

Fig. 2.—Dimethyl sulfoxide with *cis*-4-*t*-butylcyclohexanol.

It is interesting to note that not only is the chemical shift of the hydroxyl proton a function of stereochemistry, but the slope of the line relating the chemical shift with concentration in carbon tetrachloride is also. As was previously pointed out,¹⁰ one would expect the hydroxyl group in the axial position to be less hydrogen bonded than in the equatorial position. In the axial position the hydroxyl group can probably be bonded best with the hydrogen directly away from the plane of the ring. The slopes for *cis*-4-*t*-butylcyclohexanol and *trans*-4-*t*-butylcyclohexanol are 2510 and 3160 c.p.s./ N_{ROH} respectively. The slopes for

1-ethynyl-*cis*-4-*t*-butylcyclohexanol and 1-ethynyl-*trans*-4-*t*-butylcyclohexanol are 690 and 1060 c.p.s./ N_{ROH} respectively. This phenomenon is currently being investigated for the purpose of determining whether the slope of the concentration-chemical shift relationship can be useful in confirming and assigning stereochemistry.

Experimental

Carbon tetrachloride was distilled at atmospheric pressure in a dry system under nitrogen. Pyridine and dimethyl sulfoxide were distilled from calcium hydride under reduced pressure. The dimethyl sulfoxide was stored over Linde Molecular Sieve 4A. Tetramethylsilane was added to all solvents to produce solutions that were approximately 0.001 mole fraction in internal standard.

All glassware was dried and placed in a vacuum desiccator. All manipulations were carried out under a nitrogen atmosphere to eliminate uptake of atmospheric moisture. Solutions were prepared in 2- and 5-ml. volumetric flasks and the weights of compound and solvent were determined by difference.

Spectra were obtained with a Varian Associates A-60 spectrometer. The probe temperature was 40°. The chemical shifts were determined to 0.2 c.p.s. The position of the *t*-butyl hydrogen and solvent signals where applicable were used as additional internal references.

[CONTRIBUTION FROM MONSANTO CHEMICAL CO., CENTRAL RESEARCH DEPARTMENT, ST. LOUIS, MISSOURI]

Equilibrium Rearrangement of Perchlorocarbon Compounds

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By heating any perchlorocarbon compound or mixture of compounds having an over-all mole ratio of chlorine to carbon between 1 and 4, an equilibrium is reached in a closed condensed fluid system between hexachlorobenzene, carbon tetrachloride, and smaller amounts of hexachloroethane; no carbonization was observed under any conditions investigated. The equilibrium constant is reported for the temperature in the 400–460° range and data on the kinetics of decomposition of octachloropropane are discussed in terms of a probable free-radical mechanism. The aromatization reaction which gives rise to hexachlorobenzene is shown to be reversible.

In the past, high-temperature reactions of perchlorocarbon compounds have been studied by an open system or flow techniques.^{2,3} Some short-time studies have also been made under pressure.^{4,5} However, the present work is believed to be the first investigation of the interconversion of these compounds under conditions where chemical equilibration is demonstrable. The equilibrium involves both aromatic and aliphatic carbon structures—with the proportions of the various compounds present in equilibrium depending only on the ratio of chlorine to carbon in the starting mixture. In those studies^{2,6} in which activated carbon was used as a catalyst, it is not clear whether carbon is formed during the reaction. Therefore, no such catalyst was employed in the studies reported below.

Experimental Section

Reagents.—The materials used were the purest grade commercially available products and were further purified when gas

chromatography indicated more than 1% of impurities. The carbon tetrachloride was Baker and Adamson reagent grade material, and the tetrachloroethylene (redistilled), hexachlorobenzene, and hexachloroethane were Eastman White Label products. The octachloropropane from Columbia Organic Chemicals, Columbia, S. C., was found to have 11.5% C and 88.5% Cl, with no H or O (theory: 11.3% C, 88.7% Cl). The hexachlorobutadiene, hexachloropropene, and hexachlorocyclopentadiene, obtained from K and K laboratories, Jamaica 33, N. Y., exhibited the physical constants reported in the literature.

Equilibration.—The reactions were conducted in sealed Pyrex tubes (o.d. 6 mm., i.d. 4 mm.) which were placed inside steel guard-tubes during heating. [The 1-mm. glass wall thickness was found to withstand adequately the pressures (up to ca. 200 atm.) developed.] In all cases, the tubes were sealed so as to have the liquid nearly filling their entire volume (ca. 95%) at the reaction temperature so that, for practical purposes, only a single phase was considered to be present. Heating was carried out for the desired length of time in one of three furnaces held at 345 ± 15°, 405 ± 4°, and 455 ± 4°. Occasional visual observation of the heated tubes indicated that those having high values of $R \equiv \text{the Cl/C over-all mole ratio}$ were supercritical. In order to fix the zero time in the kinetic studies of the decomposition of octachloropropane and of hexachloroethane, the sealed glass tubes were inserted in the steel guard-tubes which had been preheated to the reaction temperature. At the end of a given run, the tube was quenched in cold water. For these two rate studies, the furnace temperatures were maintained at 350 ± 3° and 400 ± 3°, respectively.

Analysis.—A Microtek GC-2500 dual column gas chromatograph was used for analysis, employing a thermal-conductivity detector and a variable-temperature programmer. The 5-ft. long column was packed with a sorbent consisting of 10% Dow-

(1) On leave of absence from the Plastics Division of Monsanto, 1962.

(2) M. Schmeisser, H. Schröter, and H. Schilder, *Chem. Ber.*, **95**, 1648 (1962).

(3) V. V. Korshak, Yu. A. Strepikheev, and L. F. Verlatova, *J. Gen. Chem. USSR*, **17**, 1626 (1947); *Chem. Abstr.*, **42**, 3721b (1948); J. A. Krynetsky and H. W. Carhart, *J. Am. Chem. Soc.*, **71**, 816 (1949); D. R. Bidinosti and R. F. Porter, *ibid.*, **83**, 3737 (1961).

(4) F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 295 (1950).

(5) M. G. Gonikberg, V. M. Zhulin, and V. P. Butuzov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 730 (1956); *Chem. Abstr.*, **51**, 1815c (1957); M. G. Gonikberg and V. M. Zhulin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 510 (1957); *Chem. Abstr.*, **51**, 16,274h (1957).

(6) A. M. Goodall and K. E. Howlett, *J. Chem. Soc.*, 2599 (1954).

TABLE I
 CHLOROCARBON EQUILIBRIA

Temp., °C.	Starting materials (mole %)							Equilibrated products (mole %)					$K \times 10^{-11}$ (mole fract.)
	R = C ₁ C	CCl ₄	C ₂ Cl ₄	C ₂ Cl ₆	C ₃ Cl ₆ ^e	C ₄ Cl ₆ ^e	C ₆ Cl ₆	R = C ₁ /C	CCl ₄	C ₂ Cl ₄	C ₂ Cl ₆	C ₆ Cl ₆	
405 ^a	3.50	96.9	0	0	0	0	3.1	3.47 ^c	93.5	0.3	2.9	2.9	9
	3.00	92.3	0	0	0	0	7.7	3.05 ^c	89.3	.2	3.5	6.7	2.2
	3.00	0	0	100	0	0	0	3.01 ^c	88.2	.4	4.2	7.0	0.4
	2.50	85.7	0	0	0	0	14.3	2.51 ^c	81.9	.4	3.8	13.7	0.8
	2.00	75.0	0	0	0	0	25.0	2.03 ^c	71.9	.5	3.3	24.0	1.0
	2.00	0	100	0	0	0	0	2.33 ^d	78.5	.5	3.8	17.0	0.6
	2.00	0	0	0	100	0	0	2.23 ^d	77.3	.4	3.2	19.0	7.1
	1.50	54.5	0	0	0	0	45.5	1.49 ^c	50.0	.0	3.5	46.1	0.014
	1.50	0	0	0	0	100	0	1.63 ^d	56.6	.6	4.2	38.2	0.008
	455 ^b	4.00	100	0	0	0	0	0	4.00	100	0	0	0
3.00		92.3	0	0	0	0	7.7	3.11	90.8	0	3.1	6.0	7.2
3.00		0	0	100	0	0	0	3.09 ^c	89.9	0	3.5	6.4	2.3
2.00		75.0	0	0	0	0	25.0	1.97	71.3	0	3.2	25.5	1.2
455 ^a	1.00	0	0	0	0	0	100	1.00	0	0	0	100.0	...

^a The data correspond to 5 months at this temperature. ^b Three weeks instead of 5 months. ^c The equilibrium mixtures contained 0.3–0.4% of an unknown of molecular weight ≈ 245 . ^d Insoluble white solid present. ^e C₃Cl₆ is hexachloropropene and C₄Cl₆ is hexachlorobutadiene.

Corning 710 silicone gum on a Chromosorb substrate. The temperature was programmed so as to increase from 80 to 280° at a rate of 20°/min. Integration was carried out by direct measurement of the recorded peak areas. Small corrections for differences in the thermal conductivity of the various constituents of a mixture were established by running known mixtures of widely varying composition.

Before opening, each reaction tube was cooled in Dry Ice. The contents of the tubes were removed quantitatively and dissolved in a minimum amount of mesitylene. This solvent was employed to facilitate introduction of the sample into the gas chromatograph and to assure uniform sampling. Mesitylene was chosen because it did not interfere in the analysis by coinciding in emergence time with any of the chlorocarbons.

The conditions employed were found to give separation primarily on the basis of molecular weight. Of the compounds tested (CCl₄, C₂Cl₄, C₂Cl₆, C₃Cl₆, C₃Cl₈, C₄Cl₆, C₅Cl₆, and C₆Cl₆), only hexachlorobenzene failed to fall on a straight-line plot of emergence temperature vs. molecular weight. In this plot, a molecular weight of 150 corresponded to an emergence temperature of 55° and 300 to 145°. The hexachlorobenzene exhibited an emergence temperature of 180° instead of the 135° expected for a non-cyclic unconjugated chlorocarbon of the same molecular weight.

In all the experiments with hexachloroethane, octachloropropene, and mixtures of hexachlorobenzene and carbon tetrachloride, the ratio of chlorine to carbon in the products was within ± 0.1 of that in the starting material (see Table I) indicating good recovery of products and confirming peak assignments. In experiments starting with tetrachloroethylene, hexachloropropene, and hexachlorobutadiene, the chlorine to carbon ratio was slightly high and an insoluble white solid was present which presumably was a polymeric substance with an over-all Cl/C ratio less than 1.

Results

Equilibrium Rearrangements.—In this work, we have found that in a closed system, carbon tetrachloride, hexachloroethane, and hexachlorobenzene are the principal (>1% of the reaction mixture) stable end products of perchlorocarbon rearrangements at temperatures near 400°. Neither tetrachloroethylene, hexachlorobutadiene, nor the C₃ and higher saturated aliphatic compounds are present to an appreciable extent. Surprisingly, no carbonization occurs, even after prolonged heating (4 months) at 450°. In addition, the formation of hexachlorobenzene by aromatization of aliphatics is shown to be reversible by the ready reaction of this compound with carbon tetrachloride to form hexachloroethane.

A series of pilot runs showed that the change in composition with time became extremely slow with respect to the prior change after 3 months at 405°. But the

reactions were still proceeding in many cases after 5 months at 345°, while at 455° the reactions had effectively reached completion in ca. 2–3 weeks.

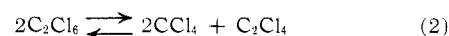
The equilibrium between the three observed compounds is given by the expression

$$K = [\text{CCl}_4]^{12}[\text{C}_6\text{Cl}_6]/[\text{C}_2\text{Cl}_6]^9 \quad (1)$$

As shown in Table I, for mixtures quenched from temperatures in the range of 400–460°, the average value of this constant⁷ is 2.7×10^{11} , with a standard deviation of 1.4×10^{11} . That this is indeed a true equilibrium condition is demonstrated by approaching it from both sides. Thus, in Table I, it can be seen that C₂Cl₆ and a 12:1 mixture of CCl₄ and C₆Cl₆ give essentially the same mixture at equilibrium. Within experimental error, the equilibrium data of Table I corresponding to 405° are not statistically different from those at 455°, so that the best estimate of the enthalpy of the reaction underlying eq. 1 is that it is between 0 and –25 kcal.

The 100-fold variation in the individual values of the equilibrium constant in Table I is probably attributable to incomplete equilibration. This variation does not seem to be caused by the effect of pressure, since the mixtures which contain the highest proportion of CCl₄ and therefore are under the greatest pressure do not show the lowest numerical values for the equilibrium constant.

Tetrachloroethylene was observed as an intermediate in the decomposition of hexachloroethane and was present in appreciable quantities during the early stages of the decomposition (Fig. 2). However, it was not seen (<1%) in the equilibrium mixtures nor was it detected in the mixtures of carbon tetrachloride and hexachlorobenzene at any stage in their approach to equilibrium. These observations show the importance of the following disproportionation in the early stages of the equilibration.



In none of the pilot studies or those reported in Table I was the formation of carbon observed. However,

(7) At the high pressures used, the equilibrium should be expressed in fugacities. However, the lack of appropriate data on hexachloroethane and hexachlorobenzene for calculating fugacities has necessitated the use of concentration terms. The extreme sensitivity of the equilibrium expression (eq. 1) to errors in the concentrations of CCl₄ and C₂Cl₆ is undoubtedly partly responsible for the large standard deviation.

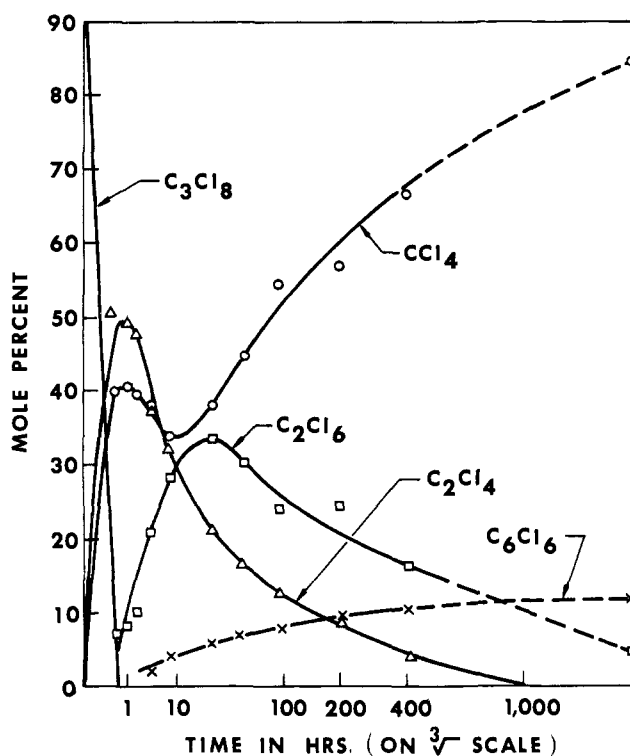
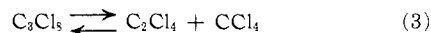


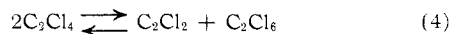
Fig. 1.—Thermal decomposition of octachloropropane at 350°.

when hexachlorobutadiene or hexachloropentadiene were heated at 405° for 5 months, a small amount of white solid was formed which was insoluble in the reaction mixture itself and in the solvent used to transfer the mixtures to the gas chromatograph. From the material balance, it would appear that this substance is an initially formed product (which undergoes further reaction extremely slowly, if at all) exhibiting an over-all Cl/C mole ratio ≤ 1 . From its properties, this material appears to be a network polymer incorporating ring structures but with little long-range π -bond conjugation.

Kinetic Studies.—The disproportionation of octachloropropane at 350° and of hexachloroethane at 400° was chosen for a detailed rate study. The results for the octachloropropane case are shown in Fig. 1, in which it should be noted that the C_3Cl_8 disappeared within half an hour and that equilibrium is reached in about 4 months. The over-all kinetic process may be formally treated in terms of disproportionation reactions, of which the initial one for Fig. 1 is



In view of the isolation of dichloroacetylene by Schmeisser, *et al.*,² this compound may reasonably be an intermediate in the formation of hexachlorobenzene, since it is known that it trimerizes to the latter.⁸ The dichloroacetylene may arise from tetrachloroethylene *via* disproportionation reactions such as those shown in eq. 4 or 5:



Reactions 2–5 may be used to explain the rate curves of Fig. 1, with the decrease (which appears after the first hour) in the amount of carbon tetrachloride being at-

(8) E. Ott and G. Dittus, *Ber.*, **76b**, 80 (1943).

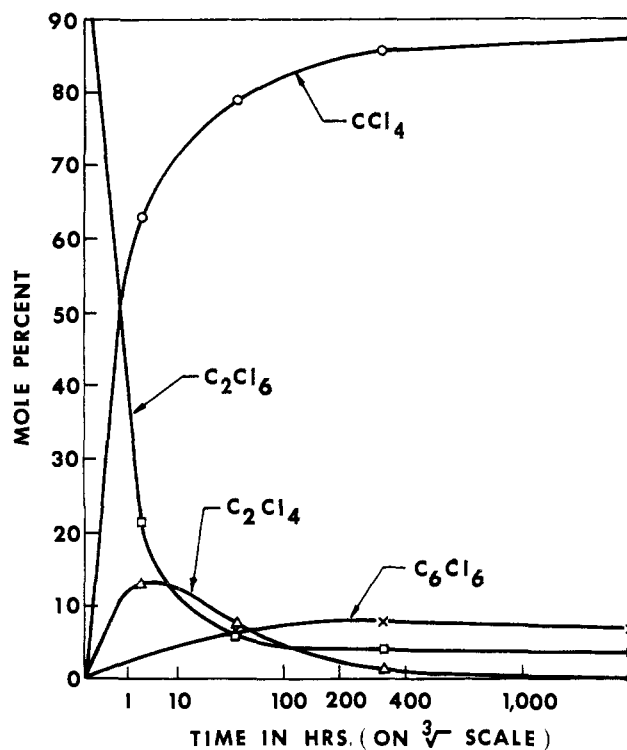
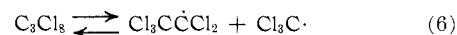


Fig. 2.—Thermal decomposition of hexachloroethane at 400°.

tributable primarily to the reverse reaction of eq. 2 as the C_2Cl_4 concentration builds up. Similarly, the data of Fig. 2 can be explained by this same set of reactions, with the reaction of eq. 2 being the initial one.

In accord with the literature,^{2,4,8} we shall assume that these disproportionation reactions proceed by a radical-chain mechanism and that C–C scission is the initiating process and predominates over C–Cl scission.^{9,10} This means that the first step in the decomposition of octachloropropane is



The radicals thus formed can produce two stable products by exchange of a chlorine atom between them (eq. 7) so that eq. 6 and 7 cover the reaction of eq. 3



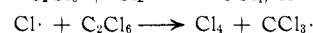
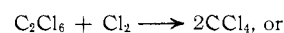
The disproportionation reactions of eq. 2, 4, and 5 are also thought to proceed by a radical chain mechanism, in which cases the $Cl\cdot$, $Cl_3C\cdot$, $Cl_2C=CCl$, and Cl_3CCCl_2 radicals are important. The data of Fig. 1 and 2 may be fitted by mathematical models based either on free-radical chains or reversible disproportionations such as eq. 2–5. However, details will not be presented here because more data than those given in Fig. 1 and 2 are needed for precise fitting of the respective rate constants.

(9) L. A. Errede and J. P. Cassidy, *J. Phys. Chem.*, **67**, 1358 (1963).

(10) One of the referees has suggested that the mechanism of equilibration may involve Cl_2 (or $Cl\cdot$) generated from the known reaction



The Cl_2 (or $Cl\cdot$) would then react as

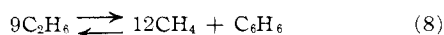


This route seems entirely plausible; in fact, it seems likely that at the temperatures studied, both $Cl\cdot$ and $CCl_3\cdot$ are important chain carriers.

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 $+200^\circ$). Notable exceptions are the rearrangements of various groups on the benzene nucleus¹¹ 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 hydrocarbons¹³ strongly suggest that a metastable equilibrium analogous to eq. 2 may have been approached in the hydrocarbon system; *i.e.*



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 ali-

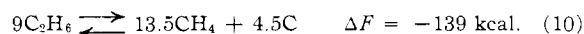
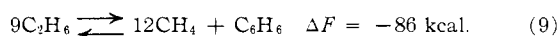
(11) *E.g.*, D. A. McCauley and A. P. Lien, *J. Am. Chem. Soc.*, **79**, 5953 (1957); H. Weingarten, *J. Org. Chem.*, **27**, 2024 (1962).

(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).

phatics 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 conditions¹⁴ 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° .



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.

(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 Olefins¹

BY LEO A. PAQUETTE²

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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

(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.

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 -halosulfones⁴ we have

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).