A solution of 4.25 g (0.01 mol) of α-picolyltriphenylphosphonium hydrochloride[7] and 2.04 g (0.01 mol) of 4-formyl-*N,N'*-diethylaminotroponeimine in 105 ml of 0.2 *M* lithium ethoxide in ethanol was allowed to stand at room temperature for 7–10 days. The resulting deep red solution was poured onto 300 ml of ice–water and the resulting red mixture was extracted with three 300-ml portions of ether. The ether layers were combined, washed with water, and dried over anhydrous sodium sulfate. Distillation of the ether left a red, semisolid residue that was recrystallized from ethanol–water to give 1.35 g (49% yield) of orange plates. The nickel(II) chelate was prepared by reaction of the γ-substituted aminotroponeimine with a 10% excess of nickel acetate in aqueous ethanol. The product **2** was obtained in 77% yield as green clusters from benzene–ethanol. Ligands for the preparation of the chelates **1** and **3** were synthesized in a similar manner.

Method B. Preparation of Anils. The anils were prepared by condensation of 4-formyl-*N,N'*-diethylaminotroponeimine with the appropriate amine. The reaction is illustrated by the synthesis of the product derived from 4-chloro-1-aminopyrazole, which was converted to the chelate **6**.

To a solution of 1.0 g of 4-formyl-*N,N'*-diethylaminotroponeimine and 1.0 g of 4-chloro-1-aminopyrazole in 25 ml of benzene and 40 ml of absolute ethanol was added two drops of acetic acid. The solution was heated under reflux in such a manner that the alcohol was removed slowly by distillation. When 25 ml of distillate had been collected, 25 ml of absolute ethanol containing one drop of acetic acid was added to the distillation flask and the process was repeated until a total of 150 ml of distillate had been obtained. The remaining solvent was removed by distillation under vacuum and the residue was recrystallized from ether–petroleum ether to give 0.65 g of red needles, mp 135–137°. The product was converted to the nickel chelate **6** in the usual manner.

Method C. Preparation of *N,N'*-Diaryl-Substituted Aminotroponeimines. The general preparative method has been described previously.[1,2] It is illustrated by the preparation of *N,N'*-di(*p*-phenyl-α-azoxyphenyl)aminotroponeimine. A solution of 0.58 g (2.72 mmol) of *p*-phenyl-α-azoxyaniline,[8] 0.23 g (1.36 mmol) of tetrafluorocycloheptadiene (97% purity), and 0.54 g (5.44 mmol) of triethylamine in 25 ml of ethanol was refluxed for 5 hr. After cooling, the red solid was removed by filtration and recrystallized twice from benzene–cyclohexane to give 0.15 g of the substituted aminotroponeimine. The product was converted to the nickel chelate **19** in the usual manner.

B. Nmr. Proton nmr spectra were obtained at 60 MHz using a Varian HR-60 instrument. Except where otherwise stated, the solvent was deuteriochloroform. The chelate solutions were internally referenced to tetramethylsilane to avoid bulk susceptibility corrections. Calibration was by the usual audiofrequency sideband technique. Contact shifts are defined as the difference in frequency between corresponding protons in the nickel chelate and the diamagnetic zinc chelate or ligand. The assignments of the protons presented few ambiguities in the present compounds and are based on spin–spin multiplets (where observed), the relative intensities of the resonances, and intercomparisons among related compounds in the manner previously[1,2] described.

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(7) R. N. MacDonald and T. Campbell, *J. Org. Chem.*, 24, 1969 (1959).

(8) D. Vorländer and H. Schuster, *J. Prakt. Chem.*, 140, 193 (1934).

Absence of Synergism in the Addition of Dichlorocarbene to Certain Oxygen-Functionalized Cyclohexenes

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Abstract: Reported are the relative reactivities toward CCl_2 addition at 80–85° of cyclohexene (1.00), cyclohexen-4-one ethylene acetal (0.44), 1-carboethoxycyclohexene (0.11), 2-carboethoxycyclohexen-4-one ethylene acetal (0.11), 1-carboethoxycyclohexen-4-one ethylene acetal (0.028), and cyclohexen-3-one ethylene acetal (0.012). No evidence is found for cooperative or synergistic addition of CCl_2 to these olefins, mediated by the ethylene acetal function. This conclusion is discussed in the light of a previous suggestion favoring such a mechanism. The reactivity data are analyzed in terms of substituent effects which operate mainly on a highly unsymmetrical transition state for CCl_2 addition.

Reactions of carbenes with heteroatomic substrates are of current interest.[2] Such reactive species as methylene and carboalkoxycarbenes react *via* ylide intermediates with a wide variety of substrates, including ethers, whereas *dihalocarbenes* are somewhat less avid. The latter do react with amines,[3] phosphines,[4] and sulfides,[5] and the "deoxidation" of alkoxides (or alcohols) may involve either a ylide or an alkoxydihalomethide anion.[6] CCl_2 is also able to strip oxygen from dimethyl sulfoxide[7] and pyridine *N*-oxide.[8] However, although reactions of CCl_2 with benzaldehyde[9] and benzophenone[10] appear to involve carbonyl ylides, similar reactions of CCl_2 with saturated ethers seem unknown. The following observations thus assume substantial importance.

The preference for CCl_2 addition to the central as opposed to the peripheral double bond of **1** decreases

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(1) Fellow of the Alfred P. Sloan Foundation. Special Postdoctoral Fellow of the National Institutes of Health. This work was done at the Massachusetts Institute of Technology, while the author was a Visiting Scientist.

(2) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, Chapter 11.

(3) M. Saunders and R. W. Murray, *Tetrahedron*, 11, 1 (1960). Also W. E. Parham and J. R. Potoski, *J. Org. Chem.*, 32, 275, 278 (1967); D. Seyferth, M. E. Gordon, and R. Damrauer, *ibid.*, 32, 469 (1967).

(4) D. J. Burton and H. C. Krutzsch, *ibid.*, 35, 2125 (1970).

(5) W. E. Parham and S. H. Groen, *ibid.*, 31, 1694 (1966), and references therein.

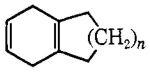
(6) J. Hine, E. L. Pollitzer, and H. Wagner, *J. Amer. Chem. Soc.*, **75**, 5607 (1953). See also: P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959); **82**, 2971 (1960).

(7) R. Oda, M. Mieno, and Y. Hayashi, *Tetrahedron Lett.*, 2363 (1967).

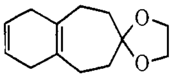
(8 E. E. Schweizer and G. J. O'Neill, *J. Org. Chem.*, **28**, 2460 (1963).

(9) C. W. Martin, J. A. Landgrebe, and E. Rapp, *Chem. Commun.*, 1438 (1971).

(10) C. W. Martin and J. A. Landgrebe, *ibid.*, 15 (1971).


1

from essentially complete (n = 1),[11] to about 4:1 (n = 2),[11] to near unity (n = 3)[12] for which an explanation based on steric hindrance has been offered.[11] In contrast to **1** (n = 3), ketal **2** shows central/peripheral reac-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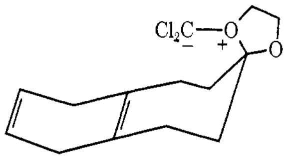
tivity of ~3,[12,13] and it was suggested that "the ketal oxygens might coordinate with the dichlorocarbene and might thus assist in directing the carbene to the central double bond."[12] Such coordination requires that ylide **3** be an intermediate, and though Dreiding



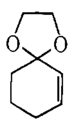
3

models demonstrate that the trivalent center of **3** can approach to ~1 Å of a central, sp^2 carbon atom, both the lack of precedent for this synergistic addition, and the required attack of an anionic carbon on a tetraalkylated double bond seem cause for concern.

Studies of CCl$_2$ additions to 3-substituted cycloalkene (C$_6$–C$_9$) alcohols, methyl ethers, and acetates gave no evidence for intermediate ylides which could transfer CCl$_2$ to the double bond;[14] dichlorocyclopropanation was mainly trans to the substituent[14] and, with 3-methoxycyclohexene, addition was retarded by a factor of 5.6 relative to cyclohexene.[15]

Now we report the relative reactivities of olefins **4**–**9** toward CCl$_2$. Not only do the results speak against transfer of captured CCl$_2$ from the ketal oxygens to normal double bonds (**5** and **6**) but also against the electronically more attractive transfer of ylidic CCl$_2$ in **8** (*cf.* **10**).[16,17] The results do, however, provide a striking paradigm of the sensitivity of CCl$_2$ selectivity toward substituent effects.


4



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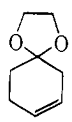

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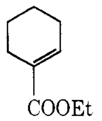

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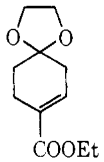

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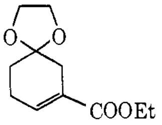

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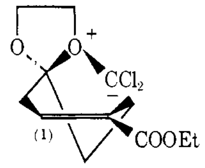
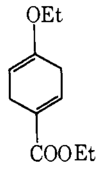


10

Results

Preparation of Olefins. Olefin **5** was prepared by the method of Garbisch[19] and **7** was obtained from the commercially available acid[20] *via* the acid chloride. Olefin **6** was obtained *via* Birch reduction of anisole, followed by ketalization.[21,22]

Following the literature,[23] a benzene solution of ethyl propiolate and 2-ethoxybutadiene[24] was heated in a bomb at 140° for 24 hr in order to prepare **11**.



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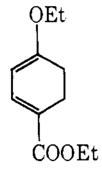

12

The product (λ_{max} 320 nm, ethanol) appeared to be mainly the isomeric **12**.[25] Nmr showed vinyl signals at δ 6.77 and 4.54 (vicinal to COOEt and OEt, respectively). Gc examination indicated that ~15% of a second component was present.

Ketalization of the mixture afforded a product which, analyzed satisfactorily for $C_{11}H_{16}O_4$, had M$^+$ at m/e 212, and showed ir absorptions at 5.84 and 6.01 μ (α,β-unsaturated ester). Though homogeneous on five packed gc columns, it was cleanly separated into two main components on a 100 ft Apeizon L Golay column at 152°. The major/minor ratio was ~5.2, and these peaks accounted for 92% of the gc trace.

The nmr spectrum (CCl$_4$) featured a multiplet at δ 6.75 (1 H, vinyl); three lines of a quartet centered at 4.16 (ester methylene, J = 7 Hz), the upfield line of which was partially obscured by the ketal singlet at 3.92 (total, quartet and singlet, 6 H); a narrow, featureless multiplet at 2.34 (4 H, allylic); a crude triplet at 1.68 (2 H, isolated methylene, J ~ 6 Hz); and a sharp triplet at 1.27 (3 H, ester methyl, J = 7 Hz).

The vinyl resonance at δ 6.75 is indicative of a proton vicinal to a carboethoxy group as in **8** or **9**.[26] The nmr

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(11) J. J. Sims and V. K. Honwad, *J. Org. Chem.*, **34**, 496 (1969).

(12) W. Grimme, J. Reisdorff, W. Jünemann, and E. Vogel, *J. Amer. Chem. Soc.*, **92**, 6335 (1970).

(13) Private communication from E. Vogel to P. S. Skell, cited by P. S. Skell and M. S. Cholod, *ibid.*, **91**, 6035 (1969), footnote 22.

(14) D. Seyferth and V. A. Mai, *ibid.*, **92**, 7412 (1970).

(15) M. A. Tobias and B. E. Johnston, *Tetrahedron Lett.*, 2703 (1970).

(16) The $^-$CCl$_2$–C(1) distance in **10** is about 2.3 Å, as measured from Dreiding models.

(17) Even if CCl$_2$ were to form ylides with methoxycyclohexene, **5** and **6**, attack of the negative ylide carbon on the unactivated double bond would be electronically unfavorable. The ylides might revert, or give up CCl$_2$ to a second molecule of CCl$_2$, to CCl$_3^-$, or to other species in solution. (The observation that sulfides inhibit the addition of CCl$_2$ to olefins but are themselves recovered in good yield[18] may be an example of such a process.) With **10**, derived from **8**, the transfer of $^-$CCl$_2$ to the activated double bond could be faster and perhaps detectable as an enhancement of the overall rate of cyclopropanation.

(18) W. E. Parham and S. H. Groen, *J. Org. Chem.*, **29**, 2214 (1964); 30, 318 (1965).

(19) E. W. Garbisch, Jr., *ibid.*, 30, 2109 (1965). Gc analysis on a Carbowax column revealed contamination by 2% of cyclohexen-3-one. Less than 1% of **6** was present, however.

(20) Frinton Laboratories.

(21) Model procedures appear in A. L. Wilds and N. A. Nelson, *J. Amer. Chem. Soc.*, 75, 5360 (1953); E. A. Braude, A. A. Webb, and M. U. S. Saultanbawa, *J. Chem. Soc.*, 3328 (1958).

(22) Gc examination on a Carbowax column showed less than 1% of **5**.

(23) A. L. Logothetis and N. A. Nelson, *J. Org. Chem.*, 27, 1438 (1962); A. L. Logothetis, Ph.D. Thesis, Massachusetts Institute of Technology, 1958.

(24) E. A. Braude, E. R. H. Jones, F. Sondheimer, and J. B. Toogood, *J. Chem. Soc.*, 607 (1949).

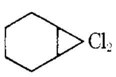
(25) Logothetis and Nelson[23] report the isolation of a mixture of **11** (λ_{max} 256 nm) and **12** (λ_{max} 322 nm) in which **11** predominated. Our isolation of **12** may reflect a rearrangement catalyzed by contact of the reaction mixture with the metallic bomb, which occurred during the reaction despite the use of a glass liner.

(26) The analogous resonance appears at δ 6.85 in the spectrum of **7**. The presence of isomers other than **8** or **9** is precluded by the absence, under high amplification, of any other vinyl resonances between δ 6.75 and 4.16.

spectrum, which can be generated by a superimposition of the spectra of **7** (less isolated methylene resonances) and **6** (less vinyl resonances) is consistent with **8**, **9**, or a mixture of both olefins. Formulation as the mixture follows from its gc resolution (see above) and from a double resonance experiment in which the allylic protons at δ 2.34 were irradiated, causing collapse of the vinyl multiplet to *two singlets* ($\Delta\delta$ 6 Hz) in a ratio of $\sim$6 :1.

That **8** was the major component of the mixture in hand follows from the expected sense of addition in the Diels–Alder reaction of 2-ethoxybutadiene and ethyl propiolate.[27] Additionally, the initial dihydrobenzene derivative(s) has been transformed to *p*-ethoxybenzoic acid.[23] The implicit claim of exclusivity in the formation of 1,4-disubstituted **11** (**12**)[23] is, however, not supported by our work.

Dichlorocarbene Additions. Substrates **4–7** were converted to cyclopropanes **13–16** by treatment with ethyl trichloroacetate and sodium ethoxide (or methoxide).[28] The products were purified by distillation or preparative gc. In the nmr, the ketal protons of **15** appeared as a relatively sharp singlet at δ 3.85, whereas those of **14** appeared as a multiplet at δ 3.95.[29]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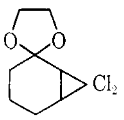
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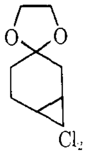
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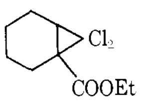
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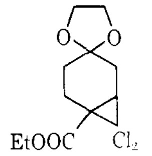
The reaction of equimolar quantities of phenyl(bromodichloromethyl)mercury[30] with **8** and **9** in refluxing benzene afforded two high-boiling products, **17** and **18**, which could be isolated by preparative gc on a Carbowax column at 210°; **18** had the shorter retention time, and the ratio **17**/**18** was 2.52 :1.[31] A mixture of the compounds gave a satisfactory C and H analysis for $C_{12}H_{16}O_4Cl_2$. Each adduct showed parent ions at *m/e* 294, 296, and 298, corresponding to the expected molecular weights and the presence of two chlorine atoms. Each showed ester carbonyl absorption at 5.75, and ketal C–O–C absorptions at 8.5–9.8 μ in the ir.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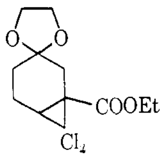
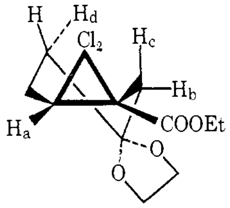

18

The 60-MHz nmr spectra of **17** and **18** were devoid of vinyl absorption and featured "unsplit" ketal signals at δ 3.87. Quartet and triplet resonances (J = 7 Hz), due to the ethoxy functions, were centered at 4.17 and 1.28 ppm. Note particularly the position and lack of splitting of the ketal resonances of these products, compared with the analogous signal of **15** at δ 3.85.

The assignment of structure **18** to the minor CCl$_2$ adduct rests on the observation of an AB quartet in its 100-MHz spectrum.[32a] This quartet represents the methylene group isolated between the ketal and carboethoxy-bearing carbon atoms. It was centered at δ 2.12 (J = 15 Hz, $\Delta\nu$ = 36 Hz). The low-field lines showed broadening suggestive of further coupling. Assuming that **18a** is a major contributor to the conformational equilibrium which describes **18**, we assign the low-field resonances of the AB quartet (δ 2.47 and 2.32) to equatorial proton H$_b$, and note the expectation of W-plan coupling of H$_b$ to H$_a$ and H$_d$.[32b] Long-range coupling to axial proton H$_c$ is not expected; it appears as two relatively sharp lines at δ 1.93 and 1.78.



18a

Such a simple feature is neither expected nor observed in the 100-MHz spectrum of the major CCl$_2$ adduct (though lines associated with an ABX pattern are present), which is therefore assigned structure **17**. The assignments mean that the major component of the starting olefin mixture (**8**) gives rise to the major component of the CCl$_2$ product mixture (**17**).

Relative Reactivity Experiments. CCl$_2$ was generated in selected mixtures of olefins **4–9**, and the corresponding product ratios were determined by gc. Relative reactivities were then calculated by the Doering–Henderson approximation.[33] Experiments involving **8** and **9** employed the **8** and **9** mixture described above, with the ratio **8**/**9** = 5.17. Corrections for purity (92%) were applied.

In most of the competition experiments, CCl$_2$ was generated by the thermolysis of PhHgCCl$_2$Br in refluxing benzene (bath at $\sim$85°). Under these conditions, **5** partially isomerized to **6** affording a product mixture which contained **14** and **15**. The thermolysis of sodium trichloroacetate in monoglyme[34] (bath at 83–85°) was therefore used to generate CCl$_2$ in competitions involving **5**. Only **14** formed from **5** under these conditions. Seyferth has shown that the selectivity of CCl$_2$ toward many olefins is essentially constant whether PhHgCCl$_2$Br in benzene or Cl$_3$CCOONa in monoglyme is employed as precursor;[35] this validates a reactivity comparison of **5** with the other substrates.

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(27) Yu. A. Titov, *Russ. Chem. Rev.*, **31**, 267 (1962); J. Sauer, *Angew. Chem., Int. Ed. Engl.*, 6, 14 (1967). The dominance of 1,4- over 1,3-disubstituted products in Diels–Alder reactions of 2-substituted dienes with monosubstituted dienophiles is invariable over the many examples cited in these reviews.

(28) W. E. Parham and E. E. Schweizer, *Org. React.*, **13**, 75 (1963).

(29) Parallel observations have been made on the difluoro analogs of **14** and **15**; R. A. Moss and D. J. Smudin, unpublished work.

(30) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y-P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

(31) Very similar results were obtained when **8** and **9** were allowed to react with phenyl(trichloromethyl)mercury in refluxing benzene for 2 days.

(32) (a) We thank Mr. M. McCreary for 100-MHz nmr spectra. (b) For pertinent discussions, see L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, pp 238 and 334 ff.

(33) W. v. E. Doering and W. A. Henderson, Jr., *J. Amer. Chem. Soc.*, **80**, 5274 (1958).

(34) W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

(35) D. Seyferth, M. E. Gordon, J. Y-P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **89**, 959 (1967).

Products and starting materials were stable to the conditions of the competition experiments for extended periods; products were also stable to the analytical conditions. Effective olefin concentrations were at least seven times those of the carbene precursor, and the relative reactivity approximation should be valid.[33] The experimentally determined relative reactivities appear in Table I; the data, adjusted to a cyclohexene standard, are gathered in Table II.

Table I. Experimentally Determined Relative Reactivities

Olefin$_a$/olefin$_b$	k_a/k_b	% av dev^a
6/4	0.435^b	1.6
7/4	0.114^b	0.88
8/7^c	0.247^d	2.9
9/8	3.92^{e,f}	3.8
5/6	0.0272	2.9

^{a} Two experiments were carried out in each case. ^{b} From these data, k_6/k_7 is calculated to be 3.82. The experimental value was determined as 3.66. ^{c} Olefin **9** was also present. ^{d} In this case only, the thermal conductivity detector was not calibrated for relative response. The reported value is therefore ~10% *too high*. The detector's response to isomers **17** and **18** was assumed to be equal; the reactivity values for **8** and **9**, adjusted to k_4 = 1.00 and presented in Table II, will also be high by ~10%. ^{e} k_9/k_8 was 3.75 and 4.14 in two experiments in which **7** was present. In the absence of **7**, k_9/k_8 was 3.86. The mean of these three values is recorded. ^{f} Note that the ratio of **17**/**18** increased as the conversion of **8** and **9** to products increased, consistent with exhaustion of the supply of the more reactive minor substrate component, **9**, which is the source of **18**. At [**8** and **9**]/[PhHgCCl$_2$Br] = 15.6, **17**/**18** was 1.34; at equimolarity, **17**/**18** was 2.5. Conversion in the latter case was ~50%.

Table II. Relative Reactivities, Cyclohexene Scale

Olefin	Rel reactivity	Olefin	Rel reactivity
4	1.00	**9**	0.11^a
6	0.44	**8**	0.028^a
7	0.11	**5**	0.012

^{a} See Table I, footnote *d*.

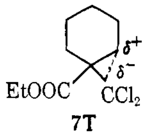
Discussion

Relative Reactivities. It is immediately clear that ketal olefins **5** and **6** exhibit no special reactivity toward CCl$_2$ (Table II). This finding augments the conclusions of previous workers.[14,15] Moreover, no favorable synergistic interaction of the ketal and carboethoxy groups of **8** is apparent. The observed relative reactivity of **8** (0.028) is actually *smaller* than the product of the reactivities of **6** and **7** (0.048) indicating that the deactivating influences of the 1-carboethoxy and 4-ketal groups reinforce each other in **8** (see below). The addition of CCl$_2$ to **8** does not, therefore, appear to proceed *via* **10**.

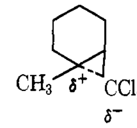
Note that **9** reacts nearly four times faster with CCl$_2$ than does **8**. This observation is underlined by an alternative formulation. The results for **5** and **6** clearly show that the introduction of a ketal group deactivates cyclohexene toward CCl$_2$ addition. Transformation of **7** to **9** requires the introduction of a ketal group, and yet **7** and **9** react with CCl$_2$ at comparable rates!

Consider a highly unsymmetrical transition state (TS) for the CCl$_2$ addition, one in which considerable positive charge resides mainly on *one* olefinic carbon. Such a TS has been postulated[36] based on the electrophilic[33] selectivity of CCl$_2$; it is supported by the observation of $\rho^* \sim -4.3$ for the addition of CCl$_2$ to simple alkenes,[37] and by the very specific steric effects which can be observed in those additions.[38] The unsymmetrical TS is also in accord with theoretical treatments.[39]

Applied to the reaction of CCl$_2$ and **7**, this concept elicits TS **7T**, which avoids placing positive charge α to the carboethoxy group. This helps to rationalize the surprising facts that the strongly electron-withdrawing 1-carboethoxy group deactivates cyclohexene only by a factor of 9,[40] whereas the weakly donating 1-methyl substituent activates by as much as 8–8.5 times.[41] In the latter case the TS is approximated by **19T**.



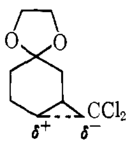
7T



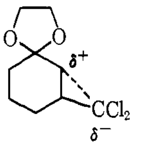
19T

The carboethoxy group deactivates by effectively removing one olefinic carbon as an initial site for carbene attack, while it is simultaneously the source of an unfavorable inductive effect which operates at that same carbon during addition. Note, too, that 1-carboethoxy deactivates cyclohexene *more* than does 1-acetyl,[40,41] even though the latter is a stronger electron-withdrawing group by the resonance effect.[42] This supports our emphasis on TS analysis of the relative reactivities, in which inductive effects are paramount, as opposed to ground-state analysis, in which resonance effects would be more important.

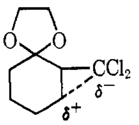
Similarly, **6T** represents the CCl$_2$ + **6** TS, in which the bulk of the induced positive charge resides on the distal[43] rather than on the proximal[43] olefinic carbon; inductive destabilization by the ketal group is thus minimized. The reactivity decrease of 2.3 (**4**/**6**) can be understood on a largely "statistical" basis: **4** has two



6T



5T



5T′

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(36) For discussions, see R. A. Moss, "Selective Organic Transformations," Vol. I, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1970, p 35 ff; R. A. Moss, "Carbenes," Vol. I, M. Jones, Jr., and R. A. Moss, Ed., Wiley-Interscience, New York, N. Y., in press. See also W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, 28, 2200 (1963); P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, 78, 3409, 5430 (1956).

(37) P. S. Skell and M. S. Cholod, *ibid.*, **91**, 7131 (1969).

(38) (a) R. A. Moss, R. W. Kleinman, and K. L. Williamson, *Chem. Commun.*, 927 (1970); (b) R. A. Moss and A. Mamantov, *Tetrahedron Lett.*, 3425 (1968).

(39) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); R. Hoffmann, private communication.

(40) The only related substituent studied is 1-acetyl, which deactivates cyclohexene by a factor of 3.3.[41]

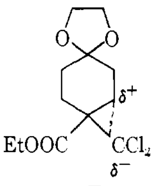
(41) O. M. Nefedov and R. N. Shafran, *Izv. Akad. Nauk. SSSP, Ser. Khim.*, 538 (1965). Reactivities were determined under conditions of temperature and precursor comparable with those employed in our study.

(42) σ_R and σ_I are 0.15 and 0.28, respectively, for COCH$_3$, but 0.11 and 0.32 for COOEt. See J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968,p 238 ff, for a discussion.

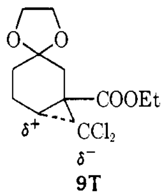
(43) Distal and proximal refer to the distance from the ketal group.

equivalent olefinic carbons and **6** has one site for attack which is substantially better than the other, *i.e.*, it effectively has one site for attack.[44] Moreover, the dramatic deactivation of **5** (**4**/**5** = 83, **6**/**5** = 38) results from a combination of inductive and steric effects. TS **5T** is strongly destabilized by the unfavorable inductive effect, whereas alternative **5T′** surely suffers from steric hindrance at the ketal center.[45]

For ketals **8** and **9** we draw TS **8T** and **9T**. We see that **8** should indeed be less reactive than predicted by the product of the reactivities of **7** and **6**, for although COOEt engenders the same deactivation in **8** and **7**, it also directs the induced positive charge to the proximal olefinic carbon of **8**. With **6**, the charge can develop on the distal carbon. Inductive deactivation by the ketal group is therefore more serious in **8** than in **6**.



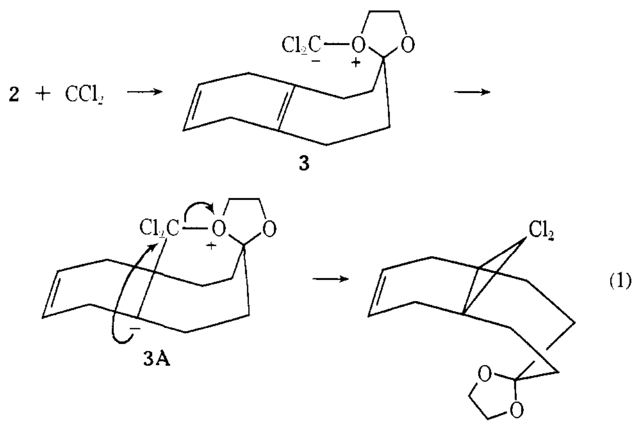
8T



9T

That the reactivities of **9** and **7** are comparable finds explanation in the observation that the induced positive charge in **9T** resides on the distal "para" carbon, for which we conclude that inductive destabilization by the ketal group is not large. A similar conclusion follows from the analysis of **6T** (see above). We have analyzed the relative reactivities in detail, because the analysis provides one of the clearest examples of the utility of the unsymmetrical transition state concept.[36, 39]

The Problem of Synergism. The synergistic conception of CCl_2 addition to **2**[12] finds no support in the present or related work.[14, 15] In an attempt to understand this, let us analyze a cooperative carbene addition in terms of three factors. Assume that the ylide → cyclopropane transformation requires an addition–elimination sequence.[46] Applied to **2** and **3**, this generates eq 1. The factors to consider are (1) the atom to which the carbene first coordinates, (2) the strain involved in the addition of the ylide to the double bond, and (3) the stereoelectronic situation for conversion of the betaine (**3A**) to the cyclopropane.

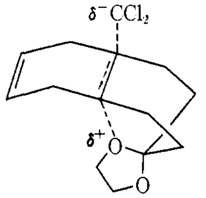


(1) The observations of Landgrebe, *et al.*,[9, 10] appear to require carbonyl ylide intermediates in the reactions of CCl_2 with benzaldehyde and benzophenone. This implies that ylides such as **3** and **10** are not, *a priori*, unreasonable transients in the reactions of **2** and **8** with CCl_2.

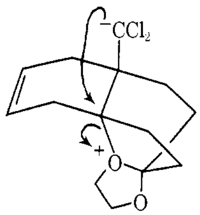
(2) Extraordinary strain is not encountered in constructing Dreiding models of **3A**, or of the corresponding betaines derived from **6**, **8**, or **9**. The ylide derived from **5**, however, could add only at the distal olefinic center; bonding at the proximal center would create prohibitive strain.

(3) If, however, the displacements which would convert **3A** and its analogs to products must occur from the *rear*[47] of the Cl_2C^{-}–^{+}O bond, then none of these betaines can close to cyclopropanes. All require front-side displacements. Here may be the crucial factor which prohibits synergistic CCl_2 additions to **5**, **6**, **8**, and related compounds.[14, 15, 48]

Only in the case of **2** is there any evidence which, at least superficially, points toward synergistic CCl_2 additions. But other explanations can be constructed. One which retains a special role for the ketal group is represented by **20**, in which a ketal oxygen assists the electrophilic attack of CCl_2 which occurs from the *opposite* face of the π system. Dreiding and space-filling models of **21** can readily be constructed, and no stereoelectronic problem attends displacement of the oxonium center by dichloromethide in **21**.



20



21

We are continuing our search for cooperative carbene addition reactions.

Experimental Section[49]

Olefins. Cyclohexene was obtained from Aldrich Chemical Co. and was percolated through a column of Woelm neutral alumina and Linde 4A molecular sieves immediately prior to use.[51]

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[44] Remote substituent effects in the related electrophilic addition of 2,4-dinitrobenzenesulfenyl chloride to 4-substituted cyclohexenes are elegantly discussed by H. Kwart and L. J. Miller, *J. Amer. Chem. Soc.*, **83**, 4552 (1961).

[45] It is difficult to estimate the magnitude of this effect, but steric hindrance to CCl_2 additions can be substantial. For example the reactivity ratio (−10°) *tert*-butylethylene/1-butene is 0.029.[38b]

[46] R. S. Matthews and T. E. Meteyer, *Chem. Commun.*, 1576 (1971), provide a pretty example of such a sequence.

[47] L. Tenud, S. Farooq, J. Seibl, and A. Eschenmoser, *Helv. Chim. Acta*, **53**, 2059 (1970), and references cited there.

[48] It is a pleasure to acknowledge the important contribution of Professor J. E. Baldwin to the development of this argument.

[49] Nmr spectra were determined with Varian T-60 or HA-100 spectrometers as solutions in CCl_4–TMS. Chemical shifts are reported in δ units. Ir spectra were determined on CCl_4 solutions with a Perkin-Elmer Infracord. Uv spectra were determined on ethanol solutions with a Cary-14 spectrophotometer. Mass spectra were run on a Hitachi-Perkin-Elmer RMU-6L spectrometer.[50] Except as noted, gc work employed an F & M Model 810 instrument. Columns frequently used included 6 ft × 0.25 in., 10% SE-30 on 80–100 Chromosorb P, and 6 ft × 0.25 in., 10% Carbowax 20M on either 80–100 Chromosorb W or 70–80 Anakrom ABS. Microanalyses were performed by Mrs. N. F. Alvord. All reactions were carried out under a nitrogen atmosphere.

[50] We thank Drs. H.-J. Förster and C. Hignite for these determinations.

[51] Reagent grade benzene was similarly treated.

Cyclohex-1-en-4-one Ethylene Acetal (6).[21,52] This compound was made by the cited model procedures using the following quantities of reagents: 400 ml of NH_3 and 150 ml of dry ether, 27 g (0.25 mol) of anisole, 4.5 g (0.65 g-atom) of Li wire, and 44 ml (0.75 mol) of absolute ethanol. After hydrolysis of the Birch product mixture, the crude product was extracted with three 100-ml portions of benzene. The benzene solution was subjected to the ketalization procedure of Agosta,[52] using 17 g (0.27 mol) of ethylene glycol and 1 g of dry oxalic acid. The crude product was distilled at the water pump over a 10-cm micro-Vigreux column. The fraction with bp 78–80° (14 mm) was shown by gc on the Carbowax column (120°) to contain about 90–92% of the desired product. Cyclohexanone ethylene acetal (6%) and ~2% of 1-cyclohexen-3-one ethylene acetal were also present, as were traces of anisole, cyclohexen-3-one, and its ketal.

The high boiling fraction (17 ml) was carefully distilled on a Nester/Faust Teflon annular spinning-band column to afford six new fractions, of which the latter three (bp 88 (34 Torr), 89 (36 Torr), and 86° (31 Torr)) were of 97.5, 99, and 99% purities. Approximately 10 g of highly pure 1-cyclohexen-4-one ethylene acetal was thus obtained: nmr 5.53 (multiplet, 2 H, vinyl), 3.86 (singlet, 4 H, ketal), 2.15 (envelope, 4 H, allyl), 1.65 (crude triplet, $J \sim 6$ Hz, 2 H, methylene).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.38; H, 8.87.

1-Carboethoxycyclohexene (7). This olefin was prepared from 10 g (79 mmol) of cyclohexene-1-carboxylic acid[20] and 25 g (197 mmol) of oxalyl chloride (2 hr of reflux) with isolation of the intermediate acid chloride (bp 94–99° (15 Torr)). The latter was slowly added to a stirred solution of 6.4 g (81 mmol) of pyridine in 40 ml (685 mmol) of absolute ethanol. The exothermic reaction was moderated with an ice bath. After addition was completed, stirring was continued for 3 hr.

The product solution was diluted with 250 ml of water, and the resultant mixture was extracted with 4 × 50 ml of ether. The ethereal extracts were combined and dried over 4A sieves. The solvent was stripped, and the residue was distilled at 58–60° (1.7 mm)[53] to give 9.8 g (80%) of water-white liquid **7**. Gc (Carbowax) indicated a purity >98%, and the ir spectrum showed absorptions at 5.84 (ester) and 6.08 μ (C=C): nmr 6.85 (multiplet, 1 H, vinyl), 4.10 (quartet, $J = 7$ Hz, 2 H, $-OCH_2-$), 2.18 (multiplet, 4 H, allyl), 1.60 (multiplet, 4 H, methylene), 1.25 (triplet, $J = 7$ Hz, 3 H, methyl).

1- and 2-Carboethoxycyclohexen-4-one Ethylene Acetals (8 and 9). 2-Ethoxybutadiene[23,24] (bp 92–94°,[54] 8.2 g, 84 mmol), 8.2 g (84 mmol) of ethyl propiolate (Aldrich, 96%), *ca.* 50 mg of hydroquinone, and 90 ml of benzene were sealed under a nitrogen atmosphere into a glass-lined bomb. The bomb was heated to ~140° for 24 hr. Upon opening the cooled bomb, it was found that about half of the contents had leaked into the space between the liner and the steel bomb. Ether was used to collect all of the product solution. The ether was stripped, and the residue was distilled over a 10-cm Vigreux column. A total of 7.69 g of product, bp 68–70° (0.17 mm), was collected and identified as **12**.[55]

The entire product (39 mmol) was refluxed with 2.45 g (39 mmol) of ethylene glycol and 320 mg of dry oxalic acid in 25 ml of benzene in a Soxhlet extractor charged with Type 4A molecular sieves. After 4 hr, 200 mg of glycol, 100 mg of oxalic acid, and 20 ml of benzene were added, and reflux was continued for 12 hr more. The product solution was washed twice with 50-ml portions of a 3.5% aqueous K_2CO_3 solution, and then with water. It was dried over 3A sieves. Benzene was stripped, and the product was distilled over a short-path apparatus to afford 5.97 g of **8** and **9**, bp 78–80° (0.12 mm).[55] The yield, based on 2-ethoxybutadiene, was 33%.

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.24; H, 7.60. Found: C, 62.25; H, 7.75.[56]

Cyclopropanes. The procedure described by Parham and Schweizer[28] was used to convert olefins **4–7** to dichlorocyclopropanes **13–16**.

7,7-Dichloronorcaran-3-one Ethylene Acetal (14). Olefin **5**[19] (288 mg, 2.05 mmol), 1.58 g (4 equiv) of ethyl trichloroacetate (Eastman), and 5 ml of benzene were stirred under nitrogen and treated with 560 mg (4 equiv) of sodium ethoxide, added in three portions over 1.5 hr. After work-up,[28] gc on an SE-30 column at 142° showed the presence of a single high-boiling product in about 50% conversion. Preparative gc afforded pure **14**.

The ir showed 8.5, 9.0, 9.65, and 9.78 μ (s, ketal). The mass spectrum featured a molecular ion series at *m/e* 222, 224, and 226 in the distribution 9:6:1; nmr 3.92 (multiplet, 4 H, ketal) and 2.32–1.20 (multiplet, "sharp" lines appear at 2.05, 1.90, 1.77, and 1.52 (very intense), 8 H).

Anal. Calcd for $C_9H_{12}Cl_2O_2$: C, 48.44; H, 5.42. Found: C, 48.09; H, 5.39.

7,7-Dichloronorcaran-4-one Ethylene Acetal (15). This compound was prepared from 3.2 g of **6** (23 mmol), 2.75 g of sodium methoxide (2.2 equiv), 10 ml of benzene, and 8.7 g of ethyl trichloroacetate (2 equiv). The latter was added in one portion to the cold (0°), stirred mixture of **6** and base. After 4 hr, 3 ml of benzene was added to the viscous, brown mixture, and stirring was continued for 5 hr. Finally, stirring was continued for an additional 3.4 hr at 25°. An aqueous work-up, followed by extraction with petroleum ether (30–50°), allowed the isolation of a high boiling residue which was distilled over a short-path apparatus to afford 1.84 g of clear liquid, bp 105–107° (2 mm). The yield based on **6** was 36%. An analytical sample was obtained by redistillation at 72° (0.08 mm).

The ir showed strong absorptions in the region 8.6–9.9 μ, assigned to the ketal function. A parent ion series was observed in the mass spectrum at *m/e* 222, 224, and 226 in the distribution 9:6:1; nmr 3.85 (singlet, 4 H, ketal) and 2.34–1.22 (multiplet, 8 H).

Anal. Calcd for $C_9H_{12}Cl_2O_2$: C, 48.44; H, 5.42. Found: C, 48.59; H, 5.51.

1-Carboethoxy-7,7-dichloronorcarane (16). This compound was prepared from 3.00 g (19.4 mmol) of **7**, 7.44 g (2 equiv) of ethyl trichloroacetate, and 10 ml of benzene, to which was added (at 0°) 2.9 g (2.2 equiv) of sodium ethoxide in four portions over 4 hr. Stirring was maintained during the addition and subsequently for 2 hr. The reactants were then warmed to 25° and stirred for 2 hr. Work-up (as above) afforded a residue which was distilled over a short-path apparatus at 61° (0.12 mm) to give 1.71 g of a clear liquid. Gc analysis (SE-30, 148°) showed the product to consist of about 15% unreacted **7** as well as ~85% of a single higher boiling product. Preparative gc then afforded pure **16**. The crude yield was 32%.

The ir spectrum showed ester carbonyl absorption at 5.79 μ. The mass spectrum featured a parent ion series at *m/e* 236, 238, and 240 in the approximate distribution 9:6:1; nmr 4.18 (quartet, $J = 7$ Hz, 2 H, $-OCH_2-$), 3.78–1.00 (multiplet), and 1.33 (triplet, $J = 7$ Hz, ester methyl). The entire upfield region integrated for 12 protons.

Anal. Calcd for $C_{10}H_{14}Cl_2O_2$: C, 50.65; H, 5.95. Found: C, 50.44; H, 5.93.

1- and 2-Carboethoxy-7,7-dichloronorcaran-4-one Ethylene Acetals (17 and 18). This mixture was prepared by stirring and refluxing a benzene solution (10 ml) of 0.500 g (2.36 mmol) of **8** and **9** (5.17:1) and 1.04 g (1 equiv) of $PhHgCCl_2Br$ (Alfa Inorganics) for 7 hr. The cooled product mixture was filtered and the precipitate was washed with petroleum ether. The solid PhHgBr weighed 0.71 g (84%). The stripped, yellow filtrate weighed 0.9 g. It was submitted to gc on the Carbowax column, from which **17** and **18** were isolated, as described above. The conversion of **8** and **9** to **17** and **18** was about 50%, and the **17**/**18** ratio was 2.5.[57] Most of the physical data characterizing **17** and **18** are given above; details of the 60-MHz spectra not mentioned there include: **17**, multiplets extending from 2.65 to 1.78 and from 1.78 to 1.08; **18**, multiplets extending from 2.72 to 1.62 and from 1.59 to 1.08. Only the high-field lines of the AB quartet are clearly seen in the 60-MHz spectrum of **18**, they appear at 1.95 and 1.68. The integral ratios of high-field/(ester methylene and ketal) protons are 1.63 (**17**) and 1.71 (**18**); the theoretical ratio is 1.66.

Anal. Calcd for **17** and **18**, $C_{12}H_{16}O_4Cl_2$: C, 48.83; H, 5.46. Found: C, 48.54; H, 5.28.

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[52] W. C. Agosta and W. L. Scheiber, *J. Amer. Chem. Soc.*, **93**, 3947 (1971).

[53] Lit. bp 109° (35 mm); S. Dev, *J. Ind. Chem. Soc.*, 33, 769 (1956).

[54] Literature boiling points range from 92.5–93.5 to 96.5°. See ref 23.

[55] Further discussion appears in the Results section.

[56] The analytical sample was purified by gc.

[57] A third product, of shorter retention time than either **17** or **18**, was noted in preparative runs, but *not* in competition experiments (where the olefin/mercurial ratio was very high). This product could also be produced from **17** by gc at high injector temperatures. Its mass spectrum featured a parent ion series at 250, 252, and 254 (9:6:1), suggesting that it was the ketone derived from 17.

Competition Experiments. The general conditions, procedures, and results are described above. Several additional points will be described in a general procedure.

Carbene precursor (50–100 mg) and a stirring bar were contained in a 10-ml flask, which was fitted with a reflux condenser capped with a gas inlet tube. The latter was connected to a nitrogen-vacuum manifold. A carefully weighed mixture of olefins A and B (200–700 mg of each) was diluted with 4 ml of benzene, and the benzene solution was injected onto the solid precursor. The stirrer was started, and the flask was immediately lowered into an oil bath preheated to ∼83°. Slow reflux and stirring was maintained for 3.5–7 hr. Then, the product mixture was cooled (0°) and filtered through a medium sintered glass funnel. Gc analysis was immediately performed on the filtrate. Competition **5**/**6** was performed in the same general manner, except that the CCl_2 precursor was sodium trichloroacetate (dried at <1 mm, 90°, 18 hr) and the solvent was dimethoxyethane distilled first from $LiAlH_4$ and then from sodium.

In runs involving **4**, **6**, and **7**, only unreacted olefin and the expected cyclopropanes were observed in the product mixtures. Runs involving **5**, **8**, and **9** gave more complicated product mixtures. However, prepared, determined, dimethoxyethane or benzene solutions of product mixtures **13** and **14** and **16**, **17**, and **18** could be refluxed with PhHgBr without alteration of the product ratios. Additionally, all competition experiments were run as duplicates; the second reaction mixture was subjected to twice the reflux time of the first. Reproducibility (Table I) was good.

The analytical gc conditions included injector and detector temperatures of 245–255° and 225–230°, respectively; details follow for the competition experiments of Table I.

Competition **6**/**4** was analyzed on an SE-30 column. The initial temperature was 117°. After **4**, **6**, and **13** had eluted, the column temperature was rapidly raised to 142° to elute **15**.

Competition **7**/**4** was analyzed on a Carbowax column. The initial temperature was 112°. After **4** and **13** had eluted, the temperature was rapidly raised to 151° to elute **7** and **16**.

Competition (**8** and **9**)/**7** was analyzed on a Carbowax column. The initial temperature was 151°. After **7** and **16** had eluted, the temperature was rapidly raised to 202° to elute **8** and **9**, **17**, and **18**.

Competition **5**/**6** was analyzed at Rutgers University, by Mr. Ulf Dolling on a Barber-Colman, Series 5000 gc equipped with a flame ionization detector and fitted with a 100 ft Apeizon-L Golay column. Typical operating conditions included injector 250°, column 160°, and detector 240°.

Detectors were calibrated with pure products.[58] Peak integrals were determined by cut-and-weigh of Xerox copies of the gc traces. Two traces were run for each experiment, and two copies were analyzed for each trace. Mean values were recorded.

Acknowledgments. I am very grateful to Professor D. S. Kemp and to the Massachusetts Institute of Technology for their hospitality and provision of laboratory space. Financial support by NIH and NSF is acknowledged with gratitude. Helpful discussions were held with Professors W. R. Moore, G. M. Whitesides, and Mr. D. C. Roberts.

(58) See, however, footnote *d* in Table I.

Mechanism of Quenching of the Uranyl Fluorescence by Organic Compounds

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Received December 16, 1971

Abstract: Quenching constants of the uranyl fluorescence by aromatic molecules and aliphatic alcohols were obtained from the Stern–Volmer plots in solutions at room temperature. Quenching by the aromatic quenchers, which have no excited states lying below that of the uranyl ions, occurred very efficiently without chemical changes. There was no kinetic isotope effect, *i.e.*, $K_q(C_6H_6)/K_q(C_6D_6) = 1.0$, which would indicate no contribution of vibrational factors of aromatic quenchers in the rate-determining step. Relative quenching rates of aromatic quenchers showed close correlations with Yukawa–Tsuno's σ values, with ionization potentials, and with rates of thermal aromatic nitrations, suggesting an important role of electron donor–acceptor interactions. Further, close correlation of relative quenching rates with relative π complex stabilities of alkylbenzenes suggested the formation of a π complex between the quenchers and the excited uranyl ions, though there would be no affinities in the ground state. On the other hand, quenching by aliphatic alcohols appeared to involve a chemical process (α-hydrogen abstraction), on the basis of kinetic isotope effects, positive activation energies for the photoredox rates, and correlation of the photoredox quantum yield with the sum of Taft's σ values, $\Sigma\sigma^*$. From these facts it was suggested that quenching of the uranyl fluorescence by aromatic quenchers and aliphatic alcohols took place *via* nonelectronic–electronic energy transfer; quenching by aromatic quenchers appeared to proceed through physical radiationless decay of an exciplex intermediate, while quenching by aliphatic alcohols seemed to proceed through a chemical decay of a similar intermediate.

The role of exciplex formation in fluorescence quenching has been widely investigated.[1] Recently, fluorescence quenching of aromatic hydrocarbons by olefins which have no excited states lying below the excited levels of the fluorescers has been observed

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