. An alternative description involving a charge-transfer complex between peroxy radical and phenol is presented.

Introduction

There has existed for some time two general and different views of the course of the inhibition reactions of hindered phenols in oxidizing substrates.

Hammond and Boozer[2] found that the rate of inhibition of oxidation in which the propagating species was a peroxy radical was first order in peroxy radical and half order in inhibitor. They concluded from this that the transition state of the rate-determining step involves two peroxy radicals and one molecule of phenol. They suggested that there must be a complex formed between a peroxy radical and the phenol as the rate-determining step.



I

II

Both Ingold[3a] and Shelton[3b] have observed that when the hydroxyl hydrogen is replaced by deuterium a kinetic isotope effect is observed in the rate of inhibition. The ratio k_H/k_D is somewhere between 6 and 10 at room temperature. From this both Ingold[3a] and Shelton[3b] have concluded that the rate-determining step is abstraction of a hydrogen atom from the phenol hydroxyl group by a peroxy radical with formation of a phenoxyl free radical, which subsequently reacts with a second peroxy radical. In all investigations of this problem in which the propagating species is a peroxy radical, the products observed from the inhibitor were peroxycyclohexadienones of the type II.[2-4] It seems to us that it might be possible to distinguish between these two descriptions by examination of the reactivity of phenoxy free radicals under conditions which parallel, as closely as experimental

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[1] This work was presented before the 147th National Meeting of the American Chemical Society, Philadelphia Pa., April, 1964.

[2] G. S. Hammond, C. E. Boozer, *et al.* *J. Am. Chem. Soc.*, **77**, 3233, 3238 (1955);

[3] (a) K. U. Ingold and J. A. Howard, *Can. J. Chem.*, **40**, 1851 (1962); (b) J. R. Shelton and D. W. Vincent, *J. Am. Chem. Soc.*, **85**, 2433 (1963).

[4] T. W. Campbell and G. M. Coppinger, *ibid.*, **74**, 1469 (1952); A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).