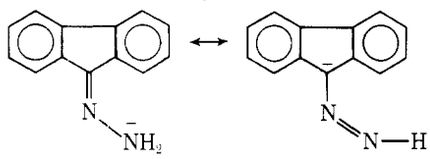
Table II. Kinetic Results for the Wolff-Kishner Reaction of Fluorenone Hydrazone (II), Dibenzotropone Hydrazone (III), and Dibenzosuberone Hydrazone (IV)

Expt no.	Hydrazone	$[HyH]_0$, M	$[RO^-Na^+]$, M Init	$[RO^-Na^+]$, M Final	Temp, °C	$t_f/t_{1/2}$	$k_1 \times 10^5$, s^{-1}	$k_2 \times 10^2$, $M^{-1}\ s^{-1}$
121	II	0.060	0.0274	0.0254	131.0	8.7	148	6.22
117	II	0.040	0.0945	0.0920	111.3	8.3	99.9	1.17
119	II	0.049	0.0587	0.0575	111.3	7.1	63.2	1.19
120	II	0.041	0.0248	0.0224	111.3	1.2	24.7	1.14
123	II	0.047	0.1031	0.1005	91.2	6.6	16.9	0.178
122	II	0.058	0.0592	0.0584	91.2	1.9	9.37	0.171
142	III	0.043	0.0108	0.0106	195.2	8.4	40.3	4.50
141	III	0.032	0.0770	0.0755	195.2	12.3	339	5.32
145	III	0.033	0.123	0.122	171.8	7.8	90.8	0.860
146	III	0.033	0.114	0.114	150.5	5.8	17.2	0.171
147	III	0.035	0.136	0.136	150.4	7.1	18.4	0.153
110	IV	0.043	0.0865	0.0815	195.6	8.1	66.1	0.94
109	IV	0.039	0.1310	0.1265	195.6	10.9	106	0.981
111	IV	0.033	0.154	0.152	171.6	5.6	19.4	0.147
137	IV	0.035	0.126	0.124	171.5	5.1	16.5	0.153
113	IV	0.028	0.697	0.697	171.6	13	124	0.206
138	IV	0.027	0.158	0.158	150.6	1.6	3.94	0.0281
139	IV	0.028	0.492	0.486	150.6	6.4	12.0	0.0279

late catalyst as described elsewhere.[1] Compounds I, III, and IV were studied in the temperature range 150.4–195.6 °C, while II, because of its higher reactivity, was studied in the temperature range 91.2–131.0 °C. A comparison of the rate constants (at 150.5 °C) and of the activation parameters is given in Table I.

While the relative rates of the Wolff-Kishner reaction of I–IV show significant differences, it is apparent from the comparison of the activation parameters that, except for the case of II, the rates are governed primarily by the differences in the enthalpies of activation. The entropies of activation of I, III, and IV fall into a narrow range of -3.75 ± 0.65 eu and it can be assumed that the transition states of the rate-determining steps of all three compounds have similar structures. The relatively small increase in the enthalpies of activation as we proceed from I to III and IV appears to reflect the increasingly more costly proton transfer from a hydroxylic solvent molecule to the sp^2 carbon atom of the hydrazone moiety. It is apparent, however, that the antiaromaticity of the potential dibenzotropyl carbanion has a small effect on the reactivity of III.

The behavior of fluorenone hydrazone (II), on the other hand, stands out in accord with the expected highly stabilized carbanion character of the hydrazone anion:



The results listed in Table I clearly demonstrate that the proposed high electron density at the carbon terminal of the hydrazone anion of II causes a significant decrease in the enthalpy of activation, most likely because of the relatively easier transfer of a proton from oxygen to carbon. The more positive entropy of activation in the case of II suggests that, again because of the relatively greater stability of the fluorenyl carbanion, the transition state lies closer to the product of the rate-limiting step, i.e., the nitrogen molecule is more highly separated in the case of II than in the analogous systems I, III, and IV.

Experimental Section

Materials. The preparation of benzophenone hydrazone and the purification of butyl carbitol have been described elsewhere.[1]

Fluorenone hydrazone was purchased from Aldrich Chemical Co. and crystallized from ethanol before use.

Dibenzotropone hydrazone and **dibenzosuberone hydrazone** could not be prepared in the usual manner[3] since this procedure yielded the corresponding alcohols in 40–60% yield. The hydrazones were obtained by allowing the ketones to react for 2 h with an excess of 95% hydrazine in refluxing ethylene glycol under nitrogen. The reaction mixture was cooled and diluted with water, and the hydrazones were extracted with benzene and recrystallized from petroleum ether. Dibenzotropone hydrazone (III), mp 78 °C.

Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 82.42; H. 5.31; N, 12.44.

Dibenzosuberone hydrazone (IV), mp 82 °C.

Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 80.90; H, 6.19; N, 12.50.

Kinetic Experiments. The apparatus, procedure, treatment, and accuracy of the data and the results for benzophenone hydrazone were reported elsewhere.[1] The kinetic results obtained with the hydrazones of fluorenone (II), dibenzotropone (III), and dibenzosuberone (IV) are summarized in Table II.

Acknowledgment. We wish to thank the National Science Foundation for partial support under GP-11480, The MHW Laboratories, Garden City, Mich., for the microanalyses, and the University of Detroit for a Teaching Fellowship (for C.E.A.).

Registry No.—I, 5350-57-2; II, 13629-22-6; III, 61047-37-8; IV, 61047-38-9; dibenzotropone, 2222-33-5; dibenzosuberone, 1210-35-1; hydrazine, 302-01-2.

References and Notes

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Structure Assignments and Reactivities of Bromochlorocarbene–Olefin Adducts

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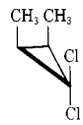
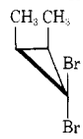
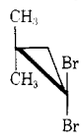
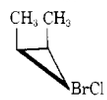
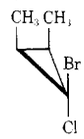
Bromochlorocarbene appears to have been the first dihalocarbene with dissimilar halogens to have been added to olefins from which geometrically isomeric adducts are possible

Table I. ^{1}H and ^{13}C NMR Chemical Shifts[a]

Registry no.		Ring protons	Methyl protons	C-1	C-2, C-3	Methyl C
1120-67-8		1.72	1.24	67.13	26.99	8.11
3591-57-9		1.65	1.09	40.14	27.96	10.48
32264-50-9		1.65	1.12			
61216-64-6	 (mixed isomers)	1.46 1.65	1.09	57.61 51.50	27.42 27.71	10.53 8.01
61216-65-7		1.47	1.10	57.71	27.47	10.48

[a] Parts per million downfield from Me_4Si.

without altering the spatial relations of groups on the originally olefinic carbons.[2] The early reports[2,3] indicated that both isomers had been formed from indene,[2] cyclopentene, and cyclohexene,[3] and the behavior of the isomers differed so greatly toward silver ions as to become subsequently exemplary of certain electrocyclic reactions.[4] A more recent report[5] has criticized the absence of experimental details in the early work. The latter workers were unable to achieve the separations claimed in one of the early reports.[3]

In other carbene–olefin additions that lead to isomer pairs structure assignments have been based on the postulate $J_{HH(HF)cis} > J_{HH(HF)trans}$ for vicinal spin coupling constants in cyclopropanes.[6] As this rule cannot be applied to the bromochlorocarbene–olefin adducts, direct evidence for structural assignments for such isomer pairs has not appeared previously, and those assignments that have been made[4] are dependent upon analogies to relative reactivities of compounds where the structure assignments were based on the above postulate.

The matter of separability of the isomer pairs was studied using the bromochlorocarbene adducts of *cis*-2-butene, cyclohexene, cyclopentene, and styrene. In each of the four cases partial separation (60% valley between isomer peaks) was achieved by isothermal GLC using a 76 m × 0.12 mm open tubular column and retention times of 1–3 h. The gas chromatograms showed both isomers to be present in each case in ratios of 1.0 ± 0.2 where the uncertainty range is of instrumental origin.

^{1}H NMR spectra of the purified isomer pairs also indicated the lack of formational stereoselectivity,[7] and reaction kinetics described below are fitted best by an isomer ratio of unity. Virtual absence of stereoselectivity is of interest in view of the uncertainty of relative importance of steric and polarizability factors in carbene additions by Doering and Hoffmann's procedure.[8] Use of this method for the addition of fluorochlorocarbene[6a] and fluorobromocarbene[9] to cyclohexene gave products having isomer ratios of 1.5 and 1.7, respectively, with sterically unfavorable geometry predominating.

Partial reaction of the isomer pairs in ethanolic silver perchlorate solution showed one isomer in each pair to be considerably more reactive than the other. Gravimetric analysis of the precipitated silver halide and mass spectra of the organic products showed that chlorine is removed preferentially from one isomer of 6-bromo-6-chlorobicyclo[3.1.0]hexane as reported by Skell and Sandler[3] and also from the less reactive isomer of 1-bromo-1-chloro-*cis*-2,3-dimethylcyclopropane. On the other hand, neither isomer of 1-bromo-1-chloro-2-phenylcyclopropane lost chlorine; only bromine was lost to silver ions by both isomers.

The 7-bromo-7-chlorobicyclo[4.1.0]heptanes behave still differently toward silver ions in that below 65 °C both halogens are lost from about half the molecules, and the remainder lose only bromine. This observation is in conflict with an early communication[3] but is made less surprising by the recent reports that cyclohexene-1-carboxaldehyde is a minor product from similar reactions of 7,7-dibromonorcarane[10] with analogous carbonyl-containing products forming from related compounds.

The large difference in silver ion promoted solvolysis rates of the two isomers of 1-bromo-1-chloro-*cis*-2,3-dimethylcyclopropane permitted isolation of the less reactive isomer in high purity as evidenced by the absence of a strong, polarized band found near 323 cm^{-1} in the Raman spectrum of the isomer mixture.[11] Chemical shifts in the ^{1}H and ^{13}C NMR spectra of this single isomer, an equimolar mixture of both isomers, and the corresponding dibromo- and dichlorodimethylcyclopropanes are presented in Table I.

Comparison of the ^{1}H NMR spectra reveals no difference in the methyl proton signals from the two bromochloro isomers and the dibromo compound, but the multiplets attributable to the ring protons of the bromochloro isomers, though overlapped at 60 MHz, were resolved at 100 MHz.[12] The appearance of the ring proton signals at higher fields for the less reactive isomer and for the dibromo compound favors this isomer having bromine cis to the methyl groups.[13]

Stronger evidence for this assignment comes from the ^{13}C

Table II. Reaction of 1,1-Dibromo-*cis*-2,3-dimethylcyclopropane in Ethanolic Silver Perchlorate[a]

Time, s	$[H^+]$, mM	% reaction	$10^4 k$, $M^{-1} s^{-1}$
2700	1.7	4.6	2.36
9960	5.6	15.2	2.29
30 180	13.8	37.5	2.30
88 800	26.6	72.3	2.47
267 780	34.8	94.6	2.22
			2.33 ± 0.07

[a] Initial concentrations: 36.8 mM halide and 75.4 mM silver perchlorate in 80% (vol) ethanol–water at 25.0 °C.

Table III. Rate of Acid Formation from Mixed Isomers of 1-Bromo-1-chloro-2-phenylcyclopropane[a]

Time, min[b]	22	65	179	590	1429	3763
Obsd $[H^+]$, mM	10.6	19.0	26.7	33.3	40.9	47.2
Calcd $[H^+]$, mM[c]	10.3	19.1	26.7	33.0	40.3	47.2

[a] 0.0486 M dihalocyclopropane and 0.44 M silver perchlorate initially in 95% (vol) ethanol–water at 92.8 °C. [b] Timing was begun at mixing at room temperature. After 12.5 min, to allow for mixing and thermal equilibration, 6.6 mM acid had formed which has been attributed solely to reaction of the more reactive isomer. [c] Based on a 1:1 initial isomer ratio and pseudo-first-order rate constants of 1.94×10^{-2} and 7.5×10^{-4} min^{-1}.

NMR chemical shifts shown in Table I for the same set of compounds. Only the assumption that the methyl carbons are more strongly influenced by the closer halogen is required. The assignment of the signals to the carbons giving rise to them is based on the multiplicities and J_{CH} values in coupled spectra. The ^{13}C NMR chemical shifts agree roughly with values estimated by addition of monohalo substituent effects.[14] The small difference in chemical shifts of the corresponding ring carbons of the bromochloro isomers may reflect a difference in ring strains.[15]

That the less reactive isomer of 1-bromo-1-chloro-*cis*-2,3-dimethylcyclopropane has bromine cis to the methyls is in agreement with the reported trends of acetolysis rates of monohalocyclopropanes and cyclopropyl tosylates.[16] This structure assignment receives further support from a partial electron diffraction analysis of the less reactive isomer.[17]

Rate constants for the silver ion assisted reactions in aqueous ethanol depend linearly on the concentrations of both halocyclopropane and silver salt as demonstrated in Table II for 1,1-dibromo-*cis*-2,3-dimethylcyclopropane. This observation is in contrast to the recent communication of Bach and Willis[18] in which a quadratic dependence on silver ion concentration was employed and may reflect the result of differences in initial concentrations. Generally, the rates were measured using pseudo-first-order conditions with a large excess of silver ions as illustrated in Table III for the mixed isomers of 1-bromo-1-chloro-2-phenylcyclopropane.

These reactions were usually followed by the formation of titratable acid, but the same rate constant was obtained in several cases by following the rate of decrease in silver ion concentration or decrease of reactant concentration in petroleum ether extracts of the reaction solution. Thermal rearrangement prior to reaction with silver ions was excluded in the case of the methanolysis of 1,1-dibromo-*cis*-2,3-dimethylcyclopropane by the several hundredfold faster reaction of the rearrangement product, (*E*)-3,4-dibromo-2-pentene,[19] and in other cases by the equality of the rate of reactant disappearance in extracts of the reacting solutions and the rate of acid formation in the same solutions.

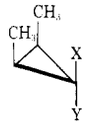
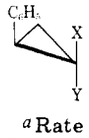
The products of these reactions in general were the alcohols and ethers expected by analogy to the product studies of Sandler[20] on reactions of dibromo- and dichlorocyclopropanes.

The structures of the 1-bromo-1-chloro-2-phenylcyclopropane isomers shown in Table IV are assigned by analogy to the dimethyl compounds so as to have the more reactive isomer be that with bromine trans to the phenyl. This assignment is preferred also by analogy to the acetolysis rates of *cis*- and *trans*-1-chloro-2-phenylcyclopropane.[16a] Presence of the second halogen would not be expected to impair the latter comparison (vide infra).

The second-order rate constants in Table IV provide three comparisons of the effect of chlorine vs. bromine as the remaining halogen. Bromine is removed faster from the more reactive isomer of 1-bromo-1-chloro-2-phenylcyclopropane (where chlorine is the remaining halogen) than from 1,1-dibromo-2-phenylcyclopropane (where bromine is the remaining halogen); the ratio k_{ClBr}/k_{BrBr} is 3.17. Similarly in the dimethyl series, k_{ClBr}/k_{BrBr} is seen to be 1.72 at 25 °C. When chlorine is removed from the dichlorodimethyl compound and from the less reactive bromochloro isomer, the ratio k_{ClCl}/k_{BrCl} is 1.25. A faster reaction when chlorine, rather than bromine, is the remaining halogen is seen also in other dihalocyclopropanes[21] and may indicate that only a small amount of positive charge is transferred to C-1 in the transition state as has been suggested for acetolysis,[16] hydrolysis,[22] and on theoretical grounds.[23] Whether the charge at C-1 is small because little weakening of the carbon–halogen bond has occurred in the activated complex or because ring opening and charge transfer to C-2 and C-3 is synchronous with carbon–halogen bond cleavage cannot be ascertained from these data. The latter possibility has been proposed by DePuy et al., however, for acetolyses.[24]

That ring opening is probably concerted with carbon–halogen bond breaking in the silver ion assisted solvolyses is a satisfactory explanation for the rather small difference in rate constants at 92.8 °C for chlorocyclopropane (2.18×10^{-7} $M^{-1} s^{-1}$) and 1,1-dichlorocyclopropane (1.3×10^{-7} $M^{-1} s^{-1}$)

Table IV. Silver Ion Assisted Solvolysis Rate Constants[a]

	X–Y			
	Br–Br	Cl–Br	Br–Cl	Cl–Cl
	100 ± 5 (25.0)	172 ± 5 (25.0)	93 ± 7 (92.8)	116 ± 8 (92.8)
	23 (92.8)[b] (3234-51-3)[c]	73 (92.8) (61158-74-5)	2.8 (92.8) (61158-75-6)	0.160 ± 0.006 (92.8) (2415-80-7)

[a] Rate constants × 10^5 ($M^{-1} s^{-1}$) in 95% ethanol initially containing 0.42 ± 0.03 M silver perchlorate. Temperatures in parentheses. [b] Extrapolated from lower temperatures. [c] Registry no.

in 0.42 M ethanolic (95%) silver perchlorate. In view of the well-known low reactivity of *gem*-dihalides toward silver ions[25] this difference would otherwise by surprisingly small.

An approximate value of 970 for k_{Br}/k_{Cl} at 92.8 °C for removal of bromide and chloride from the dimethylcyclopropyl compounds was obtained using an activation enthalpy of 20.6 kcal/mol for the more reactive bromochloro isomer. For bromo- and chlorocyclopropane the ratio was 400 ± 25, and for acetolyses of the monohalo compounds at 100 °C the ratio has been reported to be 32.[16c] According to Hammond's postulate,[26] the larger ratio for the silver ion promoted ethanolyses would seem to indicate greater progress along the reaction coordinate than has been postulated for the effect of alkyl substituents in the acetolysis reactions.

Experimental Section

Infrared spectra were determined on neat liquids using Beckman IR-5A and Perkin-Elmer 521 spectrophotometers. ^{1}H NMR spectra were recorded with JEOL Minimar and Varian A-60 and HA-100 spectrometers using 15–20% carbon tetrachloride solutions. ^{13}C NMR spectra were obtained on 20% hexadeuterioacetone solutions using a JEOL FX-60 spectrometer. Analytical GLC was performed with a Hewlett-Packard 5700-A gas chromatograph using a 76 m × 0.2 mm open tubular column coated with OV-17. An Autoprep 700 with a glass 2.7 m × 8 mm column packed with SE-30 on Chromosorb was used for preparative separations. Hewlett-Packard 5930 and Perkin-Elmer 270 GS–mass spectrometers were used. Microanalyses were performed by Galbraith Laboratory, Knoxville, Tenn.

Halocyclopropanes. Dihalocyclopropanes were prepared by carbene addition to the appropriate olefins except for 1,1-dichlorocyclopropane, which was prepared with chlorocyclopropane by vapor phase photochlorination of cyclopropane.[27] The dihalocarbenes were generated from the appropriate haloform and potassium *tert*-butoxide alcoholate.[8] The physical properties of the adducts agreed with published values[3,5,8,20,28] for each compound. Cyclopropyl bromide was obtained from Aldrich Chemical Co. and was found to contain less than 2% impurities.

1-Bromo-1-chloro-*cis*-2,3-dimethylcyclopropanes. Chlorodibromomethane (0.34 mol) was added over 1 h to a stirred mixture of 0.50 mol of potassium *tert*-butoxide alcoholate, 1 mol of *cis*-2-butene, and 250 ml of petroleum ether (bp 38–57 °C) held at −10 °C. Stirring was continued for 3 h while the temperature rose to room level. The mixture was washed with water (3 × 50 ml) and dried before being distilled first through a 0.5-m Vigreux column and then through a Teflon annular still under reduced pressure. The yield was 50 g (0.27 mol, 80%): bp 72–73 °C (38 mm); n^{25}D 1.4856; d^{25} 1.453; IR (film) 3020, 2936, 1127, 945, 717 cm^{-1} (s).

Anal. Calcd for C_5H_8ClBr: C, 32.73; H, 4.40. Found: C, - 32.58; H, 4.39.

Reaction of *endo*-1-Bromo-*exo*-1-chloro-*cis*-2,3-dimethylcyclopropane in Methanolic Silver Perchlorate. The less reactive isomer (1.22 mmol) in 4 ml of methanol containing 3.61 mmol of silver perchlorate was heated in a sealed vial at 64 °C for 27 h. The precipitate was collected in a Gooch crucible, washed, and dried at 120 °C to a constant weight of 183.4 mg (1.28 mmol silver chloride equivalent). The remaining silver salt in the combined filtrate and washings was precipitated with excess 0.3754 M aqueous sodium chloride. The resulting mixture was extracted (2 × 2 ml) with petroleum ether. Aliquots of the aqueous layer (17 ml) were neutralized with 0.0107 M methanolic sodium methoxide and required 6.85 ± 0.01 ml per ml of aqueous solution indicating the formation of 1.25 mmol of acid during the reaction. The neutralized aliquots were titrated by Mohr's method to determine by difference that 1.22 mmol of silver ions had been consumed in the reaction. GC–MS of the petroleum ether extracts showed one major component with molecular ion masses of 178 and 180 in a ratio of about one, consistent with an assignment of this major product as 3-bromo-4-methoxy-2-pentene. The chromatograms also showed a minor component that had molecular ion masses of 134 and 136 in a ratio of 3:1 as expected for 3-chloro-4-methoxy-2-pentene. The ratio of bromopentene to chloropentene in the petroleum ether extracts was 9:1.

Kinetic Studies. Temperatures were constant within 0.1 °C. Runs at 25 °C were quenched by pipetting aliquots into excess aqueous sodium chloride. The quenched mixtures were then titrated first with methanolic sodium methoxide to the thymol blue end point and then with silver perchlorate by Volhard's or Mohr's method. For runs at elevated temperatures aliquots of the reaction solutions were first cooled to 0 °C and sealed in glass ampules before being immersed in the constant temperature bath. Thermal expansion was approximately corrected for with the formula $k = (1 + 10^{-3}t)k_{app}$ where t is the bath Celsius temperature and k_{app} is the uncorrected, observed rate constant.

Registry No.—Bromochlorocarbene, 13590-47-1; *cis*-2-butene, 590-18-1; cyclohexene, 110-83-8; cyclopentene, 142-29-0; dibromocarbene, 4371-77-1.

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Syntheses of the Syn and Anti Isomers of [2.2](1,4)Naphthalenophane-1,13-diene

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A synthesis of *anti*-[2.2](1,4)naphthalenophane (**3**) was first reported by Cram in 1963,[1] and later, via an improved method, by Brown and Sondheimer.[2] In 1969, Wasserman and Keehn reported a synthesis of *syn*-[2.2](1,4)naphthalenophane (**1**) and its thermal conversion on melting to *anti*-[2.2](1,4)naphthalenophane (**3**).[3] It was suggested that the