Nucleophilic Reactivity of the Carbon–Carbon Double Bond. VI. Products from 5-Hexenyl, Cyclopentylmethyl, and Cyclohexyl Cations with Different Leaving Groups

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The products of acetolysis of 5-hexenyl, cyclopentylmethyl, and cyclohexyl *p*-nitrobenzenesulfonates are compared with those formed in similar media from carbonium ions with uncharged leaving groups. Cyclohexylmercuric acetate produced cyclohexene and cyclohexyl acetate in a ratio identical with that from the sulfonate, but cyclopentylmethylmercuric acetate failed to react at a comparable rate or to produce analogous products. Cyclopentylmethylamine and cyclohexylamine diazotization with isoamyl nitrite in acetic acid produced cyclohexene and cyclohexyl acetate and other products. No cyclization occurred with 5-hexenylamine.

Related carbonium ion intermediates formed from precursors differing either in structure or in leaving group have sometimes been observed to give products differing in relative amounts.[1,2] It has been suggested that nucleophilicity of the leaving group, especially in solvents of low nucleophilicity, affects the ratio of products formed by elimination to those formed by substitution.[2] Alternatively, partial internal return of the leaving group from the ion pair after rearrangement of the cation may be responsible for product differences.[3–5] When the carbonium ion is formed by paths as different as the π route and the σ route,[6] the position of the anion may be significant. For bicyclic cations, it may be difficult to assess the relative importance of anion proximity and cation conformation.[7]

If the effect of the leaving group is steric rather than electrostatic, a neutral leaving group would cause product differences of the same kind as a charged leaving group.[8]

We have conducted experiments utilizing two methods of generating carbonium ions with neutral leaving groups, solvolysis of alkylmercuric acetates and diazotization of alkylamines. These were done under conditions directly comparable with the acetolyses of 5-hexenyl, cyclopentylmethyl, and cyclohexyl tosylates,[5] in order to determine the effect of leaving groups on the product ratios.

Results

The product analysis for acetolysis of 5-hexenyl, cyclopentylmethyl, and cyclohexyl *p*-nitrobenzenesulfonates and corresponding alkylmercuric acetates and for deamination of the appropriate alkylamines are compared in Table I.

The reactions occurred in homogeneous solutions in all cases, at closely comparable concentrations, and at temperatures near 80°. Product stability under the reaction conditions was shown to depend upon the absence of acids stronger than acetic acid in the medium; so the solutions were "buffered" by the addition of anhydrous sodium acetate in sufficient amount to react with the *p*-nitrobenzenesulfonic acid formed during the reaction of the sulfonate esters and in low concentration in other cases simply to assure the absence of strong acid. The product ratios are known to be affected slightly by added salts, but not substantially by concentrations of less than 0.03 M.[5]

A careful inspection of the 5-hexenyl *p*-nitrobenzenesulfonate product evinced no trace of cyclopentylmethyl acetate. A measurable quantity of five-membered ring closure could have provided a second parameter in addition to the cyclohexene/cyclohexyl acetate ratio for the detection of differences in the reaction intermediates. Under conditions capable of detecting 0.1%, no cyclopentylmethyl acetate could be seen in the chromatogram.

Acetolysis of cyclohexylmercuric acetate proceeded cleanly as reported by Jensen.[9] A longer reaction period was required when the solution contained sodium acetate to prevent secondary product interconversion. The product ratio was identical with that from the classical cyclohexyl cation derived from the *p*-nitrobenzenesulfonate. Cyclopentylmethylmercuric acetate reacted slowly, as shown by the formation of some sludge containing mercury, but no analogous organic products were found.

The results of some typical diazotization experiments are given in Table II. When isoamyl nitrite was used to diazotize cyclohexylamine, the product ratio was almost invariant with changes in the mole ratio or with added base. Consequently, product studies were made with equimolar amounts of amine and isoamyl nitrite and with a low concentration of sodium acetate present to assure product stability.

Diazotization of cyclohexylamine produced 64% cyclohexylacetate, 33% cyclohexene, and 3% bicyclo[3.1.0]hexane. The latter was observed in the aqueous diazotization of cyclohexylamine to the extent of 2%, but is reportedly formed in more substantial amount in "aprotic" diazotization.[10]

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[1] (a) J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951); (b) D. Semenow, C. H. Shih, and W. G. Young, *ibid.*, **80**, 5472 (1958); (c) W. B. Smith and W. H. Watson, *ibid.*, **84**, 3174 (1952).

[2] (a) D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957); (b) D. J. Cram and M. R. V. Sahyun, *ibid.*, **85**, 1257 (1963); (c) S. Winstein and M. Cocivera, *ibid.*, **85**, 1702 (1963); (d) P. S. Skell and W. L. Hall, *ibid.*, **85**, 2851 (1963).

[3] (a) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1397, 1992 (1961); (b) H. L. Goering, J. T. Doi, and K. D. McMichael, *ibid.*, **86**, 1951 (1964).

[4] S. Winstein, F. Gadient, E. T. Stafford, and P. T. Klinedienst, Jr., *ibid.*, **80**, 5895 (1958); C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

[5] P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *J. Amer. Chem. Soc.*, **87**, 1308 (1965).

[6] S. Winstein and P. Carter, *ibid.*, **83**, 4485 (1961).

[7] P. D. Bartlett, E. M. Nicholson, and R. Owyang, *Tetrahedron*, **22**, Suppl. 8, Part II, 399 (1966).

[8] H. L. Goering and G. N. Fickes, *J. Amer. Chem. Soc.*, **90**, 2848, 2856 (1968).

[9] F. R. Jensen and R. J. Ouellette, *J. Amer. Chem. Soc.*, **83**, 4477, 4478 (1961); **85**, 363, 367 (1963); F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968.

[10] O. E. Edwards and M. Lesage, *Can. J Chem.*, **41**, 1592 (1963); L. Friedman, reported at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstracts ORGN 99.

TABLE I

PRODUCTS OF ACETOLYSIS OF *p*-NITROBENZENESULFONATES AND ALKYLMERCURY ACETATES COMPARED WITH ALKYLAMINE DEAMINATION PRODUCTS, MOLE PER CENT[a]

Substrate (Registry no.)	Reaction time, hr	Yield, %	1-Methylcyclopentene	Cyclohexene (A)	5-Hexenyl acetate	Cyclopentanemethyl acetate	Cyclohexyl acetate (B)	Other products	A/B
			p-Nitrobenzenesulfonate Acetolysis[b]						
5-Hexenyl (788-97-6)	86	94	0	4.7	83.7	0	11.6	0	0.40
Cyclopentylmethyl (788-96-5)	52.3	83	15.1	61.9	0	0	18.0	0	3.4
Cyclohexyl (788-92-1)	0.7	82	0	87.0	0	0	13.0	0	6.7
			Alkylmercury Acetate Acetolysis[c]						
Cyclopentylmethyl (34825-68-8)	691	0	0	0	0	0	0	0	
Cyclohexyl (10341-90-9)	135	49	0	87.0	0	0	13.0	0	6.7
			Alkylamine Deamination[d]						
5-Hexenyl[e] (34825-70-2)	1.0	60	0	0	55	0	0	1,5-Hexadiene, 22 1-Hexen-5-yl acetate, 20 Unknown, 3	
Cyclopentylmethyl[f] (6053-81-2)	1.0	57	7	25	0	9	49	1-Methylcyclopentyl acetate, 7 Unknown, 3	0.51
Cyclohexyl (108-91-8)	1.0	66	0	33	0	0	64	Bicyclo[3.1.0]hexane, 3	0.52

[a] By gas chromatography of pentane extracts, using an internal standard. Product yields normalized to add to 100%. [b] Initial concentration 0.17 *M*, sodium acetate 0.27 *M*, 80.8°. [c] Initial concentration 0.22 *M*. Cyclopentylmethylmercuric acetate gave 14% yield of free mercury in the form of brown sludge after 691 hr, but no organic product could be found by the usual extraction and analysis procedure. 5-Hexenylmercuric acetate acetolysis was not tried. [d] Initial concentration 0.18 *M*, reacted with isoamyl nitrite, initially 0.20 *M*, sodium acetate 0.011 *M*, 79.7°. [e] Phenylthiourea derivative, 34825-65-5. [f] Phenylthiourea derivative, 34825-67-7.

TABLE II

DIAZOTIZATION OF CYCLOHEXYLAMINE[a]

Reagent	Mole ratio[b]	Medium	Yield, %	C_6H_{10}[c]/Cyclohexyl acetate
IAN[d]	1.02	HOAc	55	0.52
$NaNO_2$	1.0	HOAc	30	0.44
IAN	1.02	0.011 *M* NaOAc/HOAc	66	0.54
IAN	1.02	0.27 *M* NaOAc/HOAc	60	0.54
IAN	1.02	0.011 *M* NaOAc/HOAc	60	0.56
IAN	1.12	0.011 *M* NaOAc/HOAc	66	0.57
IAN	1.20	0.011 *M* NaOAc/HOAc	62	0.54
IAN	1.29	0.011 *M* NaOAc/HOAc	58	0.50

[a] The reactions occurred at 70.68° for 1 hr in anhydrous acetic acid with an amine concentration of about 0.175 *M*. [b] Diazotization reagent/cyclohexylamine. [c] C_6H_{10} consists of cyclohexene and a minor amount of bicyclo[3.1.0]hexane, which were not resolved in these gas chromatograms. [d] Isoamyl nitrite. Unreacted isoamyl nitrite was detected in glc analyses as well as a 15% yield of isoamyl acetate and less than 1% of pentenes apparently derived from isoamyl nitrite. A certain amount of isoamyl acetate was formed by acetolysis of isoamyl nitrite but control samples indicated that the initial rate was only $^1/_{220}$th the diazotization rate at the concentrations used.

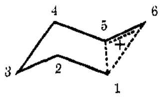
Diazotization of cyclopentylmethylamine produced, in addition to products from cyclohexyl cation, 7% of 1-methylcyclopentyl acetate. Cyclohexene and cyclohexyl acetate were produced in the ratio of 0.51.

5-Hexenylamine upon diazotization produced 1,5-hexadiene and 1-hexen-5-yl acetate, which were not found in detectable amount from acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate. Neither cyclohexene nor cyclohexyl acetate could be detected in the product extract under conditions at which 1% of either would have been distinct.

All of the diazotization reactions were of 1 hr duration and the results probably do not represent the maximum yield attainable.

Discussion

The acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate occurs with kinetic enhancement compared to *n*-hexyl *p*-nitrobenzenesulfonate and results in cyclic products, 4.7% cyclohexene and 11.6% cyclohexyl acetate.[5] This implies that the π electrons of the double bond are involved in supporting the positive charge in the transition state leading to cyclic products. Charge distribution is open to question, although a preference for symmetrical transition states in carbonium ions formed by the π route was demonstrated by Bartlett and Sargent.[11] Though the cyclization of 5-hexenyl *p*-nitrobenzenesulfonate does not itself result in the formation of products having five-membered rings, derivatives substituted at C-6 do close with the formation of both five- and six-membered rings.[12] Therefore, it is reasonable to postulate a nonclassical carbonium ion such as I for the reaction intermediate which leads to cyclic products. The π and σ route intermediates, in approaching the geometry of I, still retain the leaving group in the neighborhood of the carbon atom to which it was attached. Kinetic rate enhancement shows that electron mobilization in both cases accompanies the departure of the leaving group.



I

In acetolysis of alkylmercuric acetates, rapid ionization equilibrium with the alkylmercuric cation is established, followed by rate-controlling loss of free mer-

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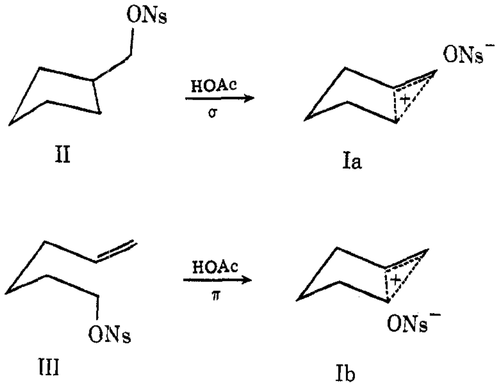
[11] P. D. Bartlett and G. D. Sargent, *J. Amer. Chem. Soc.*, **87**, 1297 (1965).

[12] E. M. Nicholson, Thesis, Harvard University, 1965; W. S. Johnson, D. M. Bailey, R. Owyang, R. A. Bell, B. Jaques, and J. K. Crandall, *J. Amer. Chem. Soc.*, **86**, 1959 (1964).



cury.[9] The utilization of the reaction for the comparison of σ and π route cations would lead to the suppression of counterion differences according to the internal return and electrostatic mechanisms, whereas steric effects might remain. That is, the mercury atom is unlikely to undergo internal return with rearrangement.

$$\mathrm{RHgOAc} \underset{\text{fast}}{\rightleftharpoons} \mathrm{RHg}^+ + \mathrm{OAc}^- \xrightarrow[\text{slow}]{} \mathrm{R}^+ + \mathrm{Hg} + \mathrm{OAc}^- \xrightarrow[\text{fast}]{} \text{products}$$

An electrostatic effect on elimination is also unlikely. However, the process failed to provide the necessary σ and π route cations because mercury is poor as a leaving group with primary carbonium ions. The reaction occurred so slowly that general deterioration of the samples was apparent.

In the one comparison obtained, acetolysis of cyclohexylmercuric acetate gave the same cyclohexene/cyclohexyl acetate ratio as cyclohexyl *p*-nitrobenzenesulfonate, both under kinetic control. Electrostatic assistance to elimination therefore seems to be absent in this process. Both processes apparently involve a classical cyclohexyl cation.

The reaction of alkylamines with nitrous acid or with alkyl nitrites is considered to be analogous to diazotization of aromatic amines except that the diazonium ion is unstable and suffers immediate loss of nitrogen with the formation of the carbonium ion.[13] The nitrogen molecule constitutes the neutral leaving group in this case.

$$\mathrm{RNH_2 + HONO + H^+ \longrightarrow 2H_2O + RN_2^+ \longrightarrow N_2 + R^+ \longrightarrow} \text{products}$$

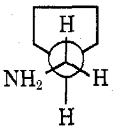
Since the products from 5-hexenyl, cyclopentylmethyl, and cyclohexyl *p*-nitrobenzenesulfonates were extremely subject to alterations of the medium,[5] it was important to run the diazotization–decomposition reactions of the amines under strictly comparable conditions. The use of nitrite esters as the diazotization reagent facilitated reaction in homogeneous solution with a comparable reaction rate at 80°.[14]

The cyclohexene/cyclohexyl acetate ratio realized from cyclohexylamine and isoamyl nitrite was 0.52, whereas sodium nitrite yielded a ratio of 0.44 for total C_6H_{10}/cyclohexyl acetate (Table II). It seems possible that the considerable evolution of gas from the latter sample may be responsible for some loss of the more volatile product.

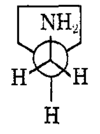
Addition of sodium acetate to the medium had little effect on the product ratio. In the comparable ester solvolyses, even lithium perchlorate led to marked alteration of the elimination–substitution ratio, in the direction of more elimination.[5] This insensitivity of the product ratio argues for an indiscriminate cation, an indication of a very exothermic product-forming step.[15]

The products formed by the reaction of isoamyl nitrite and cyclopentylmethylamine indicate that two kinds of rearrangement processes are occurring. Hydride migration leads to the formation of 1-methylcyclopentene and 1-methylcyclopentyl acetate, together about 14% of the total product. Ring expansion leads to the production of cyclohexene and cyclohexyl acetate, 25 and 49%, respectively.

The prevalence of ring expansion over hydrogen migration is explicable on the basis of a preferred conformation of the ground state, IV. Migration in diazotization of 3-phenyl-2-butylamine and [1-^{14}C]-2,2-diphenyl-2-*o*-tolylethylamine is faster than the establishment of rotational equilibrium.[2a,16] The population of conformer IV and its enantiomer should be more than twice that of V.



IV



V

The fact that cyclopentylmethylamine and cyclohexylamine gave the same ratio of cyclohexene to cyclohexyl acetate permits the assumption that the carbonium ion intermediates in the two cases are identical. This lack of memory of original structure may be due to poor charge solvation. That is, the charge is either localized or distributed over several carbon atoms of the cation, but in any case the solvent molecules in the neighborhood are not oriented to stabilize the charge. This is possible because of the different energy contour of diazotization is compared to solvolysis. According to the Hammond postulate, the structure of the transition state for diazotization, by virtue of the exothermic nature of the reaction, is similar to that of the starting material. Huisgen and Rüchardt have elaborated this to the extent of suggesting that, in the transition state for diazotization, the carbon attached to nitrogen is still essentially sp^3 hybridized.[17] It seems clear that in the passage from the respective transition states to the carbonium ion intermediate solvation from the rear is not necessary and the front side is shielded by the forming nitrogen molecule. This observation of leveling of the product ratio when a neutral molecule is the leaving group indicates that the mechanism of memory effects in this cation system is electrostatic. This same result

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(13) H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1961, Chapters 1, 2, 3, 6.

(14) G. Seidl and R. Huisgen, *Chem. Ber.*, **97**, 249 (1964); D. Y. Curtin, J. A. Kampmeier, and M. L. Farmer, *J. Amer. Chem. Soc.*, **87**, 874 (1965); L. Friedman and A. T. Jurewicz, *ibid.*, **91**, 1808 (1969), and preceding work in this series.

(15) J. D. Roberts, C. C. Lee, and W. H. Saunders, *J. Amer. Chem. Soc.*, **76**, 4501 (1954); D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957); D. Y. Curtin and M. C. Crew, *ibid.*, **76**, 3719 (1954).

(16) V. F. Raaen and C. J. Collins, *ibid.*, **80**, 1409 (1958).

(17) R. Huisgen and C. Rüchardt, *Justus Liebigs Ann. Chem.*, **601**, 1, 21 (1956); see also P. D. Bartlett and E. S. Lewis, *J. Amer. Chem. Soc.*, **72**, 1005 (1950). Moss has recently summarized suggestions that in primary diazonium ions the carbon–nitrogen bond is broken only upon attack by a nucleophile at carbon: R. A. Moss, *Chem. Eng. News*, **49** (47), 28 (1971).

TABLE III

ALKYLMERCURIC BROMIDES, RHgBr

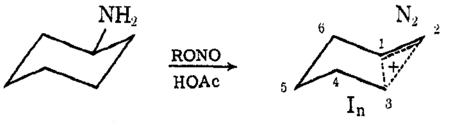
			Analysis, %							
			Carbon		Hydrogen		Mercury		Bromine	
Registry no.	R	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
10192-55-9	Cyclohexyl[a]	153.5–154.0	19.82	19.76	3.05	3.46	55.16	54.78	21.97	21.61
33631-67-3	Cyclopentylmethyl	61.0–62.5	19.82	19.77	3.05	3.43	55.16	54.81	21.97	21.80
27936-01-2	5-Hexenyl	102.5–104.0	19.82	19.87	3.05	3.32	55.16	54.60	21.97	21.80

[a] Cyclohexylmercuric bromide, mp 153°: G. Grüttner, *Chem. Ber.*, **47**, 1651 (1914).

might occur in solvolysis intermediates *if* the rearrangement led to charge development at a point sufficiently remote from the leaving group to avoid its electrostatic effect and if the activation energy for rearrangement were low enough to permit migration without concurrent solvent reorientation.[18]

Reaction of 5-hexenylamine with isoamyl nitrite gave no detectable amounts of cyclic products; so this prospective route to cyclohexyl cation failed.

Bicyclo[3.1.0]hexane was found in 3% yield from cyclohexylamine diazotization, along with 33% cyclohexene. Presumably these come from a common intermediate I_n by the competitive loss of H from two positions, C_3 (to form bicyclo[3.1.0]hexane) and C_2 (to form cyclohexene). The argument that a bicyclic intermediate is necessary to explain a bicyclic product is not compelling, but it is more convenient than a classical cyclohexyl cation. We consider the diazotization to produce a cation without benefit of solvation. Delocalization of the σ bonds follows in the sense of internal "solvation" of the charge, producing I_n. The stability of bicyclo[3.1.0]hexane under the reaction conditions, work-up, and analysis was carefully checked; so the proposal that it is an intermediate which forms other products is not correct in this case.[18a]



Experimental Section

Melting points were obtained on a Monoscop V block melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord spectrophotometer in carbon tetrachloride or chloroform solution and calibrated with respect to polystyrene film. Nmr spectra were obtained in carbon tetrachloride or deuteriochloroform solutions on a Varian A-60 spectrometer and chemical shifts in Hertz were measured from internal tetramethylsilane. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory.

***p*-Nitrobenzenesulfonates.**—The preparation and properties of cyclohexyl, cyclopentylmethyl, and 5-hexenyl *p*-nitrobenzenesulfonates have been described.[5]

Amines.—Cyclohexylamine was used as received (Eastman 2496). 5-Hexenylamine was prepared from 4-pentenyl *p*-nitrobenzenesulfonate.[5] In dimethyl sulfoxide solution 12.5 g of sodium cyanide and 29.3 g of 4-pentenyl *p*-nitrobenzenesulfonate reacted in 4.5 hr at room temperature to form 5-hexenenitrile: 6.7 g; bp 82° (51 mm); $n^{25}{\rm D}$ 1.4243 [lit.[19] bp 54–59° (16 mm); $n^{25}{\rm D}$ 1.4268]; nmr 90–150 (area 6.0), 280–320 (1.8), 320–370 Hz (0.9); ir 3.24 (m), 3.39 (s), 4.44 (m), 6.07 (s), and 6.97 μ (s). The product contained 0.4% of a lower boiling impurity (glc, LAC 446). 5-Hexenenitrile, 6.7 g, with 2.7 g of lithium aluminum hydride in ether for 1 hr gave 5-hexenylamine: 1.9 g; bp 58° (55 mm) (lit.[20] bp 125–126°); $n^{25}{\rm D}$ 1.4349; nmr 70–100 (area 6.0), 110–130 (2.0), 150–170 (2.0), 280–310 (1.9), and 320–370 Hz (0.9); ir 2.94 (s), 3.24 (m), 3.42 (s), 6.08 (s), and 6.96 μ (s). The nmr spectrum in deuteriochloroform had a sharp spike at 87 Hz which was assigned to $-NH_2$ because of ready deuterium exchange. The best 5-hexenylamine obtained had 3% of a higher boiling impurity (glc, UCON 550x/Diatoport W). The phenylthiourea derivative, recrystallized from ethyl acetate–ligroin and from ethyl alcohol, had mp 57°; ir 2.92, 3.44, 6.12, 6.28, 6.54, 6.69, and 10.9 μ. *Anal.* Calcd for $C_{13}H_{18}N_2S$: C, 66.60; H, 7.74; N, 11.95; S, 13.68. Found: C, 66.81; H, 7.74; N, 11.74; S, 13.96.

Cyclopentanecarboxylic acid was converted to cyclopentanecarboxamide by treatment with thionyl chloride and then ammonium hydroxide, mp 179–180° (subliming) (lit.[21] mp 179°). The amide, 10.4 g, with 3.5 g of lithium aluminum hydride in tetrahydrofuran was refluxed for 14 hr. The solution gave 3.4 g of cyclopentylmethylamine, bp 138–140° (768 mm), $n^{25}{\rm D}$ 1.4538 (lit.[22] bp 140°), containing trace amounts (less than 1%) of ether, tetrahydrofuran, and a third volatile impurity (glc, UCON 550x/Haloport F). The ir spectrum had bands at 3.02, 3.48, 3.56, 6.20, 6.89, and 9.3 μ. The phenylthiourea derivative was obtained as square plates from alcohol or from ethyl acetate–ligroin: slightly yellow; mp 132.5–133.0°; ir 2.97, 3.44, 3.55, 6.30, 6.54, and 6.68 μ. *Anal.* Calcd for $C_{13}H_{18}N_2S$: H, 7.74; N, 11.95; S, 13.68. Found: H, 7.61; N, 11.62; S, 13.34.

Alkylmercuric Acetates.—Cyclohexyl-, cyclopentylmethyl-, and 5-hexenylmercuric acetates were prepared *via* Grignard reagents.[23] Cyclohexyl bromide (Eastman) was redistilled before use. Cyclopentylmethanol was converted to the bromide by phosphorus tribromide.[24] 5-Hexen-1-ol obtained from PCR, Inc., contained about 10% impurities (glc, UCON) even after redistillation. It was converted to the bromide in the same way, but the bromide after distillation contained about 5% of a contaminant (glc, UCON). The Grignard reagents, free from magnesium metal, reacted exothermically with mercuric bromide to form alkylmercuric bromides (Table III). Equivalent amounts of the alkylmercuric bromide and silver acetate slurried in methanol for 4 hr at room temperature gave the alkylmercuric acetates (Table IV). Ir and nmr spectra were in agreement with the expected structures.

Products.—1,5-Hexadiene and cyclohexene were obtained commercially. Bicyclo[3.1.0]hexane was prepared in 71% yield.[25] The preparation and properties of cyclopentylmethyl, 5-hexenyl, and 1-methylcyclopentyl acetates have been described.[5]

1-Hexen-5-ol and its acetate were obtained following a procedure of Kharasch.[26] Allyl Grignard reagent with propylene oxide (Eastman) gave the products listed in Table V. Identification of the components is by nmr spectra of certain distillation fractions.

1-Hexen-5-ol was obtained 98.6% pure (glc, UCON): bp 87° (98 mm); $n^{25}{\rm D}$ 1.4293 (lit.[27] bp 138–139°; $n^{24}{\rm D}$ 1.4286); ir 3.00, 3.31, and 6.11 μ; nmr 67 (doublet, area 3), 78–110 (2),

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[18] The idea that a rearranged carbonium ion would have "open" or unsolvated character was clearly expounded by Silver, while Renk and Roberts took the opposite position: (a) M. S. Silver, *J. Amer. Chem. Soc.*, **83**, 3482 (1961); M. S. Silver, *J. Org. Chem.*, **28**, 1686 (1963); (b) E. Renk and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 878 (1961).

[19] F. B. LaForge, N. Green, and W. A. Gersdorff, *ibid.*, **70**, 3707 (1948).

[20] CIBA, Ltd., Belgian Patent 626,292 (June 19, 1963); *Chem. Abstr.*, **60**, P 9158C (1964).

[21] N. Zelinsky, *Chem. Ber.*, **41**, 2627 (1908).

[22] K. Jewers and J. McKenna, *J. Chem. Soc.*, 2209 (1958).

[23] J. H. Robson and G. F. Wright, *Can. J. Chem.*, **38**, 21 (1960).

[24] L. H. Smith, *Org. Syn.*, **23**, 88 (1943).

[25] H. E. Simmons and R. D. Smith, *ibid.*, **41**, 72 (1961); *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

[26] M. S. Kharasch, L. Biritz, W. Nudenberg, A. Bhattacharya, and N. C. Yang, *ibid.*, **83**, 3229 (1961).

[27] J. Colonge and A. Lagier, *Bull. Soc. Chim. Fr.*, 15 (1949).

TABLE IV

ALKYLMERCURIC ACETATES, $RHgOCOCH_3$

		Analysis, %					
		Carbon		Hydrogen		Mercury	
R (Registry no.)	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found
Cyclohexyl	88.0–88.5	28.03	28.38	4.12	4.20	58.52	58.58
Cyclopentylmethyl	88.5–90.0	28.03	28.20	4.12	4.19	58.52	58.85
5-Hexenyl (34825-75-7)	39.0–40.5	28.03	28.01	4.12	4.36	58.52	58.34

TABLE V

PRODUCTS OF REACTION OF ALLYL GRIGNARD REAGENT WITH PROPYLENE OXIDE

Compd	% (glc area)
2-Methyl-4-penten-2-ol	1
Propylene chlorohydrin	10
1-Hexen-5-ol	67
2-Methyl-4-penten-1-ol	8
Yield	86

110–144 (2), 185 (1), 200–240 (1), 280–320 (2), and 320–360 Hz (1). The acetate was obtained in 80% yield, bp 86° (74 mm), $n^{25}\mathrm{D}$ 1.4150 [lit.[28] bp 152° (750 mm), $n^{18}\mathrm{D}$ 1.4211].

Acetolysis Procedure.—Acetolysis and extractive work-up of the *p*-nitrobenzenesulfonates in ampoules has been described.[5] The alkylmercuric acetates were treated in the same way, except that in the absence of rate data the time period required for complete reaction was estimated from observation of the amount of mercury precipitated. The weight of free mercury served as a measure of the extent of reaction of samples, or, if brown sludge resulted, it was dissolved in dilute nitric acid and assayed by standard methods.[29] The glc analysis of the organic products usually gave a yield in agreement.

Addition of a catalytic amount of perchloric acid in the acetolyses of alkylmercuric acetates resulted in an increase in the reaction rates but the product studies were useless because secondary interconversion of the products occurred. Cyclohexylmercuric acetate in 0.01 *M* perchloric acid in acetic acid reacted completely in 2 hr at room temperature, forming 99% of theoretical mercury. Analysis of the product extract showed 90% cyclohexene and 10% cyclohexyl acetate in 75% yield. Cyclohexylmercuric acetate in 0.01 *M* sodium acetate in acetic acid required 135 hr at 80.8° to attain 61% reaction based on the weight of recovered mercury. Glc gave 87% cyclohexene and 13% cyclohexyl acetate in the product extract, with 49% yield.

Acetolysis of cyclopentylmethylmercuric acetate was much slower. In 0.01 *M* perchloric acid in acetic acid, 0.15 *M* solution failed to react at room temperature. However, treatment at 79.7° for 2 hr led to deposition of black sludge containing 51% of theoretical mercury. The organic product, 19% yield, was less than 5% cyclohexene, the rest being cyclohexyl acetate. In 0.01 *M* sodium acetate in acetic acid, a solution of 0.25 *M* cyclopentylmethylmercuric acetate at 80.8° for 691 hr precipitated only 14% of the free mercury expected, along with a substantial amount of brown sludge. The pentane extract of the solution contained no detectable amount of either cyclohexene or cyclohexyl acetate.

Diazotization of the amines was done in a flask with an efficient cold-finger condenser and magnetically stirred in the constant-temperature bath. Sodium nitrite was added in small portions, but reaction was violent with considerable foaming and gas evolution, including nitrous anhydride. The reaction was smoother when isoamyl nitrite was employed as the nitrosating agent introduced *via* syringe through a septum. Gas evolution was moderate throughout and only slightly reddish in color. The reaction mixture was homogeneous, in contrast to the situation with sodium nitrite, which required several minutes to dissolve.

Product Studies.—Product analyses were by glc with area response calibration and using internal standards for the calculation of the absolute yields of individual products. F & M Model 609 and 5750 and Varian Aerograph Model 1520 gas chromatographs with flame ionization detectors were used for the quantitative work. Identification of products was based on ir of fractions condensed from preparative gas chromatography or for minor components by comparison of retention times with authentic samples, verified on two different columns. These were usually silver nitrate in diethylene glycol on Chromosorb P for resolution of the olefins and diisodecyl phthalate on Chromosorb P for acetates. Quantitative work was generally on UCON 550x.

There were indications that methylenecyclopentane was a primary product from cyclopentylmethyl *p*-nitrobenzenesulfonate and was converted to 1-methylcyclopentene. Control samples showed this conversion to occur. However, direct injection of the acetolysis medium produced chromatograms showing somewhat variable amounts of methylenecyclopentane ranging from 2 to 4%. This led to rapid deterioration of the silver nitrate–diethylene glycol columns used for the resolution of methylenecyclopentane and 1-methylcyclopentene, probably due to precipitation of silver acetate.

The resolution of bicyclo[3.1.0]hexane and cyclohexene was best accomplished on a 10 ft × 0.25 in. 10% oxydipropionitrile on Chromosorb P column.

1,5-Hexadiene was chromatographed on a short silver nitrate column because of long retention caused by the very large complexation constant of this olefin.[30]

The stability of cyclohexene, 5-hexenyl acetate, cyclohexyl acetate, and cyclopentylmethyl acetate to the acetolysis conditions was demonstrated with control samples on which gas chromatography showed good recovery and no trace of alteration of the product. This demonstration of kinetic control of the products was reinforced by examination of the products after 2 and 4 half-lives as well as after 10. The product ratios were the same in all cases. When sodium acetate was omitted from the acetolysis medium, changes in the product ratios due to acid-catalyzed rearrangement and addition of acetic acid to unsaturated products were observed. Cyclohexene and cyclohexyl acetate samples in 0.2 *M* perchloric acid in acetic acid at 80° for 2 hr virtually reached equilibrium. The cyclohexene was 96.2% converted to cyclohexyl acetate and 3.4% of cyclohexene was found in the cyclohexyl acetate control. Both samples contained small amounts of extraneous products as well.

5-Hexenyl acetate treated with anhydrous acetic acid containing 0.01 *M* perchloric acid gave products of rearrangement and addition believed to be 4-hexenyl acetate and two isomeric diacetates because of glc characteristics.

The amount of unreacted isoamyl nitrite remaining in the diazotization product extracts was measurable. This was best done on an Apiezon N column, on which the separation from cyclohexene was still just barely adequate. A control sample containing only isoamyl nitrite in 0.011 *M* sodium acetate–acetic acid solution at 79.68° reacted slowly to form isoamyl acetate.

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