When this reaction was carried out under the same conditions in d_6-DMSO, the same product was obtained except that it contained 1.50 D/molecule.

Reaction of 2,3,4-Triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]octane (6) with Potassium *tert*-Butoxide in DMSO at 70°.—Potassium *tert*-butoxide (1.00 g, 0.009 mol) was added to a solution of 2,3,4-triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]octane (**6**, 0.79 g, 0.0023 mol) in DMSO (15 ml) with stirring under nitrogen. The reaction mixture became deep green after a few minutes and the solution was stirred at 70° for 20 hr. The solution was diluted with water and extracted with ether. The ether layer was dried over sodium sulfate. Removal of the solvent and recrystallization from 95% ethanol yielded 0.67 g (85%) of 2,3,4-triphenylbicyclo[3.2.1]-2-octene (**8a**), mp 151–154°. The uv spectrum (95% EtOH) had λ_{max} 258 nm (ϵ 9680). The nmr spectrum ($CDCl_3$) featured the following resonances: aromatic multiplet centered at τ 3.00 (15 H); benzyl proton at 6.25 (1 H) as a doublet (J = 2 Hz); stilbenyl bridgehead as a multiplet at 7.1 (1 H); the other bridgehead proton at 7.65 (1 H) as a multiplet; a multiplet centered at 8.15 (4 H) assigned to methylene proton anti to the double bond, the two protons of C-7 and the exo proton at C-6; a multiplet at 8.75 (2 H) assigned to the methylene proton syn to the double bond and the endo proton of C-6. Unsaturation tests (bromine and permanganate) were negative.

Glpc analysis (5-ft SE-30, 225°) of the crude reaction mixture and the ether extract showed only the bicyclic product (**8a**). It should be noted that it was possible to separate an authentic mixture of 2,3,4-triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]octane (**6**) and 2,3,4-triphenylbicyclo[3.2.1]-2-octene on this column.

Anal. Calcd for $C_{26}H_{24}$: C, 92 85; H, 7.15; mol wt, 336. Found: C, 92.61; H, 7.26; mol wt (mass spectrum), 336.

When the reaction was carried out under the same conditions in d_6-DMSO the same product was obtained except that it contained 0.98 D/molecule. The low field signal at τ 6.25 due to the allylic proton at C-4 was absent.

Preparation of Triphenylbishomocyclopentadiene (11).—The procedure was adopted from Prinzbach and Martin.[11] In a sealed tube under nitrogen, 2,3,4-triphenyl-*endo*-tricyclo-[3.2.1.0^{2,4}]-6-octene (**7**, 3.0 g, 0.00896 mol) was heated at 190° for 24 hr. The green-black solid was recrystallized three times from 95% ethanol to give 0.9 g (30%) the quadricyclane **11** as white crystals, mp 138–141°. The nmr and uv spectra were in complete accord with the literature spectra.

Reaction of Triphenylbishomocyclopentadiene (11) with Potassium *tert*-Butoxide in d_6-DMSO.—Potassium *tert*-butoxide (0.63 g, 0.0056 mol) was added to a solution of the quadricyclane **11**, 0.50 g, 0.00149 mol) in d_6-DMSO (15 ml) with stirring under nitrogen. The orange-red solution was stirred for 20 hr at 70° after which the solution was diluted with water and extracted with ether. The ether layer was dried over sodium sulfate. Removal of the solvent and recrystallization from 95% ethanol gave 0.45 g (90%) of the quadricyclane **11**, mp 138–141°. The nmr spectrum was identical with that of the starting compound except for the absence of the benzyl proton. A mixture melting point with an authentic sample was not depressed.

Anal. Calcd for $C_{26}H_{21}D$: C, 93.13; H, 6.87; mol wt, 335. Found: C, 93.40; H, 6.69; mol wt (mass spectrum), 335; 1.01 deuterium atom per molecule.

Registry No.—**6**, 906-84-3; **7**, 906-85-4; **8a**, 34934-84-4; **9a**, 34922-26-4; **11**, 34938-92-6.

Linear Free-Energy Relationships among Reactions Occurring on the Cyclohexyl Ring. The Bromination of C_4-Substituted Cyclohexanones

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The rates and activation parameters in bromination of C_4-substituted cyclohexanones under various reaction conditions show very little change with large variation in the nature of the remote substituent. It is shown that these exceedingly small rate effects are to be reconciled with factors inherent in the enolization mechanism of bromination. The effort to apply these rate data in a linear free-energy relationship with corresponding data for ArSCl addition and $NaBH_4$ reduction reactions occurring at a ring atom in C_4-substituted cyclohexyl derivatives has afforded some understanding of the factors which vitiate correlations of this nature.

In earlier investigations[2,3] examples were cited which indicated that in some instances conformational influences of remote substituents as well as polar effects govern the reaction rates. In one such example[3] the conclusion was drawn that a given substituent may influence the competing rate processes differentially. Thus, in the reduction of 4-substituted cyclohexanones it was shown that the substituent may exert a different influence on the transition state for reduction to a cis alcohol than in the transition state for reduction to a trans. It is conceivable, however, that cases can exist in which a given 4 substituent regulates a (common) transition state *via* two different but simultaneously active influences, namely conformational and polar. These influences, furthermore, could be considered as separable and correlatable in a linear free-energy relationship. Equation 1 may be proposed as a

$$\log k_a = (m\sigma_c + n\sigma_p)\rho_a \qquad (1)$$

possible expression for correlating such conformational and polar effects exercised simultaneously in a given transition state. Here k_a is the rate constant for the reaction a under study, σ_c and σ_p are the substituent constants expressing, respectively, the conformational and polar effects of substituents, and m and n are weighing factors related to the nature of both the substituents and the reaction under study. The parameter ρ_a has the usual significance of the reaction constant.

For the addition of ArSCl to 4-substituted cyclohexenes[2a] polar effects dominate, and it has been found that

$$(m\sigma_c + n\sigma_p) \cong n_2\sigma_p = \sigma_I \qquad (2)$$

where σ_I is the familiar inductive substituent constant,[4] reducing to the situation prevailing in rigid, bicyclic

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[1] (a) Facultad De Quimica, Universidad Nacional Autonoma De Mexico 20, D. F.; (b) Department of Chemistry, University of Delaware, Newark, Del.

[2] (a) H. Kwart and L. J. Miller, *J. Amer. Chem. Soc.*, **83**, 4552 (1961). (b) H. Kwart and T. Takeshita, *ibid.*, **84**, 2833 (1962). (c) Much of the rate data for the ArSCl addition reactions and $NaBH_4$ reductions applied in various plots in this article have been taken from the Ph.D. dissertation of S. Hsia, University of Delaware, June 1967. A publication discussing this work is presently in preparation. (d) The results of A. A. Khan from these laboratories to be discussed in a future article.

[3] H. Kwart and T. Takeshita, *J. Amer. Chem. Soc.*, **86**, 1161 (1964).

[4] R. W. Taft and I. C. Lewis, *ibid.*, **80**, 2436 (1958).

TABLE I

RATES OF BROMINATION[a] OF C_4-SUBSTITUTED CYCLOHEXANONES AND ACTIVATION PARAMETERS

C_4 substituent[b]	k[c] (10^5) sec^{-1}				$\Delta S^{\ddagger}$,	$\Delta H^{\ddagger}$,	$\Delta F^{\ddagger}$, kcal/mol			
	15°	25°	37.5°	50°	eu	kcal/mol	15°	25°	37.5°	50°
CO_2H		1.87	7.52	30.1	−10.9	20.7	23.8	23.9	24.1	24.2
CN	0.373	1.20	4.38	16.9	−15.9	19.4	24.0	24.2	24.4	24.6
CO_2Me	0.588	1.92	7.58	26.1	−14.9	19.5	23.7	23.9	24.1	24.3
BzO	0.610	1.17	7.46	23.9	−16.9	18.9	23.7	23.9	24.1	24.3
MeO	0.721	1.62	8.33	30.9	−15.5	19.2	23.6	23.8	24.0	24.2
$SiMe_3$	0.892	3.03	11.4	38.7	−14.6	19.3	23.5	23.6	23.8	24.0
H	0.987	1.92	9.70	35.3	−18.3	18.2	23.5	23.7	23.9	24.1
C_6H_5	1.07	3.29	12.0	38.6	−17.5	18.4	23.4	23.6	23.8	24.0
CH_3	1.10	2.06	12.4	43.7	−15.8	18.8	23.4	23.6	23.8	24.0
C_6H_{11}	1.21	3.29	14.6	53.2	−13.8	19.3	23.3	23.4	23.6	23.7
t-Bu	1.46	3.13	16.4	56.7	−15.7	18.7	23.2	23.4	23.6	23.8

[a] In 70% HOAc–H_2O–HCl; see Experimental Section for kinetic procedures. [b] Registry numbers are, respectively, 874-61-3, 34916-10-4, 6297-22-9, 23510-95-4, 13482-23-0, 7452-95-1, 108-94-1, 4894-75-1, 589-92-4, 92-68-2, 98-53-3. [c] Pseudo-first-order rate constant.

systems[5] in which a conformational effect cannot be a factor. On the other hand, the solvolysis of various 4-substituted cyclohexyl tosylates[3] has been found to involve both polar and conformational effects.

The bromination of ketones in acetic acid–HCl media is recognized as a first-order reaction,[6] the rate-determining step of which is formation of the enol. The basic objective of the current investigation was to gain deeper insight concerning the transition state of this particular reaction by means of kinetic studies of the characteristics of this reaction in ring systems with which we have dealt in the earlier investigations. The rates of bromination of eleven 4-substituted cyclohexanones were measured at four different temperatures within a range of 35°.

Results and Discussion

The results obtained and the activation parameters computed from these rate data are compiled in Table I. The plot of log *k* *vs.* the inductive substituent constant[4] σ_I (see Figure 1 for a typical case) not only departs from linearity but also demonstrates clearly how little change of rate is experienced, despite the very large variation in the character of the substituents encompassed by the reaction series.

A second noteworthy feature is represented by the observation that the transition state is sensitive to medium effects to the point that the substituent effect, such that it is, can be made to change sign. The competing influences which result in the insensitivity to polar effects of substituents while simultaneously exhibiting a high degree of responsiveness to medium effects can be regarded as direct consequences of the nature of the transition state. This can be seen with the aid of the analysis given in Scheme I.

In acidic media the energy pinnacle on the reaction pathway is characterized by partial breaking of the α carbon–hydrogen bond of the conjugate acid of the ketone. The degree of double-bond character associated with the α carbon and the extent of charge residing on the enol system (both) tend to increase the energy of the transition state in the presence of an electron-withdrawing substituent. Contrary to this, the electron-donor properties of the hydroxyl oxygen tend to offset the electron demand on the α carbon created by sp^2 hybridization. Similarly, the electron-donor properties of the oxygen aid in stabilizing the positive charge centers of the conjugate acid of the ketone. The latter, of course, is transferred to the solvent in the process of removing the proton from the α carbon. These features of the transition state structure allow for very considerable variation in charge distribution. Thus, there is a net increase in electron demand (as compared to the parent ketone) in highly

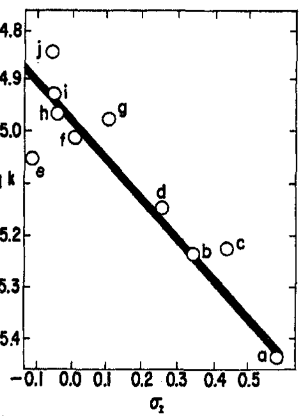
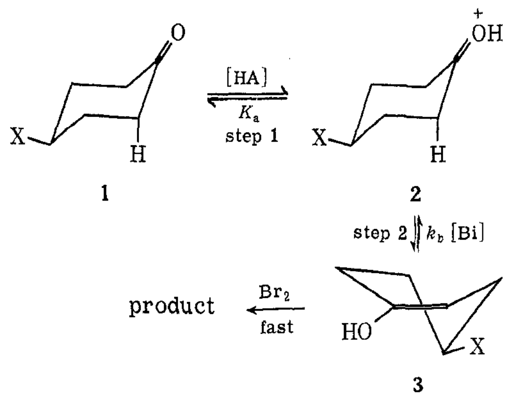


Figure 1.—Log *k* of bromination of 4-substituted cyclohexanone at 15° in 70% AcOH-H_2O-HCl *vs.* Taft σ_I values. Substituent legend in all figures: a, -CN; b, -CO_2Me; c, -BzO; d, -MeO; e, -$SiMe_3$; f, -H; g, -C_6H_5; h, -Me; i, -C_6H_{11}; j, -*t*-Bu.

SCHEME I



$(k_{obsd} = K_a k_b$, and

$$\log k_{obsd} = \log K_a + \log k_b \cong \sigma(K_a + k_b) = \sigma\rho_{-overall}$$

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[5] J. D. Roberts and W. T. Moreland, *J. Amer. Chem. Soc.*, **75**, 2167 (1953).

[6] See H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, 1965, pp 145–147, for a discussion of the mechanistic course of this reaction; H. O. House, V. Paragamian, R. S. Ro, and D. J. Wluka, *J. Amer. Chem. Soc.*, **82**, 1457 (1960).

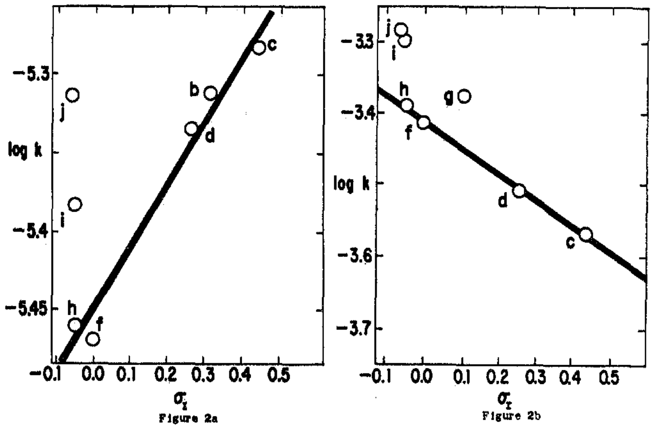


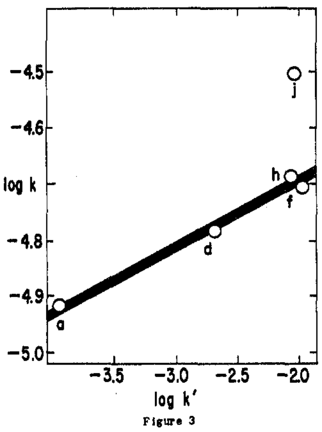
Figure 2.—(a) Log k of bromination of 4-substituted cyclohexanones at 25° in 90% AcOH-H_2O-AcONa *vs.* Taft σ_I values. (b) Log k bromination of 4-substituted cyclohexanones at 25° in 90% AcOH-H_2O-HCl *vs.* Taft σ_I values.

acidic media where the solvent itself must fulfill the role of the weak base. Conversely, when medium acidity is low and the concentration of a negatively charged base [B^-] is high, a decreased electron demand can be experienced in the enol region of the molecule to such an extent that the ρ constant will be driven to the positive side.

The data, in general, bear out these expectations. Electron-withdrawing substituents retard the bromination reaction in strong acid media and increase the rate slightly compared to H^+ in weak acid media containing significant concentrations of acetate ion. However, in both cases the correlation of log k_{obsd} *vs.* σ_I is far from satisfactory, being only fair in the acid-catalyzed reaction and very poor in the acetate-catalyzed case. In both cases, the points at greatest departure from any kind of linearity are those which correspond to the substituents of very low polarity and large bulk such as *tert*-butyl and cyclohexyl. Thus, in the instance of ArSCl addition reactions previously mentioned,[2] where the polar effect of the substituent is of paramount influence, (*i.e.*, where either $m\sigma_c$ is a linear function of $n\sigma_p$, or $n\sigma_p \gg m\sigma_0$), it is clear that eq 2 can be applied as a useful approximation. It is equally apparent, now, that, in the bromination of cyclohexanones, the conformational effect of the substituent cannot be completely ignored and can vitiate the simplification of eq 2 (*i.e.*, $n_2\sigma_p = \sigma_I$). This must be particularly true in the acetate-catalyzed reaction where *tert*-butyl deviates most widely from the line in Figures 2a and 2b (see Table II data). It is consistent with the idea that an axial β proton is removed by acetate in the transition state and the bulky substituents (of very low polarity) flatten the ring to the greatest extent. This distortion acts to promote attainment of the geometric requirement that the axial orbital develops at C_2 (through H^+ abstraction by acetate) in coplanarity with the p lobes of the trigonal carbon at C_1, but, since step 2 (ρ_{-k_b}), comprises only a part of the overall rate process which can be influenced by substitution at C_4, the true magnitude of this conformational effect on $\rho_{-\text{overall}}$ in terms of rate factors cannot be gauged because of compensation by ρ_{-K_a}.

Correlation with Rates of ArSCl Addition to Cyclohexenes.—Though the bromination of 4-substituted cyclohexanones does not conform to the simplification of eq 2, a plot of the log k_{obsd} values *vs.* those of the respective ArSCl addition reactions (which do) affords what appears to be a reasonably good correlation with the one significant deviation from linearity, namely, the *tert*-butyl substituent (in Figure 3). The critical observation here is simply that, as opposed to the other substituents studied, *tert*-butyl is of such size and nature as to induce conformational irregularities which interfere with a linear relationship. The plots in Figures 1 and 3 tell the same story. It will be noticed that in Figure 1, for example, the deviations exist for phenyl, *tert*-butyl, and trimethylsilyl. In Figure 3, for which plot phenyl and trimethylsilyl data are lacking, the one group which would be anticipated for conformational reasons to depart from the linear relation clearly fulfills this expectation.

Further study of these data leads to the following simple conclusion. With the exception of cyclohexyl, phenyl, *tert*-butyl, and trimethylsilyl, the rate effects of all the other 4 substituents examined can be correlated quite well with polar substituent constants σ_I, and that for these substituents the rate can also be related to the substituent group dipole moment. The fact that the trimethylsilyl moment correlates reasonably well with the log of the bromination rate constant in Figure 6 (as will be seen in a subsequent section of this discussion) but shows no correlation with σ_I reflects a lack of total correspondence between σ_I and the dipole moments of this group. Since such groups,



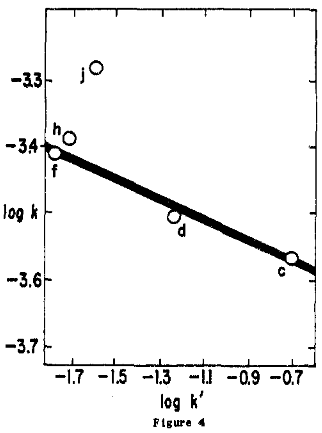


Figure 3.—Log k of bromination of 4- substituted cyclohexanones at 25° in 70% AcOH-H_2O-HCl *vs.* log k' of addition of ArSCl to 4-substituted cyclohexanones.

Figure 4.—Log k of bromination of 4-substituted cyclohexanones at 25° in 90% AcOH-H_2O-HCl *vs.* log k' of $NaBH_4$ reduction.

TABLE II
RATES OF BROMINATION OF C_4-SUBSTITUTED CYCLOHEXANONES COMPARED AT 25° IN VARIOUS MEDIA

	k^a (10^5), sec^{-1}	
C_4 substituent	More acidic medium[b]	Less acidic medium[c]
$C_6H_5CO_2$	27.3	0.521
MeO	31.2	0.462
H	38.8	0.336
C_6H_5	42.3	0.933
CH_3	40.9	0.345
C_6H_{11}	50.6	0.411
t-Bu	52.4	0.483

[a] Pseudo-first-order rate constant. [b] In 90% HOAc-H_2O-HCl; see Experimental Section for kinetic procedures. [c] In 90% HOAc-H_2O-NaOAc.

which tend to produce departure from the linearity of the free-energy relationship, are neither strongly polar nor sufficiently bulky to effect complete control of the ring conformation,[2a] a constant relationship between their σ_I and μ values could not in most cases have been anticipated.

Correlations with Rates of Sodium Borohydride Reduction of Cyclohexanones.—It has earlier[2b,c] been shown that both rate and the reduction product stereochemistry are strongly affected by the polarity of the C_4 substituent. Figures 4 and 5 demonstrate now that the rates of $NaBH_4$ reduction of C_4 substituted cyclohexanones also can be correlated with the respective bromination rates. Again we observe that *tert*-butyl stands above the line delineated by all the remaining substituents for which comparative data are available. This *tert*-butyl case represents still another instance where the conformational control exerted by the substituent is totally unrelated to its polar characteristic in the transition state. For most substituents the conformation of the ring in the transition state is strongly controlled by interaction of the permanent dipole of the C_4 substituent and the charge developed at the seat of reaction (C_1) extending into the low dielectric of the ring cavity.[2,3,5] Thus, we have at hand additional indication that a charge–dipole interaction of sufficient magnitude can be responsible for the simplification of eq 2; *i.e.*, under these circumstances $m\sigma_c$ is function of $n\sigma_p$. In general, circumstances which vitiate this simple correlation can be identified readily as points of departure in plots like Figures 4 and 5.

Correlation of Bromination Rates with Substituent Dipole.—Figure 6 represents a plot of the rates of bromination in the acid-catalyzed reaction *vs.* μ for all substituents for which the dipole moment value of the functionally substituted hydrocarbon CH_3CH_2X has been recorded. The linearity of the correlation must be regarded as quite satisfactory. The only point which can be said to deviate significantly from the line comprising all of the other substituents is the phenyl case, where the ground-state interaction giving rise to a measurable dipole moment for ethylbenzene is still a matter of controversy. It is certainly not clear that the dipole of the phenyl ring in the activated state would be the same since it originates largely as a result of some polarizability phenomenon. Conversely, we can deduce that the permanent (ground state) dipoles of the remaining functional groups correlated in this series would interact in the same way with a charge developing at a remote (C_1) center in the reaction transition state. This correlation affords further support for the conclusions reached above. That is to say, when both the 4-substituent dipole and the charge developed at the reaction center in the transition state are of sufficient magnitude, a dominant influence on reaction rate will result from charge stabilization directly at C_1 (field effect), and indirectly through control of the ring conformation arising through exercise of the resulting coulombic restraint. One could scarcely have expected a linear relationship of log k and μ were it not for the fact that the substituent dipole in the transition state constituted a degree of regulation on both of these factors comprising the total energy of the transition state, and the fact that the conformational effect of the substituent in the transition state is related to the degree of this charge–dipole interaction (*i.e.*, again, $m\sigma_c$ is a function of $n\sigma_p$).

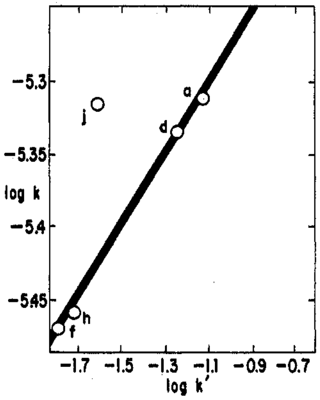


Figure 5

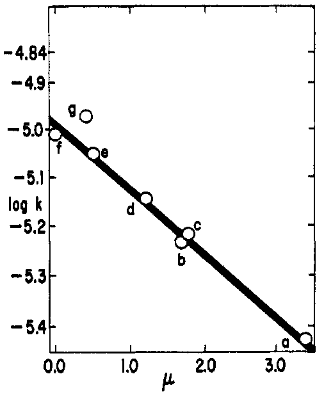


Figure 6

Figure 5.—Log k of bromination of 4-substituted cyclohexanones at 25° in 90% $AcOH-H_2O-AcONa$ *vs.* log k' of $NaBH_4$ reduction.

Figure 6.—Log k of bromination of 4-substituted cyclohexanones at 15° in 70% $AcOH-H_2O-HCl$ *vs.* the dipole moment (μ) CH_3CH_2R.

Experimental Section

Kinetic Procedures.—An exact amount of the C_4-substituted cyclohexanone was weighed into a 100-ml volumetric flask necessary to obtain a final concentration of substrate in the range of 0.01–0.02 M. To this was added about 85 ml of solution "A" (see below) and the flask was immersed in the constant-temperature bath. After sufficient time was allowed to reach temperature the flask was made up to volume with exactly 10 ml of solution "B" and additional solution "A," as required. Samples (10 ml) were withdrawn at time intervals suited to the bromine consumption rate in the reaction and titrated in the usual way with standard thiosulfate.[7]

Three rate determinations were performed for each of the various substrates at each of the temperatures and reaction conditions selected, and the results were averaged. The straight-line relationship of the usual psuedo-first-order plot held to at least 70% of completion in all cases. Beyond this point a slight deviation was often noted because of the incidence of polybromination and the catalytic effects of the hydrobromic acid formed by the reaction.[8]

Anhydrous acetic acid was prepared by treating 10 l. of 95% AR grade with 822 g of acetic anhydride and 200 g of AR chromic anhydride. The solution was refluxed for 30 min and distilled through a 25-cm glass bead column at 580 mm. The product boiling at 107–110° (collected for use) melted at 16–17°.

Solution "A" was prepared in three variations. A_1 consisted of 3.6 l. of anhydrous acetic and 0.4 l. of H_2O (corresponding to 90% acetic acid; density = 1.0605 at 20°). A stream of HCl gas (dried by bubbling through a H_2SO_4 wash bottle) was passed into this acetic acid until a concentration of 0.082 N HCl was attained. A_2 consisted of 2.8 l. of acetic acid and 1.2 l. of H_2O (corresponding to 70% acetic acid; density = 1.0690 at 20°). A stream of dry HCl gas was then passed into this solution until a concentration of 0.067 M HCl was reached. A_3 consisted of 3.6 l. of acetic acid and 0.4 l. of H_2O to which was added 80 g of anhydrous sodium acetate, corresponding to a 2% concentration in the 90% acetic acid medium.

Solution "B" was prepared in three variations. B_1 consisted of 0.5 l. of solution A and 9.6 g of purified (AR) bromine. B_2 consisted of 0.5 l. of A_2 solution and 9.6 g of bromine. B_3 consisted of 0.45 l. of anhydrous acetic acid, 0.05 l. of H_2O, and 9.6 g of bromine. In each of the above cases, the exact concentration of bromine was determined by sodium thiosulfate titration before use.

Preparation of the Cyclohexanone Substrates and Intermediates.—The structues and purities of all of the cyclohexanones

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(7) D. P. Evans, *J. Chem. Soc.*, 785 (1936).

(8) D. H. R. Barton, J. F. McGhie, M. K. Pradham, and S. A. Knight, *ibid.*, 876 (1955).

used for the kinetic measurements were established in all cases by means of ir, nmr, and glpc criteria.

4-Carboxycyclohexanone was prepared by oxidation of the precursor alcohol with Jones reagent[9] at 15°. The product recrystallized from benzene–hexane melted at 67–68°.[10]

4-Carbomethoxycyclohexanone was prepared in analogous fashion starting from 4-carbomethoxycyclohexanol. The product was distilled under reduced pressure and the fraction used for kinetic study had bp 74–75° (0.3 mm).

4-Benzoxycyclohexanone was prepared by the method of Jones and Sondheimer:[11] after recrystallization from ether–hexane, mp 58–59°; dinitrophenyl hydrazone mp 159–160°.

4-Methoxycyclohexanone was prepared according to directions of Helfer[12] by chromate oxidation of 4-methoxycyclohexanol. The latter was obtained by reduction of hydroquinone monomethyl ether with Raney nickel and hydrogen following familiar procedures.[13]

Cyclohexanone was purified *via* the Girard T reagent.[14]

4-Phenylcyclohexanone was synthesized by a two-step procedure starting from *p*-phenylphenol reduction[15] to a cis–trans mixture of 4-phenylcyclohexanol. The mixture was oxidized to the ketone using the Jones reagent.[9] The product[15] used for kinetic studies had mp 73–74°.

4-Methylcyclohexanone was purified (as a commercial sample) by distillation, $n^{20}\text{D}$ 1.4448.[16]

4-Cyclohexylcyclohexanone was obtained in a two-step procedure[15] beginning with reduction of *p*-phenylphenol with palladium/charcoal and hydrogen at 1500 psi and 150°. The reduction product mixture was oxidized with Jones reagent[9] in the usual way to ketone product which was isolated and purified by means of the Girard T reagent according to the method described by Büchi and Pappas,[17] mp 27–28°.

4-*tert*-**Butylcyclohexanone** was prepared according to directions of Winstein and Holness,[18] mp 45–46°.

4-Cyanocyclohexanone and 4-trimethylsilylcyclohexanone were provided by Dr. A. A. Khan[19] who prepared them according to methods in the literature. Their structures and purities were confirmed in the usual ways before use in kinetic procedures.

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[9] E. R. H. Jones and K. Bowden, *J. Chem. Soc.*, 39 (1946).

[10] W. H. Perkin, Jr., *J. Amer. Chem. Soc.*, **85**, 416 (1904).

[11] E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 616 (1949).

[12] L. Helfer, *Helv. Chim. Acta*, **7**, 950 (1924).

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Structural Constraints on Electrocyclic Reactions of Unsaturated Ketenes. Synthesis and Irradiation of 2,4,4,5-Tetramethylbicyclo[4.2.0]octa-1,5-dien-3-one

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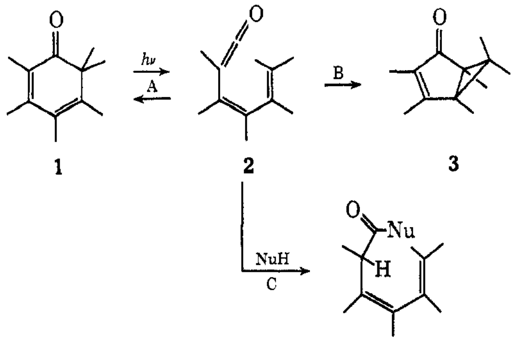
Oxidation of tetramethylbenzocyclobutene (**7**) with peroxytrifluoracetic acid–boron fluoride gave as the sole volatile cyclohexadienone (34% yield) 2,4,4,5-tetramethylbicyclo[4.2.0]octa-1,5-dien-3-one (**5**). The oxidation provides a striking illustration of the preference for *β*- (over *α*-) benzenonium ions in reactions of electrophiles with benzocyclobutenes, since both steps (electrophilic attack and methyl migration) are regiospecific. Irradiation of **5** in methanol (Pyrex) gave five methyl esters, **13** (55%) and the four stereoisomers of **14** (nearly equal amounts of each). This result contrasts with the irradiation of hexamethyl-2,4-cyclohexadienone (**1**), which under identical conditions gave no methyl esters. Reasons for the difference are discussed.

The unsaturated ketene **2**, produced by irradiation of the hexamethyldienone **1**, may react thermally in three different ways (A–C).[1,2] The particular reaction path depends on the nucleophile strength and on the solvent polarity. Methanol is not sufficiently nucleophilic to compete with the electrocyclic paths, but secondary amines divert the reaction completely along path C.[2] Of the two electrocyclic paths, B is favored by polar solvents and A by nonpolar solvents. For example, in ethanol virtually every ketene molecule produced by irradiation of **1** goes on to **3**, whereas in hexane approximately two-thirds of the ketene produced recyclizes to **1**.[2]



The reaction scheme shown for **1** is general, except that path B is only observed for heavily substituted ketenes.[1–5] This reaction path requires overlap of the ketene π-orbital lobes at C-4 with C-6, and C-1 with C-5, which can only be affected if the ketene twists appreciably from planarity and approaches the geometry of the bicyclo[3.1.0]hexenone product (*i.e.*, **3**).[4] To examine structural constraints on the electrocyclic reaction (B), we have studied the effect of incorporating two adjacent substituents into a ring. This would be expected to limit the conformations accessible to the ketene, and therefore affect the cyclization reaction. We report here on the synthesis and irradiation of the

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