Cyclopentylcarbene-α-*d*. Stereochemistry at the Carbene Carbon in Intramolecular Carbene and Carbenoid Insertion[1]

E. ALEXANDER HILL

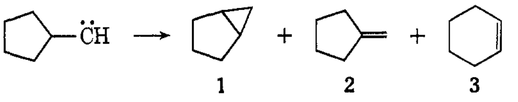
Department of Chemistry, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201

Received December 2, 1971

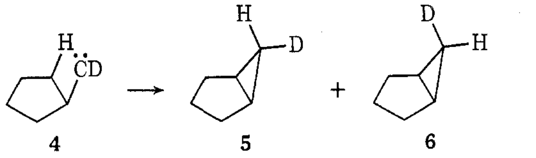
Bicyclo[3.1.0]hexane is the major product formed from cyclopentylcarbene 1, or related carbenoids, generated by (a) the decomposition of the tosylhydrazone of cyclopentanecarboxaldehyde; (b) the action of sodium on cyclopentylmethyl chloride; (c) the reaction of cyclopentyllithium with methylene chloride; and (d) the reaction of cyclopentylmagnesium chloride with methylene chloride. Using a deuterium label in the carbene precursors, it was found that the stereochemistry of bond formation at the carbene carbon varies with carbene or carbenoid source. Observed stereochemistry is rationalized on the basis of likely transition-state geometries.

Knowledge of the stereochemistry of organic reactions often provides illuminating insight into their mechanisms. In the case of carbene insertion into a saturated C–H bond, it has been found previously that the reaction occurs with retention of configuration at the C–H bond being attacked.[2,3] In the present study, we report findings concerning another aspect of the stereochemistry of carbene or carbenoid insertion—the steric preference for formation of the new bonds to the "bivalent" carbon.

In previous work, we have found that three probably "carbene-derived" products—bicyclo[3.1.0]-hexane, methylenecyclopentane, and cyclohexene—are formed in the reaction of cyclopentylmethyl chloride with metallic sodium (eq 1).[4] In the first of these, two stereochemical outcomes at the "carbene carbon" are possible: the hydrogen originally attached to this carbon may be either exo or endo in the final bicyclic product. In eq 2, this is illustrated in the instance of a deuterated carbene. The relative preference for 5 *vs.* 6 may provide valuable insight into the nature of the transition state for the insertion. In this paper, we report the product distribution and stereochemical preference for several variations of "carbene-generating" reactions in the cyclopentylmethyl system.



(1)



(2)

Results

In Tables I and II, the products of a variety of "cyclopentylcarbene" reactions are summarized. Reactions studied were the decomposition of the tosylhydrazone of cyclopentanecarboxaldehyde with base under several sets of conditions, the reaction of cyclopentylmethyl chloride with sodium metal, and the reactions of cyclopentyllithium and cyclopentylmagnesium chloride with methylene chloride. Product distributions were determined by gas chromatography or nmr, and the identity of the products was confirmed by nmr spectra of the mixed or separated products. In the tosylhydrazone decomposition, the three products 1, 2, and 3 were detected by gas chromatography. The methylenecyclopentane fraction contained an additional alkene, most probably 1-methylcyclopentene formed by base-catalyzed isomerization. Both are included as methylenecyclopentane in Tables I and II. The methylene chloride reactions produced complex product mixtures, with the same products present in the C_6 portion. Methylcyclopentane was formed in the cyclopentylmethyl chloride[4] and cyclopentylmagnesium chloride reactions.

The deuterated carbene 4 and corresponding carbenoids were generated in similar fashion. Deuterated precursors were cyclopentanecarboxaldehyde-α-*d*, cyclopentylmethyl chloride-α,α-d_2, and methylene chloride-d_2. The stereochemistry of deuterium in products 5 and 6 was determined by nmr. From published data, it is expected that the secondary *endo*-cyclopropane proton in 5 should be at higher field than the exo hydrogen in 6.[5] Furthermore, the cis vicinal coupling constant in cyclopropanes is expected to be somewhat larger than the trans constant.[5] Consequently, a triplet absorption at δ 0.15 ppm ($J = 3.9$ Hz) is assigned to the endo proton of 5 and triplet absorption at δ 0.30 ppm ($J = 7.9$ Hz) to the exo proton of 6. The spectrum was determined in various cases at 100 MHz, which gave complete separation of the two triplets, or at 60 MHz, with deuterium decoupling to sharpen the overlapping absorptions.

Discussion

It may be seen from Tables I and II that the stereochemistry of deuterium in the bicyclo[3.1.0]hexane product (1) is highly dependent upon the carbene or carbenoid precursor. In the tosylhydrazone decompositions, which have the greatest likelihood of a free carbene intermediate,[3] there is a small but definite preference for formation of 5, with the deuterium exo. The organometallic routes show the opposite stereo-

---

[1] (a) This research was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society. (b) Reported in part at the 154th National Meeting of the American Chemical Society, Miami, Fla., Sept 1967, Abstracts S-107.

[2] (a) J. A. Landgrebe and D. E. Thurman, *J. Amer. Chem. Soc.*, **91**, 1759 (1969). (b) W. Kirmse and M. Buschhoff, *Chem. Ber.*, **102**, 1098 (1969). (c) D. Seyferth and V. M. Cheng, *J. Amer. Chem. Soc.*, **93**, 4072 (1971). (d) For examples of other stereochemical outcomes, see V. Franzen and R. Edens, *Justus Liebigs Ann. Chem.*, **729**, 33 (1969).

[3] For reviews of carbene chemistry, see J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964; W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; D. Bethel, *Advan. Phys. Org. Chem.*, **7**, 153 (1969).

[4] H. G. Richey, Jr., and E. A. Hill, *J. Org. Chem.*, **29**, 421 (1964).

[5] P. G. Gassman and F. V. Zalar, *Tetrahedron Lett.*, 3251 (1964); W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967), and references cited therein.

TABLE I

BASIC DECOMPOSITION OF CYCLOPENTANECARBOXALDEHYDE TOSYLHYDRAZONE

Solvent	Base	Yield, % N$_2$	Yield, % Hydrocarbon	C$_6$H$_{10}$ product distribution[a] **1**	**2**	**3**	**2/1**	endo D/exo D (**6/5**)[a]
Ethylene glycol	NaOCH$_3$	86		3	15	82	(5)	
DEC[b]	NaOCH$_3$	87	10	36	18	46	0.50	
DEC[b,c]	NaOCH$_3$	82	10	36	20	44	0.56	1.05 ± 0.10[d]
DEC[b] + 1 equiv of CH$_3$OH	NaOCH$_3$	60	10	32	18	50	0.56	
DEC[b]	NaOCH$_3$ (6 equiv)	82	30	71	27	2	0.39	
DEC[b,c,e]	NaH	85	30	73	27	0	0.37	0.6 ± 0.10[d]
C$_{16}$H$_{34}$	NaOCH$_3$	70		22	15	63	0.68	
C$_{16}$H$_{34}$	NaH	90[f]	10	36	21	43	0.59	
C$_{16}$H$_{34}$	NaH	90[f]	10	36	25	39	0.69	0.85 ± 0.05
								0.95 ± 0.05
C$_{16}$H$_{34}$[c]	Na salt[g]	90	12	73	26	1	0.36	0.61 ± 0.05
C$_{16}$H$_{14}$	C$_4$H$_9$Li[h]	75	25	54	28	48	0.52	
C$_{16}$H$_{14}$	Li salt[i]	55	10	68	30	2	0.44	
C$_{16}$H$_{14}$	*j*			67	33		0.49	
NMP[c,k]	NaH	80	30	70	28	2	0.39	*l*
None	Na salt[g]	80	50	69	30	2	0.44	
None[c]	Na salt[g]	90	45	70	30		0.43	0.68 ± 0.05
None	Li salt[i]	75	42	58	39	3	0.67	
None[c]	Li salt[i]	75	35	62	35	3	0.56	0.67 ± 0.05
				56	43	1	0.77	0.68 ± 0.05

[a] Uncertainties in product distribution ±5%; uncertainties in **6**/**5** ratio estimated by examination of nmr tracings. [b] Diethylcarbitol. [c] Tosylhydrazone from α-*d* aldehyde. [d] Partial exchange of deuterium. [e] Solvent stored over molecular sieves; run on undried solvent sample gave ~20% cyclohexene and **6**/**5** ratio of 1.0. [f] Nitrogen plus hydrogen. [g] Na salt prepared with NaH in THF; THF removed under vacuum. [h] Butyllithium in hexane added to tosylhydrazone suspended in C$_{16}$H$_{34}$; no reaction until heating. [i] Li salt prepared with C$_4$H$_9$Li in THF; THF removed under vacuum. [j] Isolated diazo compound. [k] *N*-Methylpyrrolidone. [l] Complete exchange of *d* in **1**.

TABLE II

ORGANOMETALLIC "CYCLOPENTYLCARBENE" REACTIONS

Reactants	C$_6$H$_{10}$ product distribution **1**	**2**	**3**	**2/1**	endo D/exo D (**6/5**)[a]
c-C$_5$H$_9$CH$_2$Cl + Na	74	24	2	0.32	2 ± 0.3
c-C$_5$H$_9$Li + CH$_2$Cl$_2$	60	40	0	0.67	1.8 ± 0.2
c-C$_5$H$_9$MgCl + CH$_2$Cl$_2$	50	45	5	0.9	3.6 ± 0.3

[a] Uncertainties estimated by examination of nmr tracings.

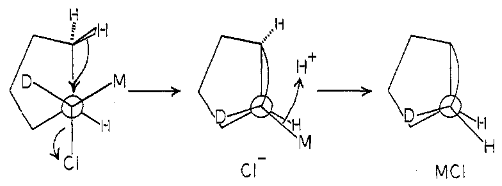


Figure 1.—Rationalization of insertion stereochemistry in cyclopentylcarbenoid insertions. Representation in two stages is for purposes of clarity.

chemical preference, most strikingly so in the magnesium case. This difference may probably be interpreted to imply that the precursor to products in all three organometallic routes is not the free carbene, but, instead, an α-halo organometallic compound, or carbenoid. Such species have been shown to be the product-determining intermediates in numerous instances of cyclopropane formation from alkenes[3,6] and are suggested in some cases of insertion into a C–H bond.[7] A less likely alternative is that carbenes are intermediates in all cases, but that different modes of generation produce the carbene in different rotational conformations. If insertion and rearrangement were to occur more rapidly than internal rotation, then different product distributions and stereochemistries could result.

Rationalizations of the product stereochemistries may be made on the basis of possible transition-state structures for insertion.

For the carbenoid intermediates in the organometallic routes, the insertion may be pictured as simultaneous nucleophilic and electrophilic substitution processes at the carbenoid carbon (see Figure 1). The nucleophilic displacement of chloride by the electrons of the C$_2$–H bond should occur with inversion of configuration at C$_\alpha$ (first stage of Figure 1). The electrophilic substitution, protolysis of the carbon–metal bond by the C$_2$ H proton, would be expected to occur with retention of configuration at C$_\alpha$ (second stage of Figure 1). Since the electron-deficient metal of most organometallic compounds is involved in solvation or aggregation, the metal would probably be the bulkiest of the groups on the carbenoid carbon, and so the conformation shown in Figure 1 should predominate. From this conformation, the insertion product, **6**, with endo deuterium should then be expected. Though the process in Figure 1 is drawn in two stages for purposes of clarity, we envision the insertion as a single step. However, the generally electrophilic nature of carbenoids suggests that in the transition state for insertion the electronic displacements represented in the

---

(6) (a) G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964). (b) L. Friedman, R. J. Honour, and J. G. Berger, *ibid.*, **92**, 4640 (1970). (c) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964). (d) G. Kobrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967). (e) See also G. Kobrich, H. Buttner, and E. Wagner, *ibid.*, **9**, 169 (1970), for an alternate explanation of some results.

(7) M. J. Goldstein and W. J. Dolbier, *J. Amer. Chem. Soc.*, **87**, 2293 (1965); L. Y. Goh and S. H. Goh, *J. Organometal. Chem.*, **23**, 5 (1970).

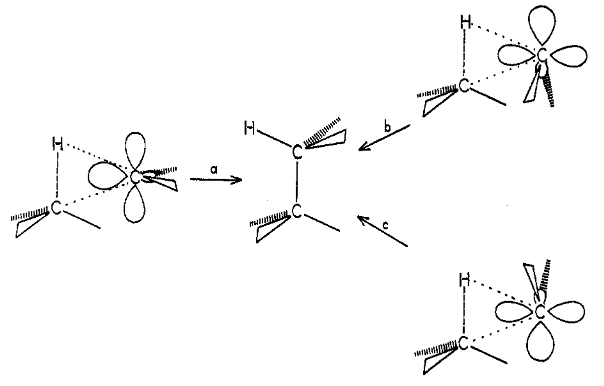


Figure 2.—Triangular "Skell–Doering" transition state for carbene insertion. Reaction paths b and c are in better accord with orbital symmetry considerations. In all cases, the reacting carbene orbitals, the CH bond, and the new C–C and C–H bonds are all coplanar.

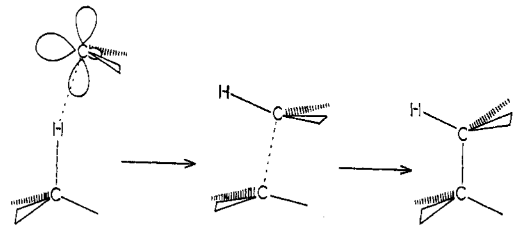


Figure 3.—Abstraction-like "Benson–Hoffman" reaction coordinate for carbene insertion. The transition state is calculated to resemble the first structure shown.[12]

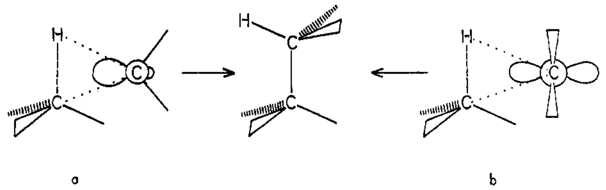


Figure 4.—Unfavorable insertion transition-state geometries. Reacting orbitals in these structures are not coplanar. The carbene p-orbital in a and hybrid orbital in b are perpendicular to the plane of the paper.

first stage of Figure 1 may be more advanced than those in the second stage. Somewhat similar considerations have led to a proposed transition-state geometry for the addition of a carbenoid to a carbon–carbon double bond.[6a]

For the insertion of a free carbene into a C–H bond, the literature contains conflicting opinions. In the pioneering studies of Skell and Woodworth[8] and Doering and Prinzbach,[9] a triangular addition-like reaction path was originally presumed (interpreted as path a in Figure 2). More contemporary considerations of orbital symmetry would prefer "nonlinear cheletropic" reaction paths[10] (b and c in Figure 2). Here, the symmetry "match-ups" would be the vacant carbene p orbital with the filled CH σ orbital, and the filled carbene hybrid orbital with the σ^* orbital. The projection of the hybrid orbital points toward either the hydrogen (path b) or the carbon (path c) of the C–H bond. Benson and DeMore[11] have concluded that an alternative abstraction-like reaction coordinate is more consistent with the high efficiency of insertion reactions. Extended Hückel calculations by Dobson, Hayes, and Hoffmann[12] support this picture as the path of minimum energy. They predict the reaction path shown in Figure 3, with the transition state approximating the structure a. Though the reaction coordinate resembles an abstraction–recombination sequence, the calculations suggest substantial C–C bonding *before* shift of the hydrogen and transfer of electron density from the σ bond to the carbene p orbital. The energy is relatively insensitive to distortion from this geometry, and, indeed, a continuum of transition-state structures differing little in energy may be visualized between extremes pictured in Figures 2 and 3.[13] However, where the insertion is intramolecular, yielding a cyclopropane ring, the triangular *vs.* abstraction question is no longer meaningful. Normal bond lengths and angles preclude approach of the carbene along the line of the C–H bond and constrain it to a position nearer to a perpendicular from the midpoint of the C–H bond (see, for example, 4 in eq 2). Since the insertion is exothermic, the transition state probably has a similar geometry.

A significant distinction in transition-state geometries exists, however, which *does* apply to the intramolecular cyclopropane-forming insertion. In all transition-state geometries drawn in Figures 2 and 3, one feature consistently recurs: all orbitals involved in the reaction lie in one plane—the carbene p and hybrid orbitals and the C–H bonding and antibonding orbitals, as well as the orbitals of the new C–C and C–H bonds being formed. Such a geometric relationship is expected to be favorable, as it gives maximum overlap between reacting orbitals. If a cyclopropane ring is being formed by intramolecular insertion, examination of models shows that it is no longer possible to have all of the appropriate orbitals of reactant and product in the same plane. However, it is reasonable that transition states most closely approaching a coplanar arrangement of orbitals would be most favorable. Figure 4 shows two triangular transition states which lack the "coplanar orbital" geometry. To maintain the same perspective as in Figures 2 and 3, these transition states are drawn with one of the carbene orbitals (p orbital in 4a and hybrid orbital in 4b) perpendicular to the plane of the paper, in which the other orbitals lie. Because the transition states of Figure 4 lack a coplanar geometry of reacting orbitals they might be expected to be higher in energy than ones resembling Figure 2. For example, in 4a, the carbene

---

(8) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956).

(9) W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1956).

(10) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, GmbH, Weinheim/Bergstr., 1970, pp 152–158; R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

(11) S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964); W. B. DeMore and S. W. Benson, *ibid.*, **2**, 219 (1964).

(12) R. C. Dobson, D. M. Hayes, and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6188 (1971).

(13) Gutsche and coworkers[14] have interpreted the distribution of products in an intramolecular insertion reaction as providing a preference for the triangular transition state of Figure 2a. A product that would appear from models to result from a near-perfect Benson–Hoffmann transition state is formed in only minor amounts, while a more strained product, whose formation almost demands a perpendicular approach of the carbene to the C–H bond, is the major isomer isolated. It would appear that the symmetry-preferred reaction path of Figure 2b would be equally acceptable.

(14) C. D. Gutsche, G. L. Bachman, W. Udell, and S. Bäuerlein, *J. Amer. Chem. Soc.*, **93**, 5172 (1971); T. A. Baer and C. D. Gutsche, *ibid.*, **93**, 5180 (1971).

p orbital is orthogonal to both the C–H bonding and antibonding orbitals.

Two possibilities for a geometry leading to insertion in cyclopentylcarbene are shown in Figure 5. In both of these, the carbene carbon occupies a pseudoequatorial conformation on the cyclopentane ring. The carbene p orbital, which is not shown in these drawings, is approximately perpendicular to the plane of the paper. The two geometries differ by a 180° rotation about the ring–carbene bond. The relative orientations of the carbene carbon and the reacting C–H bond in 5a and 5b nearly resemble 2b and 4a, respectively. (In the drawings of Figure 5, the vantage point has been changed for a clearer visualization of the stereochemistry resulting upon insertion. The vantage point in Figure 5 is equivalent to a location in the plane of the paper and to the right of the drawings in Figures 2 and 4.) Insertion from the favorable geometry of Figure 5a most smoothly proceeds to product in which deuterium originally on the carbene carbon becomes exo in the bicyclic product. This is the result found experimentally. The smaller amount of product formed with endo deuterium could be formed either *via* a transition state resembling the less favorable 5b or through a transition state in which the carbene carbon is pseudoaxial on the ring.

Several somewhat less central features of the present results may also be profitably discussed.

A complicating feature in the generation of carbenes from tosylhydrazones is the competing cationic (carbonium ion) reaction of the intermediate diazo compound, favored by a proton-donating reaction medium.[15] Data in Table I suggest that reactions which are largely carbene are characterized by formation of little or no cyclohexene and a low ratio of methylenecyclopentane to bicyclohexane ($2/1 < 0.5$). In diethylcarbitol, sodium hydride as base appears to favor the carbene process. With sodium methoxide, methanol formed in the acid–base reaction is an effective proton donor, but a large excess of methoxide decreases proton availability.[15b] In the reactions of sodium hydride or butyllithium in hexadecane, the tosylhydrazone is relatively insoluble until high reaction temperatures are reached, so that undissociated tosylhydrazone may serve as a readily accessible proton donor. The decomposition of the dry lithium salt is somewhat anomalous, since low cyclohexene yields accompany a relatively high ratio of methylenecyclopentane to bicyclohexane. It is possible that the lithium ion may act as an electrophile, or otherwise influence the course of reaction. (It was also noted that some tetrahydrofuran, used as solvent in preparation of the tosylhydrazone salts, remained with the lithium salt, but not with the sodium salt.)

A small but real variation in the stereochemical outcome occurs in the tosylhydrazone reactions. This may result from production of bicyclohexane of different stereochemical specificity in the competing cationic reaction, or, alternatively, it may reflect a sensitivity of the carbene's reaction to its environment.

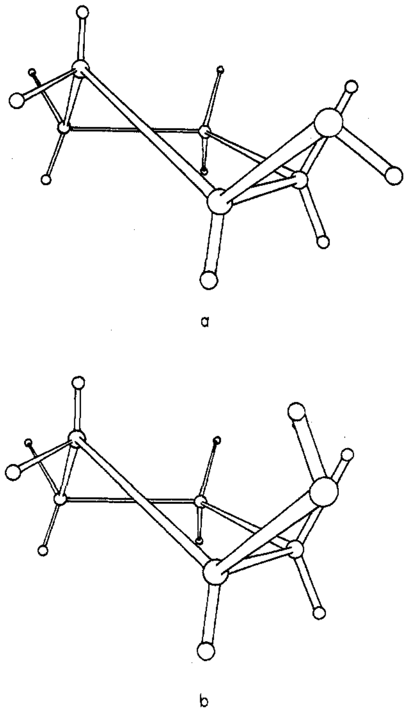


Figure 5.—Two cyclopentylcarbene conformations with the carbene carbon in pseudoequatorial position. The model in these drawings is oriented to show the carbene carbon and C–H bond as they would be seen from a vantage point in the plane of of the paper and to the right in Figures 2 and 4.

Another complication in the tosylhydrazone reactions is isotopic hydrogen exchange, shown by the presence of more complex absorption in the cyclopropane methylene region attributed to undeuterated product. In *N*-methylpyrrolidone, the bicyclohexane from deuterated tosylhydrazone was undeuterated. It is most probable that exchange of the tosylhydrazone or its salt, or of the diazo compound, had occurred, so that the stereochemical result was not affected by a selective exchange of one bicyclohexane isomer.

In the reaction of cyclopentylmethyl chloride with sodium, nmr and mass spectral analysis showed much dideuterated methylcyclopentane along with the trideuterated material expected from α elimination. This result would be consistent with competing β elimination, as would the presence of dideuterated methylenecyclopentane and an increase in the ratio of methylenecyclopentane to bicyclohexane.

Experimental Section

Nmr spectra were run on Varian Associates HA-100 and A-60 spectrometers. Deuterium decoupling on the latter instrument was done with an Nmr Specialties heteronuclear decoupler. Ir spectra were run on Beckman IR-8 and IR-5 spectrometers. Gas chromatography was carried out on an Aerograph A90-P chromatograph. Elemental analyses were done by the Schwarzkopf Microanalytical Laboratory. Melting points and boiling points are uncorrected. Assistance of Mr. H. B. Clark in the alkyl chloride–sodium reaction is acknowledged.

Cyclopentylmethyl chloride-α,α-d_2 was prepared by a method analogous to that used previously for the preparation of isotopically normal material,[4] except that reduction of ethyl cyclopentanecarboxylate was carried out with lithium aluminum deuteride. The product chloride had bp 138–139°. The nmr spectrum showed no absorption ($<2\%$) at δ 3.55 ppm, where the α hydrogens of the undeuterated compound absorb. Less than 5% cyclohexyl chloride was present.

Reaction of Cyclopentylmethyl Chloride-α,α-d_2 with Sodium.—This reaction was carried out in a manner similar to that described previously, using a small amount of dodecane as solvent.

---

[15] (a) L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, **81**, 5512 (1959). (b) R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *ibid.*, **89**, 442 (1967); see also discussion and references in ref 3.

In a reaction with undeuterated chloride, gas chromatography on silicone grease yielded three fractions: (1) 61% methylcyclopentane; (2) 9% mostly methylenecyclopentane by nmr and ir (cyclohexane was found as a minor component by chromatography on tricresyl phosphate and nmr; an additional olefinic component, absorbing in the nmr at δ 5.32 ppm, not separated from methylenecyclopentane on silicone grease or tricresyl phosphate, was tentatively identified as 1-methylcyclopentene; a published spectrum of methylenecyclopentane shows the same absorption[16]); (3) 30% bicyclo[3.1.0]hexane by nmr and ir, contaminated by ~4% cyclohexane by nmr or gc on tricresyl phosphate. The deuterated chloride gave similar results, with distributions among the fractions: (1) 88%; (2) 5%; (3) 7%. The nmr spectrum of the methylcyclopentane suggested a mixture of CHD_2 and CD_3 groups, with a splitting pattern in the former consistent with $J_{HCCH} = 6.0$ Hz, $J_{HCD} = 2.0$ Hz. The mass spectrum indicated 23% trideuteration and 77% dideuteration. The mass spectrum of the methylenecyclopentane sample indicated nearly equal amounts of mono- and dideuterated material, along with smaller amounts (~10%) of tri- and undeuterated product. The nmr spectrum of the bicyclo[3.1.0]hexane fraction at 60 MHz had a multiplet absorption at δ 0.08 to 0.45 ppm. Decoupling from deuterium sharpened the spectrum sufficiently to allow interpretation as a pair of overlapping triplets at δ 0.15 ($J = 3.9$ Hz) and 0.30 ppm ($J = 7.9$ Hz). Analysis of the areas of the components of the multiplet as the A part of an AB_2 spectrum[17] yielded a ratio of the two triplets of 1.0:2.0 (±0.3). The nmr spectrum of this fraction also showed ~8% cyclohexene in the sample.

Cyclopentanecarboxaldehyde-*α-d*. — Cyclopentanecarbonyl chloride was prepared by addition of the acid to an excess of thionyl chloride, followed by brief heating at 100°, bp 159–160.5° (lit.[18] bp 160–162°).

Cyclopentanecarbonyl chloride (42.3 g, 0.32 mol) was added dropwise over 0.75 hr to a mixture of freshly distilled aziridine (13.7 g, 0.32 mol) and triethylamine (32.2 g, 0.32 mol) in 250 ml of benzene, maintained below −12°. The mixture was allowed to warm to room temperature and stirred for 2 hr. After filtration to remove precipitated salts, the solvent was removed, and the product distilled under vacuum, bp 45° (1 mm), yield 32.7 g (74%). Distillation of the product was necessary to separate it from a material tentatively identified as the cyclopentanecarboxamide of 2-chloroethylamine.

The aziridide of cyclopentanecarboxylic acid (16.5 g, 0.119 mol) in 100 ml of anhydrous ether was added over 30 min to 1.29 g (0.0307 mol) of lithium aluminum deuteride in 50 ml of ether, maintained below 4°. After 1 hr of stirring below 10°, an excess of 6 *N* sulfuric acid was added. The ether phase was washed with aqueous bicarbonate and sodium chloride and dried over sodium sulfate. The product (8.9 g, 76%) was isolated by distillation, bp 28–30° (8 mm) [lit.[19] bp 34° (10 mm)]. The product was shown by gas chromatography to be pure. The nmr spectrum showed no detectable aldehydic proton resonance; the ir had a prominent C–D stretch at 2060 and lacked bands at 2800 and 2700 cm^{-1} present in the isotopically normal compound which had been prepared similarly.

Cyclopentanecarboxaldehyde-*α-d* tosylhydrazone was prepared by adding the aldehyde (5.0 g, 0.0505 mol) to a solution of *p*-toluenesulfonylhydrazine (9.5 g, 0.051 mol) in 19 ml of methanol, containing 8 drops glacial acetic acid. The precipitate that formed was collected, washed, and dried under vacuum, mp 90–91° dec. The isotopically normal compound was prepared in similar fashion.

Anal. Calcd for $C_{13}H_{18}N_2O_2S$: C, 58.62; H, 6.81. Found: C, 58.67; H, 6.79.

Tosylhydrazone Decomposition.—Most experiments were carried out with 1-g samples of tosylhydrazone. With sodium methoxide or sodium hydride as base, the dry reactants were mixed before addition of solvent. For formation of the lithium salts, butyllithium in *n*-hexane was added by syringe. The reaction flask was swept with nitrogen before reaction. For preparation of the dry lithium or sodium salts, tetrahydrofuran (at 0°) was used as solvent and was removed under vacuum; the salt was dried at ~20 μ before heating either dry or as a suspension in hexadecane. The decomposition was brought about by rapid heating on a Woods metal bath to ~175°. The reaction flask was attached through a cold trap (solid CO_2–acetone) to a gas buret, with which the volume of evolved nitrogen was measured approximately (±10%). After cooling to room temperature, the remaining product was transferred to the trap under 10-mm vacuum. The product was examined by nmr and gas chromatography on a Carbowax 20M column, with an internal benzene standard. In some cases, individual product fractions were isolated and examined. The methylenecyclopentane peak from solution decompositions of the tosylhydrazone with base exhibited a shoulder, and the nmr spectrum generally showed olefinic absorption tentatively ascribed to 1-methylcyclopentene formed by base-catalyzed isomerization. This was absent from pyrolyses of dry lithium or sodium salts, from pyrolysis of the preformed salts in solution, and from the reaction in *N*-methylpyrrolidone.

In one case, the diazo compound was distilled at ~100 μ to a cold trap (solid CO_2–acetone) by gradual heating of the dried lithium salt to about 125°. The ir spectrum of the orange liquid showed an intense band at 2050 and a weaker band at 1632 cm^{-1}. After this stood in CCl_4 solution, a band at 1720 cm^{-1} slowly grew in intensity. On heating in hexadecane, the diazo compound evolved gas, and a small yield of volatile products could be isolated.

Reaction of Cyclopentyllithium with Methylene Chloride.—Cyclopentyllithium was prepared by addition over 2 hr of 26.1 g (0.25 mol) of cyclopentyl chloride to lithium wire (4.5 g, 0.65 g-atom) in 200 ml of pentane with vigorous stirring in a Morton flask, under argon. After settling, the clear supernatant liquid was found to be 0.71 *M* in base.

To a portion of the above alkyllithium solution (50 ml, 35 mmol) was added methylene chloride (1.5 g, 17.5 mmol). Cloudiness developed rapidly. After the mixture stirred overnight, titration of a sample showed consumption of 95% of the base. In a similar reaction with deuterated methylene chloride, ~70% of the base was consumed. The product was poured into water, and most of the pentane solvent was removed by careful distillation through a spinning-band column. It was possible to obtain the nmr spectrum of the secondary cyclopropane hydrogens in the residue without further separation of the mixture. The product mixture was shown by nmr to contain methylenecyclopentane and bicyclo[3.1.0]hexane in a ratio of 4:6, along with a complex mixture of higher boiling components.

Reaction of Cyclopentylmagnesium Chloride with Methylene Chloride.—A Grignard reagent was prepared from 26 g (0.25 mol) of cyclopentyl chloride and 7.0 g (0.30 g-atom) of magnesium in tetrahydrofuran. The final solution was 1.5 *M* by acid–base titration. A portion of this solution (40 ml, 60 mmol) was stirred with methylene chloride overnight and then heated at reflux for 2 hr. The mixture was poured over ice and extracted with ether, and the solvent was distilled on a spinning-band column. The C_6 fraction of the residue was separated by preparative gas chromatography and its nmr spectrum examined.

Registry No.—Cyclopentylcarbene-*α-d*, 36595-06-9; cyclopentylcarbene, 7162-01-8; cyclopentanecarboxaldehyde tosylhydrazone, 36601-82-8; cyclopentylmethyl chloride, 13988-39-1; cyclopentyllithium, 23473-12-3; cyclopentylmagnesium chloride, 32916-51-1; sodium, 7440-23-5; dichloromethane, 75-09-2; cyclopentylmethyl chloride-*α,α-d$_2$*, 36601-85-1; cyclopentanecarboxaldehyde-*α-d*, 36601-86-2; aziridide of cyclopentanecarboxylic acid, 36601-87-3; cyclopentanecarboxaldehyde-*α-d* tosylhydrazone, 36601-88-4.

---

[16] Nmr Spectral Data, American Petroleum Institute Research Project 44, Spectrum No. 128.

[17] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1970, pp 123–128.

[18] G. B. Payne and C. W. Smith, *J. Org. Chem.*, **22**, 1680 (1957).

[19] E. Urion, *Ann. Chim.*, [11] **1**, 5 (1934).