Reaction of Cycloalkylmethyl Chlorides with Sodium. Fused Cyclopropanes from Cycloalkylcarbenes

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Reactions of sodium with cyclohexylmethyl, cyclopentylmethyl, cyclobutylmethyl, and cyclopropylmethyl chlorides have been studied. Bicyclic hydrocarbons containing fused cyclopropane rings, presumably formed through intramolecular insertions of cycloalkylcarbenes into C–H bonds, were found in the products of all reactions except those with cyclopropylmethyl chloride. Cyclopentene and cyclobutene, also observed as products, must have formed by rearrangements of cyclobutylcarbene and cyclopropylcarbene, respectively.

To study the reactions of cycloalkylcarbenes, we have investigated the products obtained from treating cyclohexylmethyl, cyclopentylmethyl, cyclobutylmethyl, and cyclopropylmethyl chlorides with sodium in hydrocarbon solutions. In the reaction of an alkyl chloride with sodium, a portion of the chloride is converted to an alkylsodium which then reacts rapidly with additional chloride to produce a carbene (α-elimination), olefin (β-elimination), or coupling product (Wurtz reaction).[1] A number of subsequent reactions are known for carbenes. Rearrangement to olefin (by carbon or hydrogen migration) or cyclopropane (by intramolecular C—H insertion) will produce monomeric products. Reaction with more metal alkyl or with any of the C—H, C—Cl, or C=C bonds present in other molecules in the reaction mixture will lead to products of higher molecular weight. Only monomeric products were examined in this study. As expected from the stoichiometry of the reaction, the elimination products, C_nH_{2n-2}, in any run were found to be somewhat less than one-half of the monomeric product, with products arising from the base, C_nH_{2n}, comprising the remainder.

For example, the reaction of cyclohexylmethyl chloride with sodium led to a mixture of C_7 hydrocarbons (Table I) containing methylcyclohexane as the only C_nH_{2n} product and bicyclo[4.1.0]heptane and methylenecyclohexane as the only C_nH_{2n-2} products. Methylcyclohexane presumably arises from reaction of cyclohexylmethylsodium as a base and bicyclo[4.1.0]heptane from an intramolecular insertion reaction of cyclohexylcarbene. Though methylenecyclohexane could form either from the chloride by β-elimination or from cyclohexylcarbene by hydrogen migration, it probably formed mostly from the carbene since α-elimination has been shown[1] to predominate over β-elimination in similar reactions of other primary chlorides.

Cyclopentylmethyl chloride and sodium reacted to give a similar mixture containing methylcyclopentane as the only C_nH_{2n} product, and bicyclo[3.1.0]hexane, methylenecyclopentane, and cyclohexene as C_nH_{2n-2} products. The chloride contained 6% of cyclohexyl chloride which could have been responsible for the cyclohexene observed.

A similar reaction of cyclobutylmethyl chloride gave a mixture of C_5 hydrocarbons containing methylcyclobutane and 1-pentene as C_nH_{2n} products, and bicyclo[2.1.0]pentane, methylenecyclobutane, and cyclopentene as C_nH_{2n-2} products. A control reaction of sodium with a mixture of cyclopentyl chloride and cyclohexylmethyl chloride led to substantial amounts of cyclopentane as well as cyclopentene. Therefore, in the reaction with cyclobutylmethyl chloride, the cyclopentene formed most reasonably by carbon migration in the cyclobutylcarbene intermediate and not by a β-elimination reaction of cyclopentyl chloride, which conceivably might have formed from cyclobutylmethyl chloride under the reaction conditions.

Addition of cyclopropylmethyl chloride to a phenylsodium solution led to a mixture of C_2 and C_4 hydrocarbons composed principally of 1-butene, cyclobutene, butadiene, and ethylene. Reaction of the chloride with sodium produced the same C_4 compounds, but 1-butene comprised 59% of the product. The products which apparently formed from the carbene were cyclobutene, butadiene, and ethylene. The same products plus acetylene were obtained by Friedman and Shechter[2] from the reaction of cyclopropanecarboxaldehyde tosylhydrazone with base, and the relative proportions of the products were similar despite the difference of almost 150° in reaction temperature and the different precursor of cyclopropylcarbene. Acetylene presumably formed along with ethylene in our reactions but would have remained in the reaction flask as the sodium salt.

Ring opening of the alkylsodium compounds to isomers is postulated to account for the formation of 1-pentene from cyclobutylmethyl chloride and 1-butene from cyclopropylmethyl chloride. This type of interconversion has been reported for the cyclopropylmethyl and 3-butenyl Grignard and lithium reagents,[3] and we have observed the corresponding ring cleavage of cyclobutylmethyllithium and of a cyclobutylmethyl Grignard reagent.[4] Since ring cleavages of cyclobutylmethyllithium and the corresponding Grignard reagent proceed nearly to completion,[4] the relative yields of 1-pentene and methylcyclobutane in the reaction product from cyclobutylmethyl chloride probably do not

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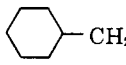
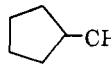
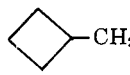
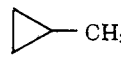
(2) L. Friedman and H. Shechter, *ibid.*, **82**, 1002 (1960).

(3) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960); P. T. Lansbury and V. T. Pattison, *ibid.*, **85**, 1886 (1963).

(4) E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963).

TABLE I

HYDROCARBON PRODUCTS FROM REACTIONS OF CYCLOALKYLMETHYL CHLORIDES

Reactants	Yield of monomeric product, %	Components in product mixture, mole %: C_nH_{2n} components: Methylcycloalkane	C_nH_{2n} components: 1-Alkene	C_nH_{2n-2} components: Bicycloalkane	C_nH_{2n-2} components: Methylenecycloalkane	C_nH_{2n-2} components: Cycloalkene
 $CH_2Cl + Na$	69	61		3	36[a]	
 $CH_2Cl + Na$	68	54		34	10	2
 $CH_2Cl + Na$	40	6	59	10	8	17
 $CH_2Cl + PhNa$	8[b]		17	*c*		47

[a] Slightly contaminated with an unidentified component. [b] This was the yield of $C_2 + C_4$ hydrocarbons. [c] Other products were butadiene (15%, contaminated with an impurity that probably was methylcyclopropane), ethylene (19%), and an unidentified component (1.5%).

reflect the composition of an equilibrium mixture of the two sodium derivatives; the presence of methylcyclobutane suggests that the rate of reaction of cyclobutylmethylsodium in the elimination reactions is comparable to its rate of ring opening. The related open-chain olefins (1-heptene and 1-hexene) were not found in the products from reactions with cyclohexylmethyl and cyclopentylmethyl chlorides.

The maximum yield of fused cyclopropane relative to isomeric olefins was found with cyclopentylmethyl chloride suggesting that a nearly coplanar arrangement of the bivalent carbon, the ring carbon to which it is attached, and the C–H bond may be favorable for insertion. With cyclobutylcarbene and cyclopropylcarbene, competition from ring expansion by carbon migration becomes important; in addition, as the ring size decreases, the bivalent carbon becomes increasingly further from the C–H bond on an adjacent carbon. The decrease in insertion by the carbene from cyclohexylmethyl chloride may be ascribed to the strain introduced in attaining a nearly eclipsed conformation. Moore, Ward, and Merritt have reported the formation in good yield of tricyclic insertion products from the reaction of 7,7-dibromobicyclo[4.1.0]heptane with methyllithium.[5] In this reaction, however, hydrogen migration is probably minimized since it would lead to a highly strained fused cyclopropene.

Experimental

Cycloalkylmethyl Chlorides.—Cyclohexylmethyl Chloride, b.p. 58–60° (18 mm.), lit.[6] 54–55° (19 mm.), was prepared from reaction of cyclohexylmethanol with thionyl chloride and pyridine as described by Kice.[6]

Cyclopentylmethyl chloride, b.p. 136–138° (731 mm.), lit.[7] 72° (25 mm.) and 60 (50), was prepared from cyclopentylmethanol in a similar manner but with a shorter reaction time and at a lower temperature. The lower layer (pyridinium salts) of the reaction mixture crystallized, facilitating the isolation of the chloride. This chloride sample was found to contain about 6% of cyclohexyl chloride by g.l.p.c. using a 100-ft. capillary column coated with SE-30 methyl silicone gum rubber (General Electric).

Cyclobutylmethyl chloride, apparently not reported previously was prepared by treating cyclobutylmethanol with thionyl chloride and tri-*n*-butylamine in ether solution using a modification of a procedure[8] used to prepare cyclopropylmethyl chloride. The ether was distilled from the reaction mixture at slightly reduced pressure. Then over 1.5 hr. the temperature was raised to 90° and the pressure was reduced to about 20 mm.; the product distilled from the reaction mixture as it formed. Redistillation gave cyclobutylmethyl chloride, b.p. 109.5–110.5° (740 mm.), that was shown by n.m.r. analysis (comparison of areas of the doublet due to the hydrogens of the chloromethyl group of cyclobutylmethyl chloride and the complex peak due to the methine hydrogen of cyclopentyl chloride) to contain less than 1% of cyclopentyl chloride. A sample prepared by a procedure similar to that used for cyclopentylmethyl chloride contained 15% of cyclopentyl chloride.

Anal. Calcd. for C_5H_9Cl: C, 57.42; H, 8.67. Found: C, 57.13; H, 8.83.

Cyclopropylmethyl chloride, b.p. 83.5–85° (719 mm.), lit.[8] 85.5° (748 mm.), was prepared as described by Caserio, Graham, and Roberts.[8] The infrared spectrum of the sample was identical with a published one.[9]

Separation and Identification of Products.—Reaction products were separated by g.l.p.c. in instruments with thermal conductivity detectors and using helium as the carrier gas. The columns used were column A, 5-ft., 25% Apiezon J (Metropolitan Vickers Co.) on firebrick; column B, 10-ft., silver nitrate in diethylene glycol on firebrick; column C, 2-ft., SE-30 methyl silicone gum rubber (General Electric) on firebrick; column D, 20-ft., 30% dipropylene glycol dibenzoate on firebrick. Fractions were collected in traps cooled in liquid nitrogen and then transferred to a vacuum line. The weights of fractions were assumed to be proportional to the peak areas on the gas chromatograms.[10,11] Identification of each fraction is described subsequently.

Reaction of Cyclohexylmethyl Chloride with Sodium.—The chloride (5.0 g.) was added over 90 min. to 1.1 g. of sodium cut into small pieces in 5 ml. of cyclohexane. The reaction mixture warmed considerably. The reaction flask was heated at 75° for 1 hr. and then was connected to a trap cooled in liquid nitrogen, and the volatile materials were transferred to the trap using a vacuum pump. Chromatography of the reaction mixture over column A gave, in order of elution, cyclohexane, a mixture of methylcyclohexane and methylenecyclohexane, followed closely by a small amount of an unknown component, and bicyclo[4.1.0]-heptane. Using column B, methylenecyclohexane was eluted after methylcyclohexane, and their relative amounts were determined. The yield of C_7 hydrocarbons was calculated by subtracting the large amount of solvent present (estimated by comparing areas of the cyclohexane peak with the areas due to C_7

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(6) J. L. Kice, *ibid.*, **80**, 348 (1958).

(7) M. Mousseron, *Bull. soc. chim. France*, [5] **15**, 84 (1948); J. von Braun and E. Anton, *Ber.*, **66**, 1373 (1933); N. Turkiewicz, *ibid.*, **72**, 1060 (1939).

(8) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

(9) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(10) L. J. Nunez, W. H. Armstrong, and H. W. Cogswell, *Anal. Chem.*, **29**, 1164 (1957); L. C. Browning and J. O. Watts, *ibid.*, **29**, 24 (1957).

(11) G. L. Tingey, Ph.D. thesis, The Pennsylvania State University, June, 1963.

components) and the small amount of unchanged chloride (estimated from comparing areas of the chloride peak and the peak due to cyclohexane and C_7 components in a chromatogram with column C) from the weight of the crude product. Methylcyclohexane and bicyclo[4.1.0]heptane were identified by comparison of their infrared spectra with those of authentic samples. Methylenecyclohexane was identified by a comparison of the infrared spectrum of the gas with that reported for a liquid sample.[12] A reaction run in the same manner using *n*-tetradecane as solvent gave very similar results.

Reaction of Cyclopentylmethyl Chloride with Sodium.—In a similar manner, 5.0 g. of chloride was added over 75 min. to 1.4 g. of sodium in 4 ml. of isooctane, and the reaction mixture then was heated gradually to 100° over 1 hr. The yield of C_6 hydrocarbons was calculated by correcting the weight of the crude product by the same procedure described for the reaction with cyclohexylmethyl chloride. Chromatography of the reaction mixture over column D gave, in order of elution, methylcyclopentane, methylenecyclopentane, and a mixture of bicyclo[3.1.0]hexane and cyclohexene. Methylcyclopentane was identified by comparison of its infrared spectrum with API 14,[13] and methylenecyclopentane by comparison of the spectrum of the gas with that reported for a liquid sample[14]; cyclohexane has the same retention time but the infrared spectrum indicates that it could not be present in significant amount. Bicyclo[3.1.0]hexane was identified by the n.m.r. spectrum of a carbon tetrachloride solution which had complex absorption from τ 8.2 to 9.0.[15] Cyclohexene has the same retention time as bicyclo[3.1.0]hexane, and its presence was detected and its amount was estimated by the presence of weak absorption at τ 4.4 (identical in position with the absorption of authentic cyclohexene). A reaction run in the same manner in *n*-tetradecane gave similar results.

Reaction of Cyclobutylmethyl Chloride with Sodium.—In a similar manner, 2.1 g. of cyclobutylmethyl chloride was added over 1 hr. to 1.1 g. of sodium in 1.4 ml. of *n*-tetradecane. Chromatography of the reaction mixture over column D gave, in order of elution, 1-pentene, methylcyclobutane, methylenecyclobutane, cyclopentene, and bicyclo[2.1.0]pentane. Cyclopentene and 1-pentene were identified by comparison of their infrared spectra with those of authentic samples. Methylcyclobutane and methylenecyclobutane were identified by comparison of their spectra with API 890 and 561, respectively.[13] Bicyclo[2.1.0]pentane was identified by the close comparison of the infrared spectrum of a carbon tetrachloride solution with that reported for the pure liquid[16] and also by comparison of its n.m.r. spectrum with one reported.[17] Cyclopentane has the same retention time as methylenecyclobutane but was shown to be absent by examination of the n.m.r. spectrum. In a similar reaction with chloride containing 15% of cyclopentyl chloride, cyclopentane (identified by comparison of its infrared spectrum with API 446)[13] was shown to comprise 14% of the product by rechromatographing the "methylenecyclobutane" fraction over column B which eluted cyclopentane before methylenecyclobutane. A reaction with 1.2 g. of cyclopentyl chloride and 4.0 g. of cyclohexylmethyl chloride led to cyclopentane (32%) and cyclopentene (68%) as the only detected C_5 products.

Reactions of Cyclopropylmethyl Chloride with Phenylsodium and Sodium.—Phenylsodium was prepared in 12 ml. of isooctane from 7.5 g. (0.067 mole) of chlorobenzene and a dispersion of 2.2 g. (0.096 g.-atom) of sodium in 4.2 g. of mineral oil. Then a solution of 1.99 g. (0.022 mole) of cyclopropylmethyl chloride in 5 ml. of isooctane was added over 45 min. Nitrogen was passed continually over the reaction mixture, and the exit gases were passed through a trap cooled in liquid nitrogen. The reaction mixture was stirred for an additional 90 min. Then the material in the trap was transferred to a vacuum line and was fractionated crudely by two distillations through a Dry Ice trap to remove less volatile components. Chromatography over column D gave, in order of elution, ethylene, 1-butene, butadiene, cyclobutene, and an unidentified peak. Ethylene was identified by its retention time. Butadiene and 1-butene were identified by comparison of their infrared spectra with API 917 and 901, respectively,[13] and cyclobutene by comparison with a published spectrum.[18] The butadiene peak had a shoulder slightly before the main peak of about one-fifth of the total peak area. The retention time of this shoulder corresponded to that of methylcyclopropane,[11] and some weak bands in the infrared spectrum corresponded to those in the infrared spectrum of methylcyclopropane.[19] Another reaction carried out by adding the chloride to sodium in cyclohexane gave in 5% yield a mixture of 1-butene (59%), butadiene (11%, with a small shoulder preceding the main peak), and cyclobutene (30%); Dry Ice was used in the trap so that ethylene would not have been collected.

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(15) Spectra were taken at 60 Mc. Chemical shifts are in parts per million relative to tetramethylsilane as 10.0.
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Condensation of Dimethyl Acetylenedicarboxylate with Malononitrile, Ethyl Cyanoacetate, and Malonate Esters

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In the presence of a mixture of pyridine and acetic acid, dimethyl acetylenedicarboxylate condenses with malononitrile and with ethyl cyanoacetate to give, respectively, pyridinium salts II and III. Under the same conditions dimethyl acetylenedicarboxylate and malonate esters yield two isomeric 1,1,2,3,4,5,6,7-octacarboalkoxycycloheptadienes. Aqueous potassium acetate converts these cycloheptadienes into the potassium salt of the strongly acidic 1,2,3,4,5-pentacarboalkoxycyclopentadiene.

In his classical studies of the chemistry of acetylenic esters Diels has shown that, in the presence of pyridine and acetic acid, dimethyl acetylenedicarboxylate readily condenses with malononitrile, ethyl cyanoacetate, dimethyl, and diethyl malonate to form a multitude of products.[1] While careful experimental work led to the isolation of a variety of products, disturbing features in several structural assignments prompted our

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