Registry No.—Benzaldehyde, 100-52-7; bisulfite, 15181-46-1; sulfite, 14265-45-3; sulfurous acid, 7782-99-2; benzaldehyde bisulfite monosodium salt, 4657-72-9.

References and Notes

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(2) Throughout this paper the term "bisulfite ion" will be used to refer to the mixture of SO_3^{2-}, HSO_3^-, H_2SO_3, and dissolved SO_2 regardless of the pH of the solution. Similarly, the adduct will be called benzaldehyde bisulfite.

(3) Reference 1c actually reports that "K_c" = $([PhCH(OH)O^-][H_3O^+])/XPhCHO] = 10^{-12.7}$ *M* at 21°. Therefore, the equilibrium constant for the addition of hydroxide is $[PhCH(OH)O^-]/([PhCHO][OH^-]) = K_c/K_w = 10^{1.4}$ M^{-1} at 21°.

(4) From a Taft correlation of alcohol acidities in aqueous solution at 25°: F. C. Kokesh, Ph.D. Dissertation, The Ohio State University, 1969. $pK_a^{chem}(R_1R_2CHOH) = -1.47(\sigma^*_{R_1} + \sigma^*_{R_2}) + 16.59$, where $\sigma^*_{OH} = 1.28$.

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(10) From a σ^I correlation of alcohol acidities in aqueous solution at 25°: F. C. Kokesh, Ph.D. Dissertation, The Ohio State University, 1969. $pK_a^{chem}(R_1R_2CHOH) = -7.19(\sigma_{R_1}^I + \sigma_{R_2}^I) + 15.42$, where $\sigma^I_{SO_3^-} = 0.13$.[11]

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Notes

Relative Reactivities in the Addition of Dichlorocarbene to Methylenecycloalkanes

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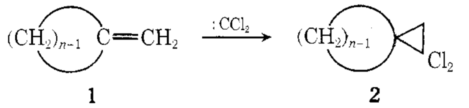
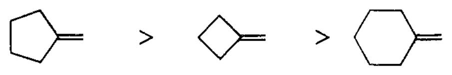
In spite of the multitude of olefins which have been subjected to attack by dichlorocarbene,[2] data have been lacking for the relative rates of addition of these species to simple methylenecycloalkanes. We now report these values for olefins **1** (n = 4–6) under a variety of conditions as summarized in Table I. The products were the dichlorospiroalkanes **2**, which were isolated and characterized (see Experimental Section). Rate constant ratios were determined by VPC procedures described previously.[3] As anticipated, the data of Table I do not show large variations with changes in the mode of generation of the carbene, the solvent, or the temperature.[4,5]



1 **2**

a, $n = 4$
b, $n = 5$
c, $n = 6$

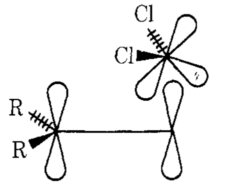
Using data at 25° for the generation of $:CCl_2$ from ethyl trichloroacetate and sodium methoxide in pentane, one obtains the following relative reactivities among olefins **1a–c**.



1b **1a** **1c**

2.44 + 0.02 1.53 + 0.1 1.00

Theoretical studies suggest that the transition state for the addition of $:CCl_2$ to an unsymmetrical olefin should resemble **3** and should represent a relatively early stage of the bond formation process.[6] The p orbital of the divalent carbon is in the same plane occupied by the π bond of the methylenecycloalkane. If one recognizes that the preferred direction of attack of $:CCl_2$ on **1c** is equatorial,[7] the already small dihedral angle between the exocyclic carbon–carbon bond and the α-equatorial hydrogens in **1c**[8] should decrease slightly so as to produce an increase in torsional strain as this olefin approaches the transition state. Similar changes in torsional strain for **1a** and **1b** should be small and ought to favor the transition state from **1a** relative to that from **1b**.



3

Changes in bond angle strain on going from ground state to transition state should involve those normally anticipated for the formation of a three-membered ring for **1c** but are more difficult to access for **1a** and **1b** because of the

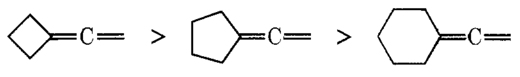
Table I
Data Summary for Competitive Addition of Dichlorocarbene to Methylenecycloalkanes

Olefin in competition with 1b	Carbene source	Solvent	Temp, °C	Time, hr	No of runs	K_{1b}/K^a
1c	Cl_3CO_2Et	Pentane	0	2	1	2.30
1c	Cl_3CO_2Et	Pentane	0–25[b]	2	3	2.48 ± 0.30
1c	Cl_3CO_2Et	Pentane	0	36	2	2.36 ± 0.09
1c	Cl_3CO_2Et	Pentane	25	2	2	2.44 ± 0.02
1c	Cl_3CO_2Et	Benzene	25	2	2	2.09 ± 0.10
1c	PhHgCClBr	Benzene	60	36	2	2.16 ± 0.05
1a	Cl_3CO_2Et	Pentane	25	2	4	1.59 ± 0.12

[a] Errors expressed as ± one-half of the range. [b] Reagents mixed at 0° followed by removal of ice bath.

lack of adequate structural and thermodynamic data on spirohexanes and spiro[2.4]heptanes. If an increase in bond angle strain in the transition state is greater for **1a** than for **1b**, then a combination of bond angle and torsional strain arguments might explain the observed reactivity sequence. If one examines nonbonded steric interactions between the chlorines and the α hydrogens of the ring in models of each transition state, the interactions appear to diminish in the order **1b** > **1a** > **1c** and cannot explain the observed reactivities. Without further data the observed results for **1a** vs. **1b** cannot be satisfactorily evaluated.

It is interesting to note that in the addition of :CCl_2 (from chloroform and potassium *tert*-butoxide, −8 to −10°) to allenes **4a–c** the order of reactivity for **4a** and **4b** is the reverse of that observed for **1a** and **1b**.[11] Unfortunately, the lack of relative reactivity data between compounds 1 and 4 precludes detailed comparisons between these series. The greater reactivity of :CCl_2 toward 1-methyleneindan compared to 1-methylenetetralin[12] is consistent with our observations for **1b** and **1c** and can be explained by considering differences in the increased torsional strain on going to the transition states.[13] Greater reactivity of **1b** relative to **1c** has also been noted for olefin reduction by diimide[14] and for epoxidation with peracids.[15] However, in the latter study the rate of epoxidation of **1a** was slower than that of either **1b** or **1c**.



4a	**4b**	**4c**
2.49	2.09	1.00

Experimental Section

Elemental analyses were performed by the Department of Medicinal Chemistry at the University of Kansas or by Galbraith Laboratories, Inc., Knoxville, Tenn., unless otherwise noted. Melting points and boiling points (capillary) are uncorrected. Infrared spectra were obtained from a Beckman IR-8 instrument with a 1604-cm^{-1} (polystyrene vs. air) reference standard. Analyses of halides by VPC were performed with an F & M Model 700 instrument (thermal conductivity detector) and the following columns: 20% QF-1 on 30–60 Chromosorb P (15 ft × 0.25 in.); 20% Carbowax 20M on 30–60 Chromosorb P (12 ft × 0.25 in.); 20% tris(cyanoethoxy)propane on 30–60 Chromosorb P (12 ft × 0.25 in.); 15% SE-30 on 30–60 Chromosorb W (10 ft × 0.25 in.); and 10% OV-210 on 80–100 Gas Chrom Q (6 ft × 0.125 in. glass column). Area measurements were performed with a disk integrator. A Varian A-60 or A-60A spectrometer was used to determine NMR spectra of compounds as solutions in carbon tetrachloride containing 3–6% tetramethylsilane.

Methylenecyclobutane (1a), bp 40.5–41.5° (lit.[16] bp 41.5–42°), was prepared from pentaerythrityl tetrabromide in 68% yield by the method of Roberts.[16]

Methylenecyclopentane (1b) was prepared from *tert*-butyl β-hydroxycyclopentaneacetate by the method of Vilkos and Abraham[17] in 83% yield, bp 75–76° (lit.[17] bp 77–78°). Ir and NMR spectra concurred with those already reported.[17,18] The desired olefin was also obtained from pyrolysis of cyclopentylmethyl acetate. However, a Wittig reaction between cyclopentanone and methyltriphenylphosphonium bromide in DMSO[19] produced a significant amount of benzene which forms an azeotrope with **1b**.

Methylenecyclohexane (1c) was prepared in 70% yield by a Wittig reaction between cyclohexanone and methyltriphenylphosphonium bromide in DMSO,[19] bp 100° (lit.[19,20] bp 98°).

1,1-Dichlorospiro[2.3]hexane (2a) was prepared by the general method of Parham[21] from methylenecyclobutane, sodium methoxide, and ethyl trichloroacetate in 47% yield: bp 153°; ir (CS_2) 3000 (s), 2950 (sh), 2860 (sh), 1420, 1245, 1200 (w), 1063 (s), 1030 (s), 1014 (s), 932 (w), 916 (w), 866, 781 (s), 747 cm^{-1} (s); NMR (CCl_4) broad absorption τ 7.0–8.1 (6 H, cyclobutyl CH_2), singlet 8.65 (2 H, cyclopropyl CH_2).

Anal. Calcd for $C_6H_8Cl_2$: C, 47.71; H, 5.34. Found: C, 47.67; H, 5.42.

1,1-Dichlorospiro[2.4]heptane (2b) was prepared as described for **1a** in 39.6% yield: bp 181°; ir (CS_2) 2975 (s), 2870 (sh), 1430, 1308 (w), 1242 (w), 1070, 1040, 1028 (doublet), 1000 (w), 963 (w), 850 (w), 758 cm^{-1} (s); NMR (CCl_4) broad absorption τ 7.5–8.6 (8 H, cyclopentyl CH_2), singlet 8.66 (2 H, cyclopropyl CH_2).

Anal. Calcd for $C_7H_{10}Cl_2$: C, 50.94; H, 6.11. Found: C, 50.73; H, 6.34.

1,1-Dichlorospiro[2.5]octane (2c) was prepared as described for **1a** in 53% yield: bp 200° [lit.[22] bp 79–80° (13 mm)]; ir (CS_2) 3005 (w, sh), 2960 (sh), 2935 (s), 2860 (s), 1420, 1275, 1210, 1150 (w), 1125 (w), 1100 (w), 1036 (s), 1021 (sh), 955, 921 (w), 891 (w), 845, 754 (s), 729 (w), 653 cm^{-1} (w); NMR (CCl_4) broad singlet τ 8.38 (10 H, cyclohexyl CH_2) singlet 8.86 (2 H, cyclopropyl CH_2).

Anal. Calcd for $C_8H_{12}Cl_2$: C, 53.65; H, 6.75. Found: C, 53.54; H, 6.85.

Competitive Addition of Dichlorocarbene to Methylenecycloalkanes. Parham Method.[21] For reaction times and temperatures of various runs, see Table I. As a representative procedure cold methylenecyclopentane (4.1 g, 50 mmol) and methylenecyclohexane (4.8 g, 50 mmol) were weighed carefully into a tared 25-ml flask which contained pentane (5 ml, olefin-free, stored over Na wire). This solution was added to a 50-ml, round-bottomed flask in which sodium methoxide (0.81 g, 15 mmol) and pentane (5 ml) were being stirred magnetically. Ethyl trichloroacetate (0.952 g, 5 mmol) was added dropwise and the mixture was stirred for the specified time.

The reaction mixture was filtered and the residual solid was rinsed with pentane; the filtrate was dried ($CaSO_4$), and the pentane and other volatile compounds were removed over a period of 10 min under aspirator vacuum with no external heating. (The product ratio in one case did not change during an additional 20 min under vacuum.)

When the above procedure was carried out at 25° for 2 hr or at 0° for 36 hr, or when other pairs of olefins were used, the amount of each olefin was 25 mmol. In still another modification of the procedure pentane was replaced with benzene. Methylenecyclobutane and methylenecyclopentane were always kept cold during the weighing process.

Seyferth Method.[23] A solution of 25 mmol each of the olefins in benzene (5 ml) was added to a 50-ml round-bottomed flask containing phenyl(bromodichloromethyl)mercury (2.2 g, 5 mmol) in benzene (5 ml). The tightly stoppered flask was stirred magnetically at 60° (oil bath) for 36 hr, sufficient time for complete decomposition of the mercurial.[24]

Analysis of Products. The high-boiling portion of the crude reaction mixture from any pair of the olefins, **1a**, **1b**, and **1c**, was injected directly into the VPC (15% QF-1 on 30–60 mesh Chromosorb P, 8 ft or 10% SE-30 on 60–80 Chromosorb P, silanized with dimethyldichlorosilane, 9 ft) and the quotients of the peak areas from four or more injections were observed as apparent values of the rate constant quotient, k_1/k_2. A detector sensitivity factor was determined with a standard mixture. Each observed rate constant quotient was corrected for detector sensitivity and the corrected values were averaged for each competition.

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Registry No.—**1a,** 1120-56-5; **1b,** 1528-30-9; **1c,** 1192-37-6; **2a,** 54788-75-9; **2b,** 54788-76-0; **2c,** 15997-13-4; dichlorocarbene, 1605-72-7; cyclohexanone, 108-94-1; methyltriphenylphosphonium bromide, 1779-49-3; ethyl trichloroacetate, 515-84-4; phenyl(bromodichloromethyl)mercury, 3294-58-4.

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Aspects of Direct Bridgehead Methylation

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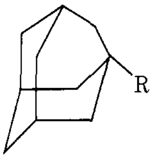
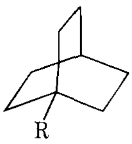
We recently required a method of synthesizing the hydrocarbons (I–III, R = CH_3) via direct quaternization of the readily available tertiary bromides. One attractive route appeared to be coupling of the appropriate halide with Grignard reagents. Despite several, largely unsuccessful, attempts[1,2] at direct alkylation of bridgehead halides, Schleyer and coworkers[3] recently described the preparation of 1-methyladamantane in high yield by treatment of 1-bromoadamantane with methylmagnesium bromide (molar ratio 1:3) in ether contained in a pressure bottle heated to 100°. These workers further reported that methylmagnesium iodide can also be used, and suggested that the method may be applicable to related alicyclic compounds.



I



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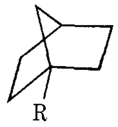
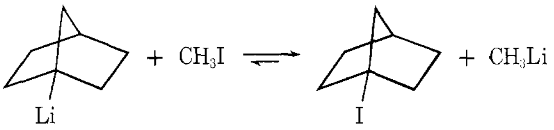


III

We repeated the experiments outlined by von Schleyer's group and similarly obtained the desired product (I, R = CH_3) in high yield (Table I). However, we found that use of methylmagnesium iodide under the same conditions gave a 3:1 mixture of 1-methyladamantane and adamantane, which are difficult to separate by VPC but which could easily be detected and analyzed by NMR (^{13}C and proton). In an attempt to apply this method to the other bridgehead bromides (II and III, R = Br) we found that longer reaction times were necessary in order to convert bicyclooctyl bromide into the methyl derivative (II, R = CH_3). Use of methylmagnesium iodide led to extensive reduction of the halide and afforded the hydrocarbons (II, R = CH_3 and R = H) in essentially equal proportions. Accordingly, this route to 1-methylbicyclo[2.2.2]octane is very attractive if methylmagnesium bromide is used as the coupling reagent.[4] As indicated in Table I, prolonged heating of 1-bromobicyclo[2.2.1]heptane in ether at 100° gave only a trace (5%) of the coupled product (III, R = CH_3), the remainder of the product being starting material. Obviously, under these conditions the coupling reaction is extremely slow, and the Grignard reagent preferentially reacts with the solvent (as confirmed by conducting a "blank" experiment).

As a possible alternative to the synthesis of 1-methylbicyclo[2.2.1]heptane, the lithio derivative (III, R = Li) was heated with methyl iodide in ether (and also hexane). The product was found to consist entirely of 1-iodobicyclo[2.2.1]heptane arising from simple halogen–metal exchange (eq 1) in which the position of equilibrium lies almost completely to the right. Similar treatment of 1-bicyclo[2.2.1]heptylmagnesium halide, whose preparation has recently been successfully performed[5] and which was not expected to undergo exchange, yielded only bicyclo[2.2.1]heptane.



(1)

The use of trimethylaluminum in the quaternization of tertiary acyclic halides has been shown[6] to be widely applicable and proceeds without the intervention to any appreciable extent of unwanted side reactions. In any case, although coupling of this kind involving bridgehead halides has not previously been reported, it seemed reasonable that in the systems under examination here, competing reactions, such as elimination, would be highly unlikely. The solvent found to be most appropriate in the study[7] of the acyclic halides was methyl chloride, in which coupling occurs rapidly at very low temperatures.

Accordingly, we treated the bromides (I–III, R = Br)