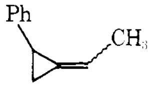
trans-**1** (35 min, 87°, trichloroethylene) partially equilibrated these isomers with *E*- and *Z*-2-phenylethylidenecyclopropane (**2**).[11] The two isomers were present in the ratio



2

18:1, as revealed by capillary GLC analysis, but it has not yet been possible to determine whether the *E* or *Z* isomer is the major component of the mixture.[12] As expected, the mixture of the isomers of **2** was optically active, having $[\alpha]^{20}$D +9.4°. It can be presumed, by analogy to the studies with Feist's ester,[1c] that this rotation results from the formation of products (**2**) via migration of C-2 of **1** in a highly stereoselective fashion with inversion of configuration. The positional selectivity that results in the failure of 2-methylbenzylidenecyclopropane to be formed from **1** by migration of C-3 is amply precedented.[1]

Photolysis[13] of the mixture of isomers of **1**, $[\alpha]^{20}$D +2.0°, for 6 h afforded a 1:1 mixture of **1** and the geometric isomers **2**; the latter were present in the ratio 1.4:1, the major component being the same as that observed in the thermolysis. The ethylidenecyclopropanes (**2**), upon GLC purification, had a rotation of $[\alpha]^{20}$D +7.0°, and recovered **1** showed $[\alpha]^{20}$D +1.0°.[14] In a second experiment, optically active **2**, $[\alpha]^{20}$D +9.4°, obtained by thermolysis of **1**, was irradiated for 6.5 h.[13] The mixture of isomers of **1** that was isolated was found to have a rotation of +1.5°.

These results clearly demonstrate that chirality is maintained during the course of both the photochemical and the thermal methylenecyclopropane rearrangements. Furthermore, if it is accepted that the latter process occurs with inversion of configuration, our preliminary results suggest that the overall stereochemistry of the photochemical reaction also involves net inversion of configuration at the pivot atom, C-2. This second conclusion is open to some question since the *E*-**2**.*Z*-**2** is significantly different in the thermal and photochemical experiments. However, the ratio of the rates of isomerization of *cis*- and *trans*-**1** is essentially independent of the mode of molecular excitation, an observation that lends support to our interpretation of the results. In addition, the report that the *E* and *Z* isomers of a chiral 2-methylethylidenecyclopropane, a pair of molecules closely analogous to *E*- and *Z*-**2**, both produce rotations in the same direction[1b] is an additional basis for our belief that the direction of rotation for the two different mixtures of *E*- and *Z*-2-phenylethylidenecyclopropane (**2**) formed in our experiments is consonant with identical net stereochemistry for both the thermal and the photochemical rearrangements.[15]

Whether the photochemical results represent the stereochemical consequence of the transformation of a electronically excited molecule of **1** to an electronically excited molecule of **2** (or vice versa) followed by relaxation to ground state or whether photoexcited **1** (or **2**) relaxes to a ground vibrational state sufficiently "hot" to permit passage through the "thermal" transition state cannot be determined from our present observations. Our results, however, do definitively exclude the development of the planar geometry calculated to be favored for triplet trimethylenemethane.[16] Moreover these results add another dimension to Kende's conclusion[2] that the photochemical methylenecyclopropane rearrangement is a phenomenon of a singlet rather than a triplet manifold.

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(4) *trans*-2,3-Dicarboethoxymethylenecyclopropane (Feist's ester) was an attractive early candidate for our study both because the stereochemical outcome of its thermal isomerization was well understood[1c,1f] and because it was reported to automerize photochemically.[5] Regrettably, in our hands this substrate suffered photoinitiated polymerization so extensive as to make isolation of the necessary quantities of rearranged products an excessively tedious task.

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(6) The structures of all new compounds prepared in the sequence have been proven by suitable spectroscopic techniques. Details will be reported in the full paper.

(7) The analysis of the stereochemistry of these two groups was facilitated by the availability of the corresponding trans isomers obtained by use of *trans*-β-methylstyrene in the first step of the synthetic scheme.

(8) That the isolation of the mixture of geometric isomers is not the result of the prior base-catalyzed isomerization of the precursor bromide is shown by the observation that the bromide having the phenyl and methyl groups trans to one another fails to eliminate to give **1**.

(9) Treatment of 2-phenylmethylenecyclopropane with potassium *tert*-butoxide in Me_2SO-d_6 under the reaction conditions used to produce **1** afforded 2-phenylmethylenecyclopropane that was at least 90% monodeuterated at the 2-position.

(10) Optical rotations were taken of hexane solutions using a Perkin-Elmer Model 141 polarimeter.

(11) A mixture of *E*- and *Z*-2-phenylethylidenecyclopropane (**2**) was available by reaction of methyllithium with 1-carboxy-1-bromo-2-phenylcyclopropane followed by reduction of the resulting ketone to the alcohol, tosylation, and treatment of the tosylate with methyllithium.

(12) Consideration of steric factors in the reaction and analogy to the literature report that rearrangement of either *cis*- or *trans*-2,3-dimethylmethylenecyclopropane affords mainly *E*-2-methylethylidenecyclopropane[1b] prompt the conclusion that *E*-**2** is the major component.

(13) A 450-W medium pressure Hanovia lamp equipped with a Vycor filter was used. The substrate was contained in hexane, and the solution was held below 27° to prevent thermal isomerization of **1**.

(14) This value, at least in part, is a consequence of the unequal rates of photochemical rearrangement of *cis*- and *trans*-**1**.

(15) We also believe that the similar magnitudes of the rotations obtained for the mixtures of **2** arising from thermal and photochemical excitation suggest that the stereoselectivities of the two processes are very similar if not identical. However, further work is required to substantiate this conclusion.

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(17) This work taken in part from the M.S. Thesis of W.A.G., University of Texas at Austin, 1974.

(18) Generous support of this research by the Robert A. Welch Foundation is gratefully acknowledged.

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Nonadditive Carbon-13 Substituent and Solvent Effects in Substituted Benzenes

Sir:

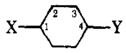
There is much current interest in carbon-13 chemical shift measurements, particularly since they seem *to mirror total carbon atom electron densities* in restricted series of compounds such as substituted benzenes.[1] However, no comprehensive study has yet been reported either on the additivity of effects in di- and polysubstituted benzenes or on the importance of general solvent effects. We report here important initial results of such studies.

Recent theoretical results, at the ab initio level, have indicated that substituent polarity leads to significant polarization of the π system (π-inductive effect) in monosubstituted benzenes.[1] Experimental carbon-13 shifts have been similarly interpreted.[1,2]

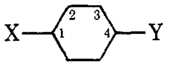
The π-inductive effect appears[3] to be manifest to a marked degree in the nonadditive behavior of ^{13}C substitu-

Table I. Para-Substituent ^{13}C Shifts in para-Disubstituted Benzenes[a]

	Fixed substituent, Y					
X	NO_2	F	OMe	NH_2	CN	H
NH_2	−9.13	−6.54	−6.83	−7.67	−12.54	−9.80
OMe	−6.76	−5.63	−5.68	−6.35	−8.47	−7.68
F	−4.03	−4.07	−3.84	−3.86	−3.81	−4.39
Cl	−1.83	−1.60	−1.36	−1.90	−1.59	−1.36
Me	−2.38	−1.82	−2.28	−2.52	−3.15	−3.05
CF_3	1.70	1.79	2.49	3.13	3.69	3.41
CN	1.75	2.14	3.34	4.22	4.31	4.35
NO_2	2.77	3.38	5.05	6.21	5.94	6.22
ρ_I	1.54	1.90	3.56	4.70	5.30	4.73
ρ_R[b]	11.34[c]	13.64	15.00	16.94	16.86[c]	20.98
$\lambda = \rho_R/\rho_I$	7.4	7.2	4.2	3.6	3.2	4.4
SD	0.4	0.4	0.4	0.4	0.7	0.6
$f \equiv$ SD/rms	10.2%	10.2%	10.5%	7.9%	10.3%	9.9%
$10^4 \Delta q_\sigma{}^{C\text{-}4}$	1634	1539	1117 (for OH)	572[d]	576	−628
$10^4 \Delta q_\pi{}^{C\text{-}4}$	−903	−65	255 (for OH)	768[d]	−558	0

[a]  Shift at C-4 for Substituent X Relative to X = H. Y is the indicated fixed substituent for each series. Shifts in dilute chloroform solutions (3%). [b] Best fit is to the $\sigma_R{}^0$ scale unless indicated. [c] Best fit given here is to the σ_RBA scale. [d] For planar aniline.

ent shifts in disubstituted benzenes. Consider a series of para-disubstituted compounds as in I, with Y a fixed sub-



I

stituent and X a series of generalized para-substituents. To what extent does the fixed substituent, Y, influence the para-substituent shifts of X? If the influence of Y is nearly a constant factor as one may tend to assume, then the para-substituent shifts of X relative to H will be little affected and we may say that additivity of shift prevails. However, we have found instead that Y exerts a major influence on the para-substituent shifts. This is clearly established by the data for the ^{13}C substituent shifts at C-4 given in Table I for a number of series having fixed Y substituents and minimum basis sets[4] of substituents X.

DSP analysis[4] of the shift data is also recorded in Table I, i.e., values of ρ_I, ρ_R, and fitting statistics are given for each series with a fixed Y substituent. The influence of Y enters mainly in the ρ_I values, which vary by 250% between Y = NO_2 and Y = CN. We note further that the influence of Y on the ρ_I value parallels the calculated[5] STO-3G ab initio σ-electron density at C-4 for the monosubstituted (Y) benzene, i.e., for X = H. Values of $10^4\ \Delta q_\sigma{}^{C\text{-}4}$ (and for comparison, the π-electron density, $10^4\ \Delta q_\pi{}^{C\text{-}4}$) are given in the lowest horizontal columns of Table I. It is our interpretation that the σ charge density at C-4 regulates the ease of π-polarization at this atomic position by the distant para-substituent, X. That is, increasing positive σ charge at C-4 (Y = CN < NH_2 < OMe < F < NO_2) increasingly reduces the π-inductive effects of the general substituent, X. This is seen in the decreasing ρ_I values in this order. Values of ρ_R also tend to decrease in this same order, but much less markedly (note that $\lambda \equiv \rho_R/\rho_I$ increases in this sequence from 3.2 to 7.4).

Professor W. F. Reynolds has kindly communicated to us the results of unpublished data for a series of p-C_6H_4Se-CH=CH_2 compounds. The C-4 shifts (0.4 M in CCl_4) for this series are well fitted by the DSP treatment with ρ_I = 9.45 and ρ_R = 30.59. C-4 shifts for a more limited number of para-substituted phenyltrimethylsilanes (50% in CCl_4) have been reported[6] and give ρ_I = 9.6; ρ_R = 28.1. Thus, as expected, enhanced ρ_I and ρ_R values are observed (even greater nonadditivity) for Y = σ-donor groups.

Nonadditive shift behavior is also found for the meta- and ortho-substituent (X) carbon-13 shifts. The influence of the fixed substituent Y, however, is less marked at these positions.[2] The ortho-substituent shifts are very poorly correlated with either the DSP treatment or with STO-3G calculated charge distributions. The meta-substituent shifts, on the other hand, are satisfactorily correlated.[1] The ρ_I values for the meta shifts are of the same sign but appreciably smaller in magnitude (~½) than the corresponding ρ_I values for the para shifts. The former tend to increase with increasing $\sigma_R{}^\circ$ value of the fixed substituent Y. The ρ_R values for the meta shifts are of opposite sign and very much smaller in magnitude (~1/10) than the corresponding ρ_R values for the para shifts. These matters, including substituent shifts for meta-disubstituted benzenes, will be given detailed consideration in a subsequent full publication.

Studies of solvent effects on carbon-13 shifts are rather sparse and mainly limited to specific effects, such as hydrogen bonding between solute (e.g., aniline) and hydroxylic solvents.[7] We have analyzed reported carbon-13 shifts for representative series of monosubstituted benzenes in aprotic solvents of varying polarity (and in methanol) and have made careful measurements of dilute solutions of chloroform. Excluding H-bonding interactions, we find that the shifts vary markedly and selectively. For example, the carbon-13 chemical shift (relative to benzene, in parts per million) for the para-carbon atom in nitrobenzene varies for dilute solutions as follows: cyclohexane, −5.7 ppm;[7] carbon tetrachloride, −5.8;[7] chloroform, −6.2; acetone, −6.3;[8] methanol, −6.4;[7] dimethylformamide, −6.8.[9] Similar changes apparently occur for all benzenes having a highly electronegative substituent, but not, for example, for toluene or anisole. A dual substituent parameter analysis indicates that the effect is mainly dependent on the inductive and not resonance nature of the substituent. For example, the analyses for series in carbon tetrachloride and acetone follow the equations:

$$\text{carbon tetrachloride}\quad 4.0\ \sigma_I + 19.8\ \sigma_R{}^\circ \quad \text{SD/rms} = 9.9\%$$

$$\text{acetone}\quad 5.1\ \sigma_I + 19.7\ \sigma_R{}^\circ \quad \text{SD/rms} = 9.3\%.$$

This is in accord with a prediction made earlier by Dayal and Taft[10] based on limited results and analogous to, but of greater magnitude than, the solvent effects observed on fluorine-19 shifts of para-substituted fluorobenzenes. We believe that these ^{13}C solvent effects are explicable in terms of increased polarization of the π-system resulting from enhanced substituent polarity as the solvent changes from cyclohexane to dimethylformamide.

Acknowledgment. We are pleased to acknowledge the helpful comments and communication of unpublished results of Professor W. F. Reynolds.

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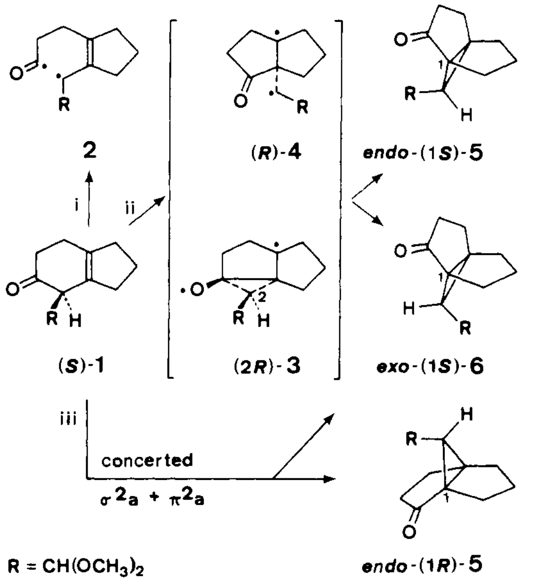
Photochemistry of a Cyclohex-3-enone. Evidence for a Stepwise Pathway in an Oxadi-π-methane Rearrangement

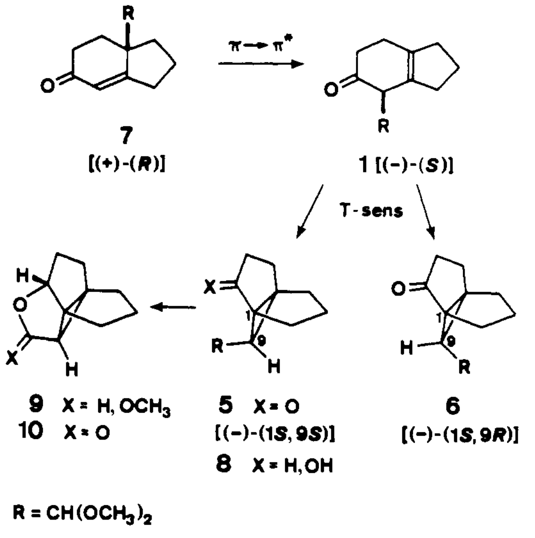
Sir:

Triplet excited β,γ-unsaturated ketones undergo an oxadi-π-methane (ODPM) rearrangement involving a formal 1,2 ($\alpha \rightarrow \beta$) acyl shift and three-ring formation through $\alpha \rightarrow \gamma$ bonding.[1] One of the early examples was reported for $\Delta^{1,9}$-2-octalone.[2] We describe now a study with the related cyclohexenone (−)-**1** designed to differentiate between the three currently debated principal mechanisms for the ODPM rearrangement which can be applied to the formation of products *endo*-**5** and *exo*-**6**. These mechanisms are summarized in Scheme I:[3] (i) α-Cleavage to the achiral diradical **2** which recombines to *racemic* endo and exo products; (ii) an alternative stepwise mechanism proceeding via intermediates of type **3** and/or **4** furnishing endo and exo products of *identical* C-1 configuration; (iii) a photochemically allowed concerted ${}_{\sigma}2_a + {}_{\pi}2_a$ cycloaddition leading to endo and exo products with *opposite* C-1 configuration.[4] The products **5** and **6** formed by the concerted mechanism iii would retain the enantiomeric purity of the starting ketone. In a reaction course of type ii a partial loss of the initial enantiomeric purity may, but need not, result for **5** and **6** depending on the extent to which certain of the steps involved are subject to stereoselective control.[5]

Scheme I



Scheme II



Irradiation of ketone *rac*-**7** with 254-nm light in methanol led to a specifically $\pi \rightarrow \pi^*$ induced 1,3-allylic shift of the dimethoxymethyl substituent[6] and formation of **1**.[7,8] Triplet sensitization of **1**, using acetone solution and 254 nm, furnished a ca. 2:1 ratio of the cyclopropyl ketones **5** and **6** (20% yield at full conversion and after chromatographic separation). Separate photolyses of **5** and **6** under the conditions of their formation resulted in the decomposition of both compounds to as yet unknown products while the two isomers did not interconvert and their ratio remained constant. The endo configuration of the dimethoxymethyl group in **5** was established by reduction with $NaBH_4$ and oxalic acid-catalyzed cyclization of the resulting hydroxyacetal **8** in methanol to **9**. Jones oxidation of **9** gave lactone **10**, ir 1775 cm^{-1} (in CCl_4). The overall yield for **5** → **10** was 44%. Application of the same reaction sequence to **6** failed to give an analogous cyclization.

Compound (−)-**1**, CD $\Delta\epsilon_{max}{}^{297}$ +3.3,[9] of 54% enantiomeric purity[10] was obtained as follows: Fractional crystallization of the hydrazide prepared from (−)-*N*-aminomenthyl carbamate[11] and the carboethoxy precursor of **7** gave partially resolved (+)-**7**, $\Delta\epsilon_{max}{}^{340}$ +3.3.[9] Photorearrangement of this compound into (−)-**1** occurred without loss of enantiomeric purity.[12]

The two ODPM rearrangement products, which were isolated after a ca. 90% conversion of (−)-**1** in the acetone-sensitized photolysis, were optically active and the enantiomeric purities were 42% for recovered **1** and 48% each for **5** and **6**. The CD exhibited identical negative Cotton effects, $\Delta\epsilon_{max}{}^{296}$ −1.3,[9] for both the endo and exo isomer, (−)-(1*S*,9*S*)-**5** and (−)-(1*S*,9*R*)-**6**, respectively.[12]

The partial racemization in the order (−)-**1** > (−)-**5** = (−)-**6** during the photolysis must be due mostly to a process competing with the ODPM rearrangement, probably to reversible α-cleavage (**1** $\rightleftarrows$ **2**). Similar acetone-sensitized epimerizations have been observed previously.[18,19] The essen-