[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF DELAWARE]

The Effect of Cyclopentane and Cyclohexane Rings on the Reaction of Tertiary Alcohols and Chlorides[1]

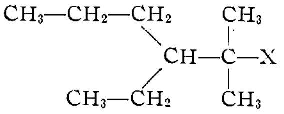
BY GLENN S. SKINNER AND FRANK P. FLORENTINE, JR.

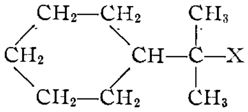
RECEIVED DECEMBER 21, 1953

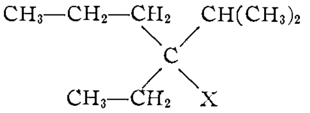
A series of comparable tertiary alcohols and chlorides of the chain and ring types, in which the functional group is linked to the ring (1,2-position) or adjacent to the ring (1,3-position), has been prepared. The alcohols reacted with hydrogen chloride to yield both olefins and teritary chlorides in all cases under the same concentration and conditions. The accepted mechanism for the solvolysis of the chlorides is used in comparing them, but since there is no accepted mechanism for the reaction of the tertiary alcohols these results are compared graphically.

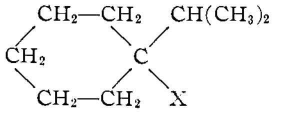
The immediate incentive for this work arose from the observation that certain esters with ring structures[2] reacted much more readily than corresponding dialkylmalonic esters to yield barbituric acid derivatives. Since this reaction is conducted in an alkaline medium we chose the formation and solvolysis of tertiary chlorides to investigate the possibility of a ring effect under acid conditions. The more stable cyclopentane and cyclohexane ring systems were selected to take account of the possible alternating effect of ring size. It was our objective to compare structurally suitable pairs of compounds under the same conditions and not to attempt explanations of the observations. Explanations have been ably presented by workers in this field.[3]

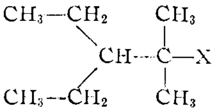
The essential structure of the selected ring compounds includes (1) an adjacent pair of tertiary carbon atoms, of which one is in the ring (1,2-position) and the other, adjacent to the ring (1,3-position), is linked to two methyl groups; and (2) the functional group which is linked to either of the tertiary carbon atoms for comparison. Similarly for the comparable open-chain compounds one of the two adjacent tertiary carbon atoms is linked to two methyl groups. Four pairs of compounds (I–VIII) thus provide a possible means of observing the relative resultant effect of moving the functional group from one tertiary carbon atom to the other.

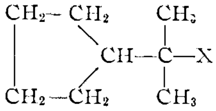

I

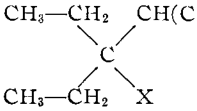

II


III

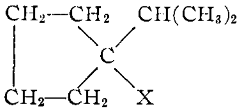

IV


V


VI


VII

X = Cl or OH


VIII

In the absence of an accepted mechanism for the reaction of the tertiary alcohols with hydrochloric acid, they are compared graphically by the change in concentration of olefin and alkyl chloride with time. Unfortunately for the purpose in hand the result is not a simple displacement. The amount of olefin formed was always large and in all cases except II exceeded alkyl chloride formation. Thus the chief reaction involved not only the functional group but also the adjacent tertiary hydrogen. While the structures of the resulting olefins were not determined, the resulting chlorides were all tertiary. The graphical comparisons thus represent a summation of several actions and until an accepted mechanism is available, reference to the relative activity of a specific bond cannot be made.

It is obvious, however, from an examination of the charts that there is a ring effect ascribable to both ring systems. For the open chain compounds, the amount of accumulated olefin always exceeds the amount of alkyl chloride. This is not true for all of the ring compounds. Also the concentration of olefin more rapidly reaches a maximum in the case of the alcohols in which the hydroxyl is linked to the tertiary carbon (1,2-position) in the ring.

The tertiary chlorides, freshly prepared from the alcohols, were solvolyzed in aqueous alcohol. The rate was followed by periodic determination of acidity and the data were found to fit the accepted[4] first-order kinetics. The chlorides III, VI and VIII were found to contain isomeric tertiary chlorides having different solvolysis rates[5] since for them the plot of log $(a - x)$ *vs.* t did not give a straight line. The avoidance of excessive amounts of the isomer was favored by the relative slowness of the rearrangement in ether. In some cases (I, II, IV, V VII) apparently pure chlorides were prepared by stopping the reaction before appreciable rearrangement had occurred. Even the rearranged chlorides were all tertiary since they were completely solvolyzed by aqueous alcohol (50%) in 6 hours at room temperature.

The treatment of 1-isopropylcyclopentanol with hydrogen chloride in diethyl ether for 6 hours resulted in a product which the hydrolysis data indicated to be a mixture of two tertiary chlorides, 62% of a relatively fast hydrolyzing and 38% of a

---

(1) Based on theses submitted by Frank P. Florentine, Jr., in partial fulfillment of the requirements for the degrees of Master of Science (1950) and Doctor of Philosophy (1951).

(2) G. S. Skinner, G. Limperos and R. H. Pettebone, THIS JOURNAL, **72**, 1648 (1950).

(3) H. C. Brown, *et al.*, *ibid.*, **73**, 212 (1951); **74**, 1894 (1952).

(4) E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

(5) H. C. Brown and R. Silber, THIS JOURNAL, **71**, 1846 (1949).

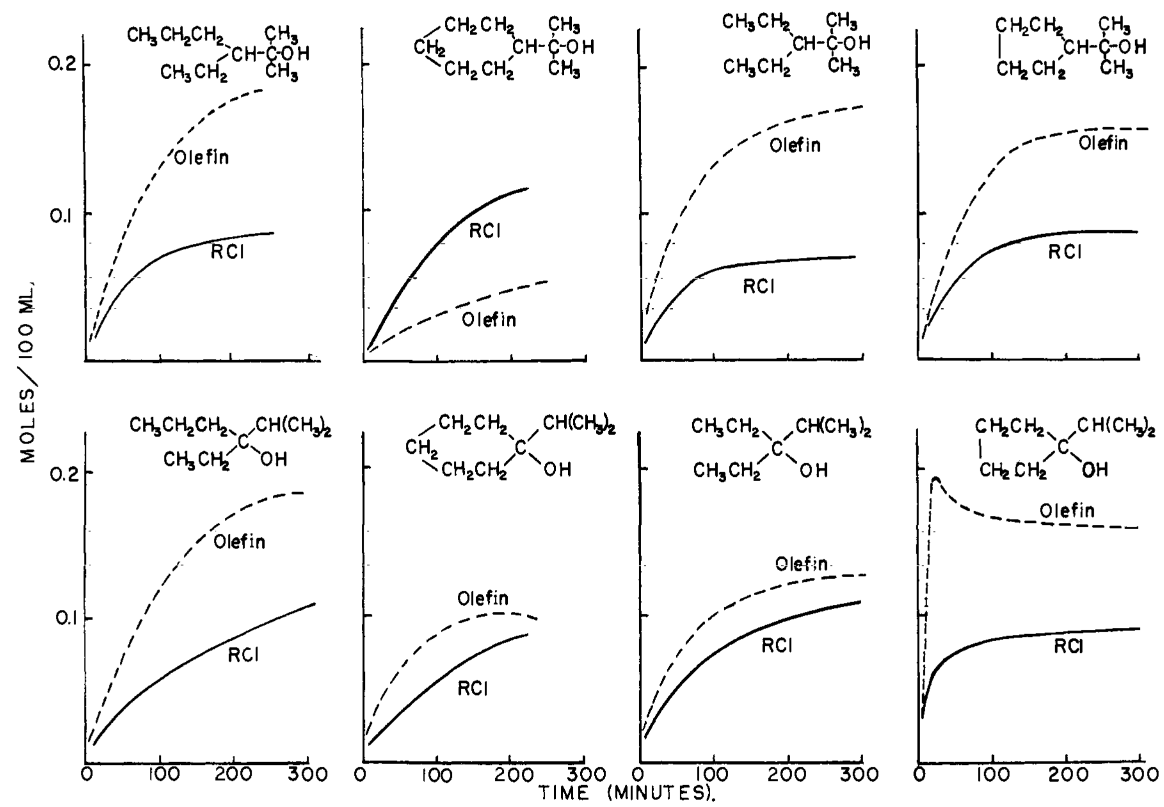


Fig. 1.—Reactions of alcohols.

slow hydrolyzing chloride. After 24 hours the preparation was reversed to 38% of the more reactive and 62% of the less reactive compound. The same mixture of the two chlorides was obtained from cyclopentyldimethylcarbinol in 24 hours. The simplest explanation of these observations (Table I) involves the conversion of the tertiary alcohol, 1-isopropylcyclopentanol to largely unrearranged tertiary chloride, which undergoes rearrangement under the reaction conditions. The rate constants were assigned to the two structures on this basis.

TABLE I

REARRANGEMENT OF CHLORIDES

Source	Time, hr.	A, %	B, %	k_A	k_B
1-Isopropylcyclopentanol	6	62	38	0.023	0.0030
1-Isopropylcyclopentanol	24	38	62	.023	.0030
Cyclopentyldimethylcarbinol	24	38	62	.023	.0030

In Table II the chlorides are paired in a manner suitable to the purpose of the work. From this it is seen that the order of reactivity for both pairs (I, III; V, VII) of chain-type compounds is the same irrespective of the position of the tertiary chlorine atom. Moving the chlorine from the adjacent tertiary carbon atom II to the tertiary carbon atom of the cyclohexane ring IV caused a decrease in the order of reactivity. A similar shift of the chlorine (VI, VIII) to the tertiary carbon atom of the cyclopentane ring caused an increase in the order of reactivity.

TABLE II

RATE CONSTANTS FOR SOLVOLYSIS OF TERTIARY CHLORIDES

	Chloride	$k_{30°}$, min.$^{-1}$
I	Dimethyl-(3-hexyl)-carbinyl	0.00317
III	Ethylisopropyl-*n*-propylcarbinyl	.00150
V	Dimethyl-(3-pentyl)-carbinyl	.00425
VII	Diethylisopropylcarbinyl	.00153
II	Cyclohexyldimethylcarbinyl	.00157
IV	1-Isopropylcyclohexyl	.00069
VI	Cyclopentyldimethylcarbinyl	.0030
VIII	1-Isopropylcyclopentyl	.023

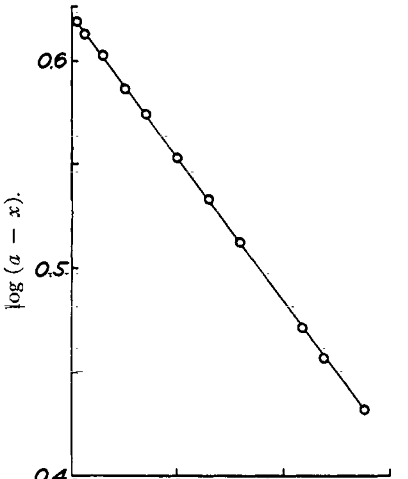


Fig. 2.—Reaction of cyclohexyldimethylcarbinyl chloride with aqueous ethanol.

Experimental

The tertiary alcohols (Table III) were prepared by standard Grignard techniques. All were purified by repeated

TABLE III

Compound	B.p. °C.	Mm.	d^{25}_4	n^{25}D	MR(obsd.)
I, dimethyl-(3-hexyl)-carbinol	71.5	14	0.8334	1.4331	45.00[a]
II, cyclohexyldimethylcarbinol[e]	85.5	15[j]	.9177	1.4663	42.95[b]
III, ethylisopropyl-*n*-propylcarbinol[f]	66.5	13	.8445	1.4369	44.76[a]
IV, 1-isopropylcyclohexanol[g]	77	13[l]	.9223	1.4665	42.64[b]
V, dimethyl-(3-pentyl)-carbinol[h]	38	2	.8346	1.4303	40.31[c]
VI, cyclopentyldimethylcarbinol	50	3	.9073	1.4567	38.44[d]
VII, diethylisopropylcarbinol[i]	59	18	.8470	1.4347	40.04[c]
VIII, 1-isopropylcyclopentanol	53	6[k]	.9085	1.4551	38.38[d]

[a] Calcd. MR 45.29. Calcd. for $C_9H_{20}O$ (I): C, 75.0; H, 14.0. [b] Calcd. MR 43.09. Found: C, 75.2; H, 13.9. [c] Calcd. MR 40.67. Calcd. for $C_8H_{16}O$ (VI): C, 75.0; H, 12.6. [d] Calcd. MR 38.47. Found: C, 74.0; H, 12.8. Calcd. for $C_8H_{16}O$ (VIII): C, 75.0; H, 12.6. [e] Matsubiara and Perkin[8] give b.p. 195° (760 mm.). Found: C, 75.0; H, 12.6. [f] Stas[9] gives b.p. 177° (760 mm.), d_{20} 0.851, n^{20}D 1.4398. [g] Vavon and Colin[10] give b.p. 76–79° (10 mm.), d_{19} 0.928, n^{19}D 1.4680. [h] Huston and co-workers[11] give b.p. 46–50° (5 mm.), d^{20}_4 0.8382, n^{20}D 1.4325. [i] Grigorowitsch[12] gives b.p. 160° (750 mm)., d_{20} 0.8295. [j] F.p. 9.5°. [k] F.p. 20°. [l] F.p. 26°.

TABLE IV

Compound, chloride	B.p., °C.	Mm.	d^{25}_4	n^{25}D	MR Obsd.	MR Calcd.	Chlorine, % Obsd.	Chlorine, % Calcd.
I, dimethyl-(3-hexyl)-carbinyl	68.5	15	0.8846	1.4388	48.36	48.63	21.53	21.81
II, cyclohexyldimethylcarbinyl	83	16	.9622	1.4679	46.38	46.43	21.81	22.08
III, ethylisopropyl-*n*-propylcarbinyl	70.5	12	.8928	1.4419	48.79	48.63	21.57	21.81
IV, 1-isopropylcyclohexyl	85.5	18	.9644	1.4691	46.28	46.43	21.94	22.08
V, dimethyl-(3-pentyl)-carbinyl	41	8	.8852	1.4352	43.84	44.01	23.80	23.86
VI, cyclopentyldimethylcarbinyl	47	8	.9545	1.4574	41.87	41.81	23.82	24.18
VII, diethylisopropylcarbinyl	41	6	.8994	1.4405[a]	43.58	44.01	23.47	23.86
VIII, 1-isopropylcyclopentyl	38	4	.9525	1.4559	41.83	41.81	23.61	24.18

[a] Brown and Silber[5] also give n^{25}D 1.4405.

fractionation at pressures low enough to avoid decomposition.

Dimethyl-(3-hexyl)-carbinol was prepared in 72% yield from ethyl ethyl-*n*-propylacetate and methylmagnesium bromide. The reaction of 3-hexylmagnesium bromide with acetone failed to yield this alcohol in isolatable amount.

Cyclohexyldimethylcarbinol from acetone and cyclohexylmagnesium chloride and ethylisopropyl-*n*-propylcarbinol from ethyl isopropyl ketone and *n*-propylmagnesium bromide were obtained in good yields.

1-Isopropylcyclohexanol.—From 0.90 mole of cyclohexanone, 1.20 moles of magnesium and 1.00 mole of isopropyl chloride, this alcohol was obtained in 25% yield only if the ketone was added in ether solution to the ethereal solution of Grignard reagent at −59 to −60°. Cyclohexanol (35%) and cyclohexylidene cyclohexanone (20%) were also formed.[6] The reaction at room temperature gave only the last two products, and no tertiary alcohol.

Dimethyl-(3-pentyl)-carbinol.—This alcohol was prepared in 90% yield from ethyl diethylacetate and methylmagnesium bromide by a procedure similar to that described for dimethyl-(3-hexyl)-carbinol.

Cyclopentyldimethylcarbinol.—The alcohol was prepared in a similar way from ethyl cyclopentanecarboxylate, in 70% yield. The reaction of cyclopentylmagnesium bromide with acetone gave less than 10% yield of tertiary alcohol.

Diethylisopropylcarbinol.—This alcohol was obtained in 79% yield from ethyl isopropyl ketone and ethylmagnesium bromide.

1-Isopropylcyclopentanol. Method I.—To a solution of Grignard reagent in 1550 cc. of ether, obtained from 1.50 moles of magnesium and 0.50 mole of tetramethylene bromide, was added dropwise at 5–10° over a period of four hours a solution of 1.00 mole of ethyl isobutyrate in 200 cc. of ether. The mixture was worked up as described by Nenitzescu and Necsoiu[7] for preparing other 1-alkylcycloalkanols; yield 58%.

Method II.—To a solution of isopropylmagnesium bromide prepared from 650 cc. of ether, 4.00 moles of magnesium and 5.00 moles of halide, was added at 5–10° a solution of one mole of cyclopentanone in 1000 cc. of ether over six hours; yield 23%.

Dehydration of Cyclohexyldimethylcarbinol.—Ten grams of the alcohol in 100 cc. of purified acetic acid was treated with 10 cc. of 50% (v./v.) sulfuric acid. After eight hours, the mixture was diluted with three volumes of water and extracted with chilled ether. The ether extract was dried over anhydrous potassium carbonate, the ether was evaporated, and the oil was distilled, taking the fraction from 158 to 170° (8 grams). Analysis by bromination indicated it to be 82% C_9H_{16}, the remaining 18% being assumed to be undehydrated alcohol.

Tertiary Chlorides.—The same general method was used for all (Table IV). The yields varied between 80% and 90%. Twenty-five grams of the tertiary alcohol was dissolved in 50 cc. of dry ether, cooled to 5°, and dry hydrogen chloride was passed in while cooling in ice, until 15 g. had been absorbed. The mixture was let stand in the ice-bath for one hour. The process of passing in hydrogen chloride was then repeated, and the mixture was let stand at room temperature for one hour. The process was repeated again, this time letting stand overnight. The ether became saturated with hydrogen chloride during the second and third introductions of gas.

The mixture was poured into ice and water. The ether layer was separated and washed with three successive portions of 40% calcium chloride solution, and dried with anhydrous potassium carbonate. The product was distilled under diminished pressure. Particularly with 1-chloro-1-isopropylcyclopentane, distillation at the lowest possible pressure was necessary to avoid degradation to olefin and hydrogen chloride.

Each material was analyzed and used within 48 hours after its isolation. On standing for a few weeks, all the tertiary chlorides began to smell of hydrogen chloride. The chlorides were analyzed gravimetrically after allowing weighed samples to react for 12 hours in the dark with an excess of alcoholic silver nitrate. All are mobile, colorless, sweet-smelling liquids.

Analytical Method for the Reaction Rates of Tertiary Alcohols with Hydrochloric Acid.—The acetic acid used as solvent was purified by the method of Eichelberger and LaMer.[13] The pure dry acetic acid was mixed with hydrochloric acid of known concentration so that the water con-

---

(6) W. A. Mosher, THIS JOURNAL, **62**, 552 (1940).

(7) C. D. Nenitzescu and I. Necsoiu, *ibid.*, **72**, 3485 (1950).

(8) K. Matsubiara and W. Perkin, *J. Chem. Soc.*, **87**, 663 (1905).

(9) J. Stas, *Bull. soc. chim. Belg.*, **35**, 379 (1926).

(10) G. Vavon and J. Colin, *Compt. rend.*, **222**, 801 (1946).

(11) R. C. Huston, R. L. Guile, J. J. Sculati and W. N. Wasson, *J. Org. Chem.*, **6**, 253 (1941).

(12) A. Grigorowitsch and D. Pavlov, *J. Russ. Phys. Chem. Soc.*, **23**, 169 (1891).

(13) W. Eichelberger and V. K. LaMer, THIS JOURNAL, **55**, 3633 (1933).

tent of the mixture could be calculated. The same batch of acetic acid–water–hydrochloric acid was used throughout this work.

This mixture (100 cc.) was pipetted into a long-necked glass-stoppered flask which was immersed in a bath at 30.00 ± 0.05°. Two 5-cc. samples were pipetted out and the chloride ion concentration of each was determined exactly as described below for samples of reaction mixture. Since the pipets were calibrated both for delivery and withdrawal, the volume of solution left in the flask was known.

A sample of the tertiary alcohol was introduced into the vessel from a weighing pipet, and the weight of the sample determined by difference in the weight of the pipet, which was also calibrated volumetrically so that the desired amount could readily be taken each time. The contents of the reaction vessel were immediately mixed by swirling. At suitable time intervals, 5-cc. samples were pipetted out and analyzed as follows.

The sample was introduced into a 250-cc. Erlenmeyer flask containing 40–50 g. of cracked ice. Two drops of phenolphthalein indicator was added, followed by rapid dropwise addition of 50% sodium hydroxide until just pink. Sulfuric acid (1 N) was added dropwise to bring the mixture just to the acid side. One cc. of half-saturated potassium chromate was added, and the mixture was titrated to the red silver chromate end-point with standard 0.1 N silver nitrate. Ice was present throughout the operation.

Suitable blanks were run on all reagents and on samples of the tertiary chloride which would be formed during the reaction. It was found that the latter hydrolyzed only to a negligible extent under the conditions of the analysis. The end-point was permanent, but not very sharp. Duplicate analyses checked within 0.2 ml. of silver nitrate solution (0.004 mole/liter of chloride).

Higher concentrations of water, hydrochloric acid or tertiary alcohol than those employed sometimes resulted in separation of phases before final equilibrium.

Olefin concentration was determined by treating 5-cc. samples with excess of 0.1 N bromine in carbon tetrachloride. After one minute, 10 cc. of potassium iodide solution (20%) and 50 cc. of water were added. The liberated iodine was titrated with standard 0.1 N sodium thiosulfate solution. The same values were obtained when a given sample was allowed to react with the bromine for ten minutes. There was no reaction of bromine with the tertiary alcohols or chlorides under these conditions. Duplicate analyses agreed within 0.003 mole/liter of olefin.

Test for Esterification.—One of the runs in which cyclohexyldimethylcarbinol was a reactant was arrested at a point representing 50% completion with respect to tertiary chloride formation. A sample (10 cc.) was neutralized with sodium hydroxide just as described for the chloride ion analysis, then extracted with ether. The ether layer was washed with water until the washings were no longer acid to phenolphthalein, and the ether was evaporated and the residue refluxed 24 hours with excess 10% sodium hydroxide in alcohol. The mixture was then made strongly acid with sulfuric acid and distilled until nearly dry. The distillate was analyzed both for chloride ion and total acidity. The values were identical (milliequivalents) indicating that no acetic acid had distilled, and therefore that the sample had contained no ester.

Tertiary Chloride Solvolysis Rates.—The method was essentially that of Hughes and Ingold.[4] The aqueous ethanol used had $d^{25}{}_4$ 0.8449 (about 78% ethanol, w./w.). The details of manipulation are well described, as is the method of analyzing isomer mixtures, by Brown and Silber.[5]

NEWARK, DELAWARE

[CONTRIBUTION FROM HICKRILL CHEMICAL RESEARCH FOUNDATION]

The Cycloheptatrienylium (Tropylium) Ion

BY W. VON E. DOERING[1] AND L. H. KNOX

RECEIVED APRIL 8, 1954

Thermal elimination of hydrogen bromide from dibromotropilidene produces cycloheptatrienylium bromide, the structure of which follows from its salt-like character, its hydrogenation to cycloheptane and its conversion by phenyllithium to 7-phenylcycloheptatriene. This stable cation is the parent of a new aromatic system which has been foreshadowed theoretically by the molecular orbital treatment of aromatic character and experimentally by the behavior of tropone, tropolone and azulene.

From the first generalization of six affinities due to Armstrong, von Baeyer and Bamberger,[2] to the present state of quantum mechanical foundation invented by Erich Hückel,[3] the theory of aromatic character has ascribed relative stability to those conjugated unsaturated cycles having six (π) electrons in a ring. The earliest attempts to test the theory centered about the hypothetically non-aromatic molecules, cyclobutadiene, $(CH)_4$,[4] and cycloöctatetraene, $(CH)_8$.[5] To date no results of theoretical significance have been forthcoming. Cyclobutadiene has resisted all efforts at synthesis and in any event would have a large, obscuring, angular strain; and cycloöctatetraene, although it has been synthesized, has a non-planar structure[6] and in consequence is impertinent to the theory.

With the five- and seven-membered rings, $(CH)_5$ and $(CH)_7$, the theoretical predictions[3,7,8] are definite: $(CH)_5^-$ should be more stable than $(CH)_7^-$ whereas $(CH)_7^+$ should be relatively much more stable than $(CH)_5^+$.[9] Experimental verification of these predictions is partial and incomplete. The well-known, remarkable acidity of cyclopentadiene[10,11] is to be compared with the failure to effect condensation with or form salts from cycloheptatriene.[12,13] One of the two anions has been prepared, therefore, and its properties are in accord with theory. In the positively charged series, neither $(CH)_5^+$ nor $(CH)_7^+$ has been prepared, but it can be inferred from the failure of cyclopenta-

---

(1) Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

(2) For a discussion and references, see W. Hückel, "Theoretische Grundlagen der organischen Chemie," Vol. I, 5th Ed., Akademische Verlag, Leipzig, 1944, pp. 507–524.

(3) (a) E. Hückel, *Z. Physik*, **70**, 204 (1931); (b) "Grundzüge der Theorie ungesättigter und aromatische Verbindungen," Verlag Chemie, Berlin, 1938, pp. 71–85.

(4) R. Willstätter and W. von Schmaedel, *Ber.*, **38**, 1992 (1905).

(5) R. Willstätter and E. Waser, *ibid.*, **44**, 3423 (1911).

(6) I. L. Karle, *J. Chem. Phys.*, **20**, 65 (1952).

(7) G. W. Wheland, *ibid.*, **2**, 474 (1934).

(8) J. L. Franklin and F. H. Field, THIS JOURNAL, **75**, 2819 (1953).

(9) The resonance energies given by E. Hückel[3] for the species in terms of β follow: $(CH)_5^-$, 2.48; $(CH)_7^-$, 2.12; $(CH)_7^+$, 3.00; $(CH)_5^+$, 1.24.

(10) J. Thiele, *Ber.*, **33**, 666 (1900).

(11) Potassium t-butoxide (pK_a 19) converts cyclopentadiene quantitatively into its potassium salt (R. S. Rouse, Yale Univ., unpublished).

(12) J. Thiele, *Ann.*, **319**, 226 (1901).

(13) E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, THIS JOURNAL, **61**, 1057 (1939).