For a reaction of the type

$$A + B \rightarrow C$$
$$A + C \rightarrow \text{products}$$

rate eq 1 and 2 can be written

$$dB/dt = -k_1[A][B] \quad (1)$$
$$dC/dt = k_1[A][B] - k_2[A][C] \quad (2)$$

Combination of eq 1 and 2 and integration leads to expression 3[28]

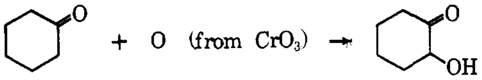
$$[C] = \alpha[B]\left[1 - \left(\frac{[B]}{[B]_0}\right)^{1/\alpha}\right] \quad (3)$$

which expresses the concentration of the reaction intermediate C as a function of the initial and residual concentration of the starting material. In eq 3 the constant $\alpha = k_1/(k_2 - k_1)$.

From eq 3 the final concentration of the intermediate C can be calculated if the final concentration of the substrate B is known and the rate constants k_1 and k_2 are available.

The final concentration of the substrate can be either determined directly (as in Table I) or estimated from the initial concentration $[B_0]$, the amount of oxidant introduced into the reaction, and the over-all stoichiometry of the reaction. In the oxidation of cyclohexanone, where adipic acid is formed as the major product, we assume that approximately one molecule of substrate is consumed per two molecules of CrO_3.

Oxidation rates for the substrate and the intermediate can usually be measured directly, but are most commonly expressed in terms of concentration changes of the oxidant rather than of the substrate and intermediate. In order to calculate k_1 and k_2 the stoichiometry under the conditions of the kinetic runs is needed. The calculation can be demonstrated for the example of 2-hydroxycyclohexanone. This intermediate is oxidized about 30 times faster than cyclohexanone. However, in the kinetic runs, cyclohexanone is used in a 100:1 ratio to oxygen available (in the form of chromic acid). When about 10% of the reaction is over, the ratio of cyclohexanone to the hydroxyketone will be 1000:1, and about 97% of the oxidant will react with the ketone and only about 3% will react with the reaction intermediate. As the reaction rates are determined from extrapolation to zero time when any curvature is observed, the experimental rate constant refers clearly to the reaction



and k_1 will therefore be equal to the experimentally determined rate constant. If, on the other hand, the intermediate is more reactive than the substrate by several orders of magnitude, the rate of disappearance of the substrate may be several times lower than the observed rate constant.

The whole treatment, although very useful and informative in evaluating the importance of different routes *via* alternative reaction intermediates, has an inherent limitation to its accuracy even if all the constants needed in eq 3 can be determined precisely. The constants k_1 and k_2 are measures of the reactivity of the substrate and intermediate toward Cr(VI). Actually, however, two-thirds of the oxidation is carried out by intermediate valence states, Cr(V) and/or Cr(IV). The present treatment would be exactly valid only if the relative reactivities of the substrate and intermediate remained the same for all valence states of chromium. We know, however, that this condition is not fulfilled precisely, even though we may accept it as a first approximation. Within the limitations and uncertainties just discussed, the treatment proved to be a valuable tool and gives at least very useful semiquantitative results.

Equation 3 is also useful in finding the optimal conditions for the detection and quantitative determination of a reaction intermediate. The maximum yield of C calculated from the condition $dC/dB = 0$, will be obtained when

$$\log [B]_0/[B] = \alpha \log k_1/k_2 \quad (4)$$

In the experiments in which we tried to verify the formation of a reactive compound and to determine its importance as an intermediate we have always used reaction conditions close to those required by eq 4.

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[28] Z. Cihla, *Collection Czech. Chem. Commun.*, **26**, 2367 (1961).

Conformational Effects in Cyclic Olefins. The Relative Rates of Iodomethylzinc Iodide Addition[1]

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The relative rates of cyclopropane formation using iodomethylzinc iodide have been determined for a number of cyclic olefins. The normal sequence cyclopentene > cycloheptene > cyclohexene is followed. The unusually low rate factors associated with alky and aryl substitution suggest a balance between small inductive and steric effects for this reaction. Norbornene reacts only 70% faster than cyclohexene. The slightly diminished rates exhibited by 4-alkylcyclohexenes are shown to be due to steric rather than inductive effects.

We have previously reported[2] the results of a kinetic study of epoxidation of a number of alkyl- and dialkylcyclohexenes. The values obtained were used in conjunction with stereochemical data to evaluate the conformational preference of 4-methylcyclohexene (equatorial conformer preferred by ~1 kcal/mole). Intrinsic in this evaluation were two assumptions: first, that the conformation of the six-membered ring,

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[1] Support by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged.

[2] B. Rickborn and S. Lwo, *J. Org. Chem.*, **30**, 2212 (1965).

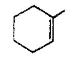
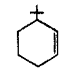
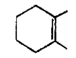
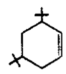
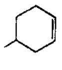
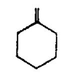
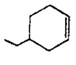
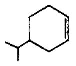
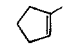
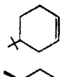
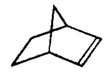
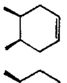
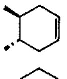
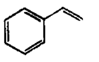
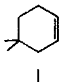
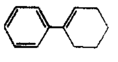
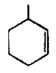
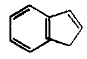
being very similar in the starting olefin and product epoxide, does not change appreciably in the transition state; and second, that inductive effects of remote alkyl groups are negligible in this reaction.

It appeared that these same criteria might also apply to the methylenation reaction discovered and developed by Simmons and Smith.[3] Although several features of this reaction are not yet fully understood, Blanchard and Simmons[4] have shown that second-order kinetics are obeyed, first order each in olefin and in organometallic reagent. The instability of the latter[4,5] creates serious difficulties in the determination of absolute rate constants. However, relative rates may be obtained using the competitive kinetic technique, *i.e.*, by allowing a pair of olefins to compete for the methylenation reagent as it is formed in solution. Blanchard and Simmons[4] have used this procedure to determine the relative reactivities of several olefins, mainly open-chain positional and geometrical isomers.

Although primarily interested in the influence of remote alkyl substituents on cyclohexene reactivity, we have expanded this study to include olefins containing other structural features of interest. The results are shown in Table I.

Table I

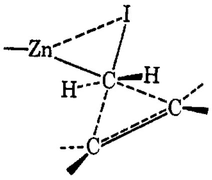
Relative Rates of Methylenation by Iodomethylzinc Iodide (Cyclohexene = 1.00)[a]

No.	Olefin	k	No.	Olefin	k
1		2.14	11		0.44
2		0.94[b]	12		0.40[c]
3		0.91	13		3.84
4		0.95	14		1.60[d]
5		0.94	15		5.14
6		0.92	16		1.70
7		0.55	17		1.18
8		0.84	18		0.95[e]
9		0.48	19		0.30[f]
10		0.58	20		0.68

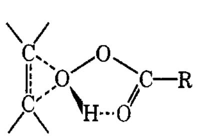
[a] Unless otherwise noted, the data were obtained by direct competition with cyclohexene. [b] This value differs considerably with that reported by Blanchard and Simmons (0.58).[4] The difference is thought to arise in the analytical procedure (see Experimental Section). [c] *cis* configuration. [d] Competition with cycloheptene. [e] Competition with 4-*t*-butylcyclohexene. [f] Competition with both styrene and 4-*t*-butylcyclohexene.

Ideally a complete understanding of the influence of structure on reactivity of an olefin involves the isolation of the various factors (strain, resonance, steric, etc.) that affect the ground and transition states. The closest approach to this has been attained by Garbisch and his co-workers[6] in a study of reduction by diimide. The success of their treatment is illustrated by the excellent agreement between calculated and observed rates covering a broad range in olefin reactivity. Clearly this quantitative approach is more difficult in the majority of olefin addition reactions, where unlike the diimide reduction, both polar and steric effects may play significant roles. Conversely, however, the relative importance of resonance, bond angle, and torsional strain, as isolated in Garbisch's work, may in certain instances be used to ascertain the relative importance of polar and steric effects on reactivity.

The transition state I has been proposed[7] for the methylenation reaction. In its geometry, I resembles (except for asymmetry along the double-bond axis) the spirano–oxygen transition state (II) for per acid epoxidation of olefins.[8–13] The results of previous workers suggested that inductive effects are relatively more important in epoxidation[12] than in methylenation,[4] and consequently a comparison of relatives rates for these reactions[2] offers an approach to the question of the nature of remote substituent effects in these and other olefin addition reactions.



I



II

Perhaps the most striking feature of the data in Table I, taking into account the range of substituents and structural features, is the invariance of the relative rates. While this insensitivity could result from a balance between large factors affecting the stability of the olefin and transition state, such repeated coincidence would appear to be very unlikely. Rather, it is suggested that the rates depend on a delicate balance of small factors, *i.e.*, that little of the olefin-stabilizing influence of a substituent is lost in the transition state, that little charge is developed, and that torsional, inductive, and steric effects, while not negligible, are relatively small.

Vinyl Substituent Effects.—The data shown in Table I are in general agreement with those of Blanchard and Simmons[4] on open-chain systems. Asymmetric

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[3] H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958); **81**, 4256 (1959).

[4] E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964).

[5] P. Turnbull, K. Syhora, and J. H. Fried, *ibid.*, **88**, 4764 (1966).

[6] E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *ibid.*, **87**, 2932 (1965).

[7] H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

[8] An alternate mechanism for epoxidation, involving an unusual 1,3-dipolar addition, has recently been proposed[9] and modified[10] by Kwart and his coworkers. Other workers[11] have pointed out that a 1,3-dipolar mechanism is not in keeping with the observed small rate factor between norbornene and cyclohexene (1.2). It seems to the present authors that available kinetic data, particularly the inductive effect of about 20–25/alkyl group in substituted olefins,[12] and the observation that the rates of epoxidation of isobutylene and 2-butene are nearly equal, also tends to rule out a 1,3-dipolar addition and to support the spirano–oxygen mechanism.[13]

[9] H. Kwart and D. M. Hoffman, *J. Org. Chem.*, **31**, 419 (1966).

[10] H. Kwart, P. S. Starcher, and S. W. Tinsley, *Chem. Commun.*, 335 (1967).

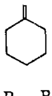
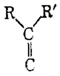
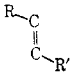
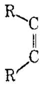
[11] K. D. Bingham, G. D. Meakins, and G. H. Whitham, *ibid.*, 445 (1966).

[12] D. Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947).

[13] B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

alkyl substitution at the double bond causes a small rate increase, while additional substitution leading to a symmetrical olefin results in a diminished rate. This effect is observed in the cyclohexene, 1-methyl-,[14] and 1,2-dimethylcyclohexene series (**1** and **2**), and also in the two cyclopentene examples (**14** and **15**). Again a balance between small inductive and steric effects is suggested, with the latter predominating in tetraalkylated olefins. An interesting comparision can be made with the series of dialkylated olefins shown in Table II.

TABLE II
COMPARISON OF RELATIVE RATES FOR DISUBSTITUTED OLEFINS (CYCLOHEXENE = 1.00)

	Diimide reduction[e]	Methylenation[f]
	3.27	3.84[c]
	2.05[a]	2.53[b]
	2.59[b]	0.42[d]
	2.65[b]	0.83[d]

[a] R = Me; R′ = n-Pr. [b] R = Me; R′ = Et. [c] Present work. [d] R = R′ = Et. [e] Reference 6. [f] Reference 4.

The close correspondence in relative rates for diimide reduction (negligible inductive and steric effects[6]) and methylenation for the unsymmetrically substituted entries stands in contrast to the behavior of the 1,2-dialkylethylenes. The slower rate for methylenation in these systems is in keeping with the unsymmetrical steric requirements of the proposed transition state.[3,4]

The relative rates of the phenyl substituted olefins (**18–20**) are not predictable in any simple manner. It might be argued that steric effects become dominant somewhat earlier when a phenyl group is present, since styrene reacts about three times faster than a typical 1-alkene,[4] whereas this order is reversed in the 1-substituted cyclohexenes (**1** and **19**). However, the low rate of 1-phenylcyclohexene may be at least in part due to higher torsional strain developed in the transition state.

Ring Size.—Garbisch[6] has shown that the cyclic olefin rate sequence $C_5 > C_7 > C_6$ can be predicted for diimide reduction. The same sequence is followed in some presumed four-center reactions (hydroboration and hydroalumination[15]). The dominant enthalpy feature in establishing this order appears[6] to be relief of torsional strain, with diminished bond-angle strain also playing an appreciable role in cyclopentene. In view of the similarities in proposed transition states for methylenation, epoxidation, and diimide reduction, the same sequence might be anticipated for all these reactions. Comparisons are shown in Table III. It is of interest that the order is followed not only by these "polycenter" additions, but also by lithium-ethylamine reduction.[16] The mechanism of the latter is unknown.

The magnitude of the rate differences for a given reaction will depend on, among other things, the degree to which the transition state geometry deviates from that of the olefin. The $C_1C_2C_3$ bond angle in cyclohexene oxide is 118.5°,[16] and a similar HCC angle may be deduced from the data given by Turner and Howe[17] for ethylene oxide. Considering this as the natural or unstrained angle for epoxides (and a similar value for cyclopropanes), calculations (using Garbisch's procedure) indicate that rate enhancement due to relief of angle strain should be small for epoxidation and methylenation. The plane described by the CH_2 group in ethylene oxide[17] lies at an angle of 22° from the plane of the parent olefin. Symmetry requires that this angle be 30° in cyclopropane. It seems reasonable, then, to argue that relief of torsional strain should also be small in the transition states for these three-membered ring forming reactions (relative to, for instance, diimide reduction) since only a fraction of this already narrow angle may be attained at this point along the reaction coordinate. The low rate factors between the cyclic olefins for both epoxidation and methylenation may be explained on this basis.

TABLE III
THE EFFECT OF RING SIZE ON THE RATE OF VARIOUS ADDITION REACTIONS (CYCLOHEXENE = 1.00)

Ring size	ICH_2ZnI	RCO_3H[a]	N_2H_2	$Li\text{-}EtNH_2$[b]
5	1.60	1.51	15.5	4.4
7	1.18	1.36	12.1	3.7

[a] Reference 12. [b] A. P. Krapcho and M. E. Nadel, *J. Am. Chem. Soc.*, **86**, 1096 (1964).

Norbornene is of particular interest, as it is very reactive ($k_{rel} = 450$) in diimide reduction.[6] Rate enhancement was estimated to be due to approximately equal contributions from relief of torsion and bond angle strain for *exo* attack. Also, Schleyer[18] has recently emphasized the role of torsional strain in discussing the strong preference for *exo* attack of the norbornyl carbonium ion. If the methylenation rate ($k_{rel} = 1.70$) for norbornene is viewed as abnormally low, one may argue that either relief of torsional strain is not appreciable in this reaction, or that rate enhancement by this factor is negated (partially) by steric effects.[19] The latter seems more reasonable, since torsional energy effects must be larger in norbornene than in other cyclic olefins, owing to smaller dihedral angles in the bicyclic olefin and the cosine potential energy function involved. It is particularly interesting to note that, in spite of the "low" rate, norbornene is reported to give *exo*-cyclopropane product.[7] *exo* selectivity is also found in epoxidation, al-

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[14] The enhanced rate of 1-methylcyclohexene weakens, but does not negate, the argument that has been presented[7] to explain the preferential attack of the acyclic double bond in limonene. Conformational effects, as discussed later in this paper, undoubtedly also play a role.

[15] Relative rates are quoted and a discussion is given in ref 6

[16] B. Ottar, *Acta Chem. Scand.*, **1**, 283 (1947).

[17] T. E. Turner and J. A. Howe, *J. Chem. Phys.*, **24**, 924 (1956).

[18] P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 699, 701 (1967).

[19] Although not obvious for this olefin, calculations using Garbisch's method indicate that bond-angle strain effects in epoxidation should be rate enhancing. In view of the approximations involved in this calculation, it is probably safer to conclude only that these effects are small. If bond-angle strain contributions were negligible in diimide reduction, a rate factor of 10–15 due to relief of torsional strain alone is anticipated; this then is more nearly the magnitude of the rate "depression" in methylenation that requires explanation as indicated above.

though this reaction is reported[20] to give about 6% of *endo* material as well.

Remote Substituent Effects.—Kwart and Miller[21] have determined the relative rates of addition of 2,4-dinitrobenzenesulfenyl chloride to a variety of 4-substituted cyclohexenes. Their work clearly demonstrates the importance of inductive effects in this reaction when highly polar substituents are involved. The authors noted the unexpected rate depression associated with remote alkyl groups, and although specific steric interactions were discussed, concluded that these effects were also primarily electronic in nature. The newly assigned positive σ_I values for the methyl and *t*-butyl groups were subsequently used in a study of 4-substituent effects on the kinetics and stereochemistry of borohydride reduction of cyclohexanones.[22] However, the relative rate ratio 4-*t*-butylcyclohexene–cyclohexene is 0.92 ± 0.03 for methylenation, epoxidation,[2] sulfenyl chloride addition,[21] and diimide reduction.[6] Clearly, since these reactions involve very different electronic demands this rate factor *cannot be ascribed to an inductive effect.* We have previously suggested that the bulky *t*-butyl group distorts the cyclohexene half-chair conformation in such a way that *trans* addition becomes less favorable than *cis* for epoxidation.[2] Similar behavior has now been demonstrated in the hydroboration of this olefin.[23] Even greater selectivity (in the same direction, *cis* addition leading to *trans* product) has been found in the diimide reduction of 1-substituted 4-*t*-butylcyclohexenes.[6] Although Garbisch has suggested that this selectivity may be due to a torsional effect associated with the 1 substituent (which in fact could account for its enhanced magnitude), it appears that a fundamental *cis*-directing influence is exerted by the 4-*t*-butyl group alone.

cis-4,5-Dimethylcyclohexene and 4,4-dimethylcyclohexene both react about one-half as fast as cyclohexene itself. This same effect has been observed in epoxidation,[2] where it was also shown that the stereochemistry (strong preference for *trans* addition) could be predicted on the basis of steric hindrance by the *axial* methyl group.[24] Similarly, the decreased rates of the 4-alkyl- (methyl-, ethyl-, and isopropyl-) and *trans*-4,5-dimethylcyclohexenes are adequately explained by steric hindrance associated with the *axial* alkyl component of the conformational mixture.

The situation is less clear for the 3-alkylcyclohexenes. The comparable rates for *cis*-3,5-di-*t*-butyl-(diequatorial) and 3-*t*-butylcyclohexenes suggest that the latter has a strong equatorial preference. Rate depression associated with a 3 equatorial substituent could be due to steric or torsional effects, or possibly distortion of the ring as suggested in 4-*t*-butylcyclohexene.

Experimental Section

Olefins.—Referring to Table I, olefins **1**, **9**, **10**, **14**, **16–18**, **20**, and cyclohexene were obtained from commercial sources; the preparations of **3** and **6–8** have been described previously.[2] Compounds **4** (bp 133–134°)[25] and **5** (bp 155–156°)[26] were prepared from the corresponding purified phenols by hydrogenation, tosylation, and elimination with 2,6-lutidine. Olefins **2** (bp 137.5°),[27] **15** (bp 75°),[28] and **19** [bp 69–70° (2.0 mm)][29] were obtained by phosphoric acid dehydration of the corresponding tertiary alcohols. Compound **11** (bp 169–170°)[30] was prepared by the coupling of *t*-butylmagnesium bromide with 3-bromocyclohexene. The method of Corey and co-workers[31] was used in the preparation of **13**.

***cis*-3-5-Di-*t*-butylcyclohexene.**—Ambient temperature and pressure hydrogenation (5% Rh on alumina) of 3,5-di-*t*-butylphenol[32] gave a mixture of ketone and alcohols (almost exclusively of the *cis*-di-*t*-butyl configuration).[33] Further reduction by lithium aluminum hydride followed by tosylation and elimination gave the olefin (**12**), bp 110–112° (21 mm).

A sample of the crude mixture from the phenol hydrogenation was oxidized with chromic acid to give the known[33] *cis*-3,5-di-*t*-butylcyclohexanone. This material showed less than 5% contamination by *trans*-ketone in vpc analysis using a TCEP column.[33b]

All of the olefins listed in Table I were purified by distillation or preparative vpc, and purities of >99% (as indicated by vpc using a variety of columns) were established. Nuclear magnetic resonance (nmr) spectra in all cases were consistent with the structures shown.

Cyclopropanes.—The cyclopropane derivatives of the olefins listed in Table I were prepared individually for use as standards. The general procedure of Simmons and Smith[3] was employed, using zinc–copper couple obtained by LeGoff's method.[34] Purification was effected by distillation of preparative vpc, again to a purity of >99%. No evidence of vpc separation of geometric isomers was observed. Nmr and infrared spectra[35] were consistent with the anticipated structures.

Kinetics.—A mixture of known, nearly equimolar amounts of two olefins and methylene iodide in ether solution was added to the zinc–copper couple under nitrogen. The solution was then refluxed, with small portions of methylene iodide being added periodically. Samples were withdrawn by syringe and injected directly for vpc analysis.[36]

A thermal conductivity detector vpc was used with a variety of columns to ensure complete separation of solvent, olefins, cyclopropanes, and unreacted methylene iodide. Peak areas in general did not correlate directly with mole percentage, nor did peak areas adjusted for molecular weight differences. Consequently it was necessary to prepare a known mixture of the four components measured in a kinetic run from standard materials. Correctional factors thus obtained were applied to

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[20] (a) H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963). (b) In epoxidation, norbornene reacts about 1.3 times faster than cyclohexene, as shown when these olefins were allowed to compete for limited *m*-chloroperbenzoic acid in ether at 25°. A similar value using a different peracid has been obtained by other workers.[11]

[21] H. Kwart and L. J. Miller, *J. Am. Chem. Soc.*, **83**, 4552 (1961).

[22] H. Kwart and T. Takeshita, *ibid.*, **84**, 2833 (1962).

[23] Unpublished work of D. K. Murphy and B. Rickborn. Alkaline peroxide treatment of the borane led to 32.2% *cis*-3-, 28.2% *cis*-4-, 20.6% *trans*-3-, and 19.0% *trans*-4-*t*-butylcyclohexanol.

[24] Although many of the compounds listed in Table I must give rise to geometric isomers on methylenation, in no case was there any indication of separation by vapor phase chromatography (vpc), using a wide variety of 0.63-cm columns. Similar but less extreme difficulties were experienced previously with isomeric epoxides;[2] models suggest that these isomers should have very similar physical properties. Separation has subsequently been effected in some instances with a capillary column.

[25] H. Pines, R. C. Olberg, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **74**, 4872 (1952).

[26] G. Stork and W. N. White, *ibid.*, **78**, 4609 (1956).

[27] C. H. Collins and G. S. Hammond, *J. Org. Chem.*, **25**, 911 (1960).

[28] H. Adkins and A. K. Roebuck, *J. Am. Chem. Soc.*, **70**. 4041 (1948).

[29] C. C. Price and J. V. Karabinos, *ibid.*, **62**, 1195 (1940).

[30] H. L. Goering, R. L. Reves, and H. H. Espy, *ibid.*, **78**, 4926 (1956).

[31] R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

[32] Gallard-Schlesinger Co.

[33] (a) M. Hanack and K. Heinz, *Ann.*, **682**, 75 (1965); (b) N. L. Allinger, H. M. Blatter, L. A. Freiberg and F. M. Karkowski, *J. Am. Chem. Soc.*, **88**, 2999 (1966).

[34] E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

[35] H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *ibid.*, **31**, 295 (1966).

[36] A potential problem, cleavage of the cyclopropane ring by Lewis acids (*e.g.*, zinc iodide) precipitated in the vpc injector port, did not occur. This was verified by the good material balances and absence of spurious peaks in the kinetic runs. Acid-sensitive compounds such as epoxides, however, were extensively rearranged when this same instrument was used without careful cleaning of the injection chamber. In spite of this objection, it was felt that direct injection was preferable to an alternate washing procedure which could introduce error due to differing olefin and product volatilities.

peak areas to determine relative mole percentages. Material balances, *i.e.*, (olefin_1 + cyclopropane_1)/(olefin_2 + cyclopropane_2) = olefin_1 (init)/olefin_2 (init) were satisfactory, indicating no detectable losses due to side reactions.

Several runs were made with many of the olefins having relative rates close to that of cyclohexene. Reproducibility was good in these cases (±3%), with individual point variations within a run having an average deviation of ±5%. Deviations were somewhat larger with olefins of more dissimilar reactivity. Data were treated by the usual first-order rate expression. No trends in relative rate ratios were observed when points were taken at various stages of reaction.

Registry No.—**1**, 591-49-1; **2**, 1674-10-8; **3**, 591-47-9; **4**, 3742-42-5; **5**, 14072-82-3; **6**, 2228-98-0; **7**, 3685-00-5; **8**, 14116-67-7; **9**, 14072-86-7; **10**, 591-48-0; **11**, 14072-87-8; **12**, 5132-52-5; **13**, 590-66-9; **14**, 142-29-0; **15**, 693-89-0; **16**, 498-66-8; **17**, 628-92-2; **18**, 100-42-5; **19**, 771-98-2; **20**, 95-13-6; iodomethylzinc iodide, 4109-94-8.

1-Aryltetrazoles. Synthesis and Properties

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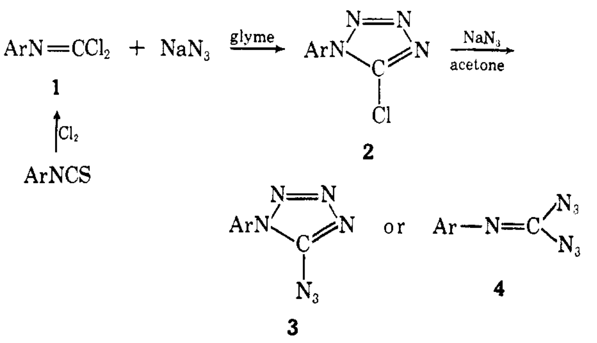
Synthetic routes to 1-aryltetrazoles were studied; the reaction of sodium azide with N-aryldichloroazomethines in dimethoxyethane solvent provides a new general synthesis for 1-aryl-5-chlorotetrazoles. A number of reactions of 1-aryltetrazoles are reported, including rearrangements and an opening of the tetrazole ring. The 1-tetrazolyl group and its 5-substituted derivatives are inductively strongly electron withdrawing (like nitro) but show only small resonance interactions, which vary with the 5 substituent. Four characteristic infrared bands between 950 and 1300 cm^{-1} are assigned to the 1-aryltetrazole system. The molecular structure of 1-aryltetrazoles is discussed on the basis of the infrared and electronic properties.

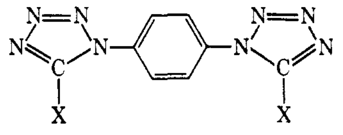
Tetrazoles have been studied extensively since they were first described in 1885[2,3] and have been used in a variety of synthetic and mechanistic programs.[3-5] 1-Aryltetrazoles have been prepared by addition of azide ion to isonitriles and by the reaction of diazonium salts with diformylhydrazine,[3] but with the exception of studies by Fallon and Herbst[6] no generally useful synthesis of 1-aryltetrazoles and their 5-substituted derivatives has been developed.

A. Synthesis. 1. 1-Aryl-5-chloro- and 1-Aryl-5-azidotetrazoles.—We now report a convenient synthesis of 1-aryl-5-chlorotetrazoles from the reaction of N-aryldichloroazomethines (**1**) with sodium azide. In glyme (1,2-dimethoxyethane) as solvent, the chlorotetrazole **2** is isolated in almost quantitative yield, but as was previously reported by Pel'kis and Dunaevs'ka[7a] for N-phenyldichloroazomethine, the use of acetone as solvent leads directly to the 1-aryl-5-azidotetrazole. Similarly when 1-phenyl-5-chlorotetrazole (**2**, Ar = C_5H_6) is treated with sodium azide in acetone, 1-phenyl-5-azidotetrazole is produced[7] (eq 1). Spectral studies, which will be discussed below, suggest that this product has the assigned tetrazole structure **3** rather than the azomethine form **4**, although under certain conditions the two forms may be in equilibrium.



(1)

A large number of N-aryldichloroazomethines can be readily converted to the corresponding 1-aryl-5-chlorotetrazoles by the azide reaction in glyme; in the present study, unsubstituted and nitro- and fluoro-substituted derivatives **2** (Ar = C_6H_5, *m*-, and *p*-C_6H_4F, *o*-,*m*-, and *p*-$C_6H_4NO_2$) as well as the bis derivative **5** have been prepared (see Table I). A number of azidotetrazoles was also prepared but not studied further because of poor stability (*e.g.*, **6** is extremely shock sensitive and explodes on rubbing with a spatula.)



5, X = Cl
6, X = N_3

On the basis of our observations of this reaction, we consider the mechanisms given in Scheme I to be the most probable and prefer course a. Azide ion reacts rapidly with the dichloroazomethine **1** (probably by an addition–elimination process) to form the chlorotetrazole **2**. The reaction of **2** with azide is considerably slower, but takes place readily in acetone in which the nucleophilic properties of azide ion are enhanced.[8] When freshly precipitated (activated) sodium azide is

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(1) This work was presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

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(3) (a) F. R. Benson, *Chem. Rev.*, **41**, 1 (1947); (b) F. R. Benson in "Heterocylic Compounds," R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N.Y., 1967, p 1.

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(8) A. J. Parker [*J. Chem. Soc.*, 1328 (1961)] notes that SNAr reactions of azide may occur more than 10^4 times faster in dipolar aprotic solvents such as acetone than in methanol or water.