pated lower absorption intensity of this conformer relative to that of It,a[3], and the mole fraction (N) of It,e was found from the optical densities (d) with the relationship:

$$1.25\, d_{It,e}/d_{It,a} = N_{It,e}/1 - N_{It,e}$$

The results are summarized in Table I. Because of the poor resolution (similar to that found with the bromo analog)[4] these values are only good to perhaps ±20%, although the relative values are much better.

Dipole moment. The apparatus used for the measurement of the dielectric constants has been described.[16] The dielectric constant and density were measured with solutions of various mole fractions of solute and these values are presented in Table III. The calculations were made following essentially the procedure of Halverstadt and Kumler[17] employing an IBM 650 Computer.[18] The molar refractivity was calculated from standard values of atomic refractivities[19] and had the value 37.20 cc. The mole fraction of each conformation was calculated using Equation 1 and the values 4.29 D and 3.17 D for μ_e and μ_a, respectively.

$$\mu^2 = N_e\mu^2_e + N_a\mu^2_a \qquad (1)$$

TABLE III

DIPOLE MOMENT DATA FOR *trans*-2-CHLOROMETHYLCYCLOHEXANONE

Benzene Solvent, 25°		
N_2	d_{12}	ϵ_{12}
0.000000000	0.872413	2.2672
0.00152136	0.872953	2.3024
0.00198221	0.873113	2.3138
0.00273943	0.873372	2.3317
0.00323172	0.873546	2.3433
0.00403953	0.873817	2.3622
$\alpha = 23.572$	$\epsilon_1 = 2.2670$	$d_1 = 0.87242$
$\beta = 0.348$	$P_{2\infty} = 387.0$ cc.	$\mu = 4.14 \pm 0.02D$

Ultraviolet studies. The data available from the earlier work (Table IV) with the isomers of II were insufficient to make possible a real quantitative analysis of the present data. If the approximation is made that ϵ for a conformational mixture is linearly related to the composition and independent of solvent, assigning $\epsilon = 15$ to It,e and $\epsilon = 49$ to It,a, the conformational compositions in various solvents are found and are given in Table I.

TABLE IV

ULTRAVIOLET SPECTRAL DATA

Compound	Octane		Dioxane		Methanol	
	λ	ε	λ	ε	λ	ε
IIt,a	306	49	306	49	—	—
IIc,e	286	17	283	15	—	—
It	295	21	289	19	283	15

Acknowledgment. The authors are indebted to Professor M. T. Rogers, Michigan State University, for kindly making available to them his apparatus for the measurement of dipole moments, and to Mr. L. A. Freiberg and Miss P. Burcar for determining the infrared spectra. This work was supported in part by a contract with the Office of Ordnance Research, U. S. Army, and in part by grant No. NSF-G6579 from the National Science Foundation.

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[16] M. T. Rogers, *J. Am. Chem. Soc.*, **77**, 3681 (1955).

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On the Rearrangement of *t*-Cycloalkyl Hypochlorites[1]

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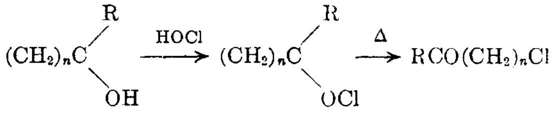
Recently the long known decomposition of *t*-alkyl hypochlorites has received renewed attention from several workers.[2] In particular, the rearrangement of *t*-cycloalkyl hypochlorites to chloro ketones[2a,b,3] interested us, as claims of generality for this reaction have been made but no report on its scope, together with experimental details, has appeared. We here report the results of an investigation on the scope of this process. 1-Methyl- and 1-phenylcycloalkanols of ring sizes five through seven were prepared and rearranged to ω-chloro ketones as shown.



$n = 4, 5, 6$; R = —CH_3, —C_6H_5

Data on the products of these rearrangements are found in Tables I and II.

Yields in Table I do not necessarily represent optimum yields, but rather those yields obtained using reported techniques.[2d,e] The low yields of III and VI reflect the considerable difficulty experienced in their isolation, as well as the apparently less favorable overall reaction with this ring size. It appears, however, that ω-chloro ketones of the types given can be prepared in this relatively simple fashion from readily obtained starting compounds.

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[1] Taken from the M.Sc. thesis of Jimmy W. Hill, Loyola University, January, 1961. Some early work was done by Messrs. G. Gapski and A. Danielzadeh.

[2] (a) T. L. Cairns and B. E. Englund, *J. Org. Chem.*, **21**, 140 (1956); (b) B. E. Englund, U. S. Pat. **2,675,402**, Apr. 13, 1954, and U. S. Pat. **2,691,682**, Oct. 12, 1954; (c) A. D. Yoffe, *Chem. & Ind.*, 963 (1954); (d) D. B. Denney and W. F. Beach, *J. Org. Chem.*, **24**, 108 (1959); (e) F. D. Greene, *J. Am. Chem. Soc.*, **81**, 2688 (1959).

[3] F. D. Greene, paper presented at the 135th Meeting of the American Chemical Society, Boston, Mass., 1959, p. 44-0 of the Abstracts.

TABLE I

ω-Chloro Ketones

$RCO(CH_2)_nCl$

R	n	Yield, %	B.P. (Mm.) or M.P.	n^t_D	d^{27}_{27}	Calcd.[a]		Found	
						C	H	C	H
(I)CH_3	4	52	52.5–54 (2.3)[b]	1.4414^{25}	1.035	—	—	—	
(II)CH_3	5	59	107–108 (17)	1.4435^{25}	1.035	56.56	8.81	56.84	8.69
(III)CH_3	6	11	92.5–94.5 (5)	1.4469^{29}	1.041	59.07	9.29	58.90	9.07
(IV)C_6H_5	4	77	49–50[c]	—	—	67.17	6.66	67.11	6.48
(V)C_6H_5	5	74	30.5–31.5	1.5268^{31}		68.40	7.18	68.50	7.34
(VI)C_6H_5	6	34	33–33.5[d]	—	—	69.47	7.63	69.67	7.65

[a] Analyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn. [b] Reported b.p. (ref. 2a) is 85.5–86.5° at 16 mm. [c] A. N. Nesmeyanov and L. I. Zakharkin [*Izvest. Akad. Nauk S.S.S.R. Odtel. Khim. Nauk*, 224 (1955); *Chem. Abstr.*, **50,** 4849*f* (1956)] report a m.p. of 49–50°. [d] Reported m.p. (ref. *c*) is 34–35°.

TABLE II

ω-Chloro Ketone Derivatives

Compound	Derivative	M.P.	Calcd. N	Found N
I	2,4-DNP (golden)	80–81.5[a]	17.80	17.66
II	2,4-DNP (yellow)	95–96	17.04	17.10
III	Semicarbazone	110–112	19.13	19.00
IV	2,4-DNP (red)	176–178	14.87	14.77
V	2,4-DNP (red)	141.5–143	14.34	14.19
VI	2,4-DNP (red)	121–123[b]	13.84	13.84

[a] Reported (ref. 2a), but no m.p. given. [b] Ref. *c* (Table I) reported a m.p. of 110–111°.

The previously reported inhibitory effect of oxygen[2e] was observed in these reactions also. 1-Phenylcyclopentyl hypochlorite in the absence of solvent underwent little change at 75–96° over a three-hour period in air. Decomposition of the hypochlorite was, however, essentially complete at 85–88° in forty-five minutes when nitrogen was bubbled through the material.

A brief study of the displacement reaction on these ω-chloro ketones was made. The results were in keeping with the proposed primary nature of these chlorides. An attempted cyclization of V to phenyl cyclopentyl ketone with dilute aqueous base failed.

EXPERIMENTAL

Melting points were determined on a calibrated Fisher-Johns melting point block. The starting alcohols are known compounds and were synthesized from the appropriate ketone *via* the Grignard reaction.[4] Their physical constants agreed with literature values and their infrared spectra were consistent with their structures.

Preparation of the t-cycloalkyl hypochlorites. The method of Greene[2e] was used since this method gave uniformly better results than the original technique of Cairns and Englund.[2a] The alcohol was added to 0° to a solution of sodium hypochlorite[5] (400 ml. per 0.1 mole of alcohol). To this solution was next added glacial acetic acid (about one-tenth the volume of sodium hypochlorite solution used) in carbon tetrachloride (30 ml. per 0.1 mole of alcohol). Vigorous stirring was commenced and continued for 3–5 hr. The separated greenish-yellow carbon tetrachloride layer was combined with three 100-ml. carbon tetrachloride extracts of the aqueous phase, washed twice with saturated sodium carbonate solution (50 ml.) and then dried over magnesium sulfate. Removal of the drying agent by filtration left the *t*-cycloalkyl hypochlorite in carbon tetrachloride solution, ready for rearrangement. The yields in Table I were the highest obtained from 0.1–0.3 mole scale experiments.

Rearrangement of the t-cycloalkyl hypochlorites. The carbon tetrachloride solution of the *t*-cycloalkyl hypochlorite was refluxed until a test for active chlorine (using a saturated solution of potassium iodide in acetic acid) was negative over a 2-min. period. Usually the greenish-yellow solution became nearly colorless during the rearrangement, especially those solutions of the 1-methylcycloalkyl hypochlorites. The period of heating was ordinarily 1.5 hr. with these compounds, albeit the rearrangement was probably completed much earlier as evidenced by the color change in 8–10 min. The decomposition of the 1-phenylcycloalkyl hypochlorites was much slower under these conditions (however, see below). Lengthy (9–14 hr.) reflux was usually employed with these compounds. Even after this time active chlorine was still detectable in the reaction material. Unfortunately, decomposition to dark colored products and evolution of hydrogen chloride was observed with longer times of reflux or on raising the temperature of reaction through gradual removal of the solvent. These reactions were therefore worked up after the mentioned reflux period.

Isolation of the ω-chloro ketones. Unchanged (or otherwise produced) alcohol, ω-chloro ketone and noncharacterized material made up the reaction product. This necessitated different techniques of isolation of the product in nearly every instance. I was isolated by removal of the solvent under reduced pressure, followed by the addition of excess saturated, aqueous sodium bisulfite solution. The addition compound formed was washed with ether and decomposed with warm sodium carbonate solution. Extraction with ether of the oil produced and eventual distillation led to the pure product. II was obtained by direct distillation of the reaction product (a small amount of potassium carbonate was added prior to distillation). III was distilled from the solvent-free reaction material under reduced pressure, but some original alcohol accompanied the product (infrared analysis). The sodium bisulfite addition compound was therefore prepared and III was isolated as described for I. Steam distillation of the solvent-free reaction material yielded crude IV. The distillate was extracted with ether and the extract was dried. Evaporation of the ether left IV as a solid, which was re-

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(4) *Cf.* W. J. Bailey and W. F. Hale, *J. Am. Chem. Soc.*, **81,** 650 (1959).

(5) Commercial bleach, 0.74*M* in sodium hypochlorite, was used.

crystallized from petroleum ether (b.p. 35–65°). V solidified when the solvent-free reaction material was chilled in ice. Recrystallization from pentane afforded pure material. VI was isolated in the same way as V, employing petroleum ether for the recrystallization. I–III are colorless oils with a pleasant odor. IV–VI are colorless, waxy solids. The infrared spectra of I–VI conform with their structures. The more volatile I–III were shown to be homogeneous by vapor phase chromatography.

The effect of air on the decomposition of 1-phenylcyclopentyl hypochlorite. The hypochlorite was prepared according to the general directions given earlier using methylene chloride as the immiscible phase. After separation and drying of the methylene chloride solution of the hypochlorite, the solvent was removed by evaporation under reduced pressure. A sample of the crude, yellow hypochlorite was then heated in an open test tube at 75–96° for 3.25 hr. After this time the potassium iodide test was still strongly positive and no change in the appearance of the sample was noticed. A stream of nitrogen was bubbled through another sample of the material held at 85–88°. In 47 min. the material was colorless and the potassium iodide test was very weakly positive. Higher temperatures led to darkened material and hydrogen chloride evolution.

Characterization of I–VI. All the ω-chloro ketones formed 2,4-dinitrophenylhydrazones easily in the usual fashion. In their reaction with sodium iodide in acetone, I–III gave precipitates within 6 min. at 50°, while IV–VI required approximately 30 min. at this temperature. All the ω-chloro ketones except IV and V developed precipitates within 30 min. in acetone solution when admixed with 5% aqueous silver nitrate solution at 25°. IV and V required 30 min. at 50° for evidence of reaction with this reagent.

Attempted cyclization of V. To V (7.83 g., 0.04 mole) in ethanol (150 ml.) there was added sodium carbonate (8.85 g., 0.08 mole) in water (150 ml.). On heating to reflux, the solution became homogeneous and some darkening took place. After 1 hr. of reflux, a cooled, acidified (nitric acid) portion of the material gave a precipitate with alcoholic silver nitrate. After 4 hr. of reflux the material was poured onto an equal volume of ice and extracted with benzene (3 times 100 ml.). The extracts were dried and the benzene removed. The residual oil (7.0 g.) was fractionated under reduced pressure. Wide boiling ranges were observed for the series of fractions obtained. Infrared examination of the fractions indicated that the lowest boiling cut (0.1 g., b.p. 106–116° at 0.5 mm., n_D^{20} 1.5295) was olefinic. The other fractions consisted of unchanged V and hydroxylic material, probably the ketol. No further examination of these substances was made.

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5,5-Dimethylcyclopentadiene[1]

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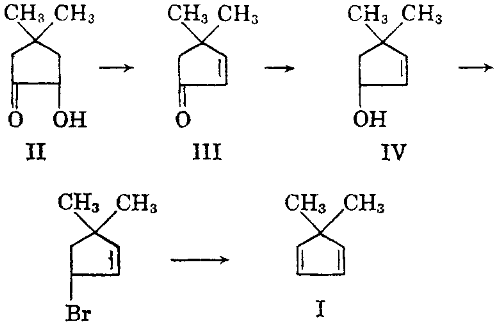
The recently reported synthesis[3] of 5,5-dimethylcyclopentadiene (I) prompts the recording of our independent and more convenient route to I, which seems well suited as a building block for the synthesis of bicyclic terpenes and related compounds. An earlier synthesis of I, b.p. 108–110° (atm. press.) has been reported[4]; however, comparison of the atmospheric boiling points of the known cyclopentane, methyl cyclopentanes, and their unsaturated derivatives shows clearly (for details, see Ref. 3) that the substance obtained by Zonis is most probably not the desired I. That this is in fact the case has been demonstrated by repetition of Zonis's work in which we obtained a material boiling in his reported range whose ultraviolet spectrum has maxima at 238, 247, 258, and 268 mμ and is wholly incompatible with the single maxima observed in the ultraviolet spectra of cyclopentadiene (240 mμ),[5] 1-methylcyclopentadiene (249.6 mμ),[6] and I as prepared below (250 mμ). Vapor liquid partition chromatography also confirms this situation.

By an adaptation of Sheehan's method[7] for the preparation of the D-ring of the steroid nucleus in an acyloin condensation, using sodium in ether–liquid ammonia, we have prepared 4,4-dimethylcyclopentan-2-ol-1-one (II) from dimethyl β,β-dimethylglutarate in 80% yield. Subsequent to this work, the preparation of II has been reported by two other groups of workers using essentially the same method.[8,9]



The sequence of reactions used is outlined below. Dehydration of II proceeds in about 80% yield using polyphosphoric acid in ten weight parts excess. When less polyphosphoric acid is used, the yield of III is considerably lower. The significance of this result lies apparently in the degree of hydration of the acid since dehydration of II using polyphosphoric acid prepared from phosphorus

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[1] This work, from the dissertation presented by W. E. T. to the graduate faculty of Lehigh University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, October 1960, was also presented before the Division of Organic Chemistry, 138th meeting of the American Chemical Society, New York, N. Y., September 1960.

[2] Armstrong Cork Company Fellow, 1958–60.

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