in the room temperature bath exhibited the same behavior. Control experiments with excess RLi or amine showed that these did not materially affect the rates. Aliquots were removed periodically, quenched with 5% HCl, diluted with hexanes for handling, dried over K_2CO_3, and analyzed by capillary GC. Known samples of **6**, **7**, and **9** vs undecane showed that no peak area correction factors were needed to convert the GC areas to molar ratios. Most analyses involved 6–10 points, covering 1–3 half-lives.

Acknowledgment. Support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Reactions of 4,4-Diphenylcarbena-2,5-cyclohexadiene and Related Systems in Dimethyl Sulfoxide

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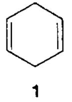
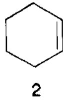
Thermal decomposition of the lithium salt of the tosylhydrazone of 4,4-diphenyl-2,5-cyclohexadienone (**10**) in dimethyl sulfoxide produces 4,4-diphenyl-2,5-cyclohexadienone, *p*-benzylbiphenyl, 3,4-diphenyltoluene, 6,6-diphenyl-1-methylene-2,4-cyclohexadiene, and *o*-terphenyl, while similar treatment of the lithium salt of the tosylhydrazone of 4,4-diphenylcyclohexenone (**26**) generates 4,4-diphenylcyclohexenone, 5,5-diphenyl-1,3-cyclohexadiene, 4,4-diphenyl-1-methylene-2-cyclohexene, and 6,6-diphenyl-1-methylene-2-cyclohexene. Thermolysis of the lithium salt of the tosylhydrazone of 4,4-diphenylcyclohexanone (**32**) in dimethyl sulfoxide yields 4,4-diphenylcyclohexene, 4,4-diphenylcyclohexanone, and 4,4-diphenyl-1-methylcyclohexanol. The kinetics of the thermal decomposition of tosylhydrazone lithium salts **10**, **26**, and **32** in dimethyl sulfoxide in the temperature range 90–125 °C were analyzed by evaluating the rate constants for the two consecutive first-order steps. The second step, for parent salts **10**, **26**, and **32**, decomposition of diazo compound to carbene, exhibited values for k_2 (110 °C) of 8.22, 197, and 363 h^{-1}, $\Delta G^{\ddagger}$s of 27.2 ± 3.1, 24.8 ± 3.1, and 24.2 ± 0.9 kcal mol^{-1}, and $\Delta S^{\ddagger}$s of −10.7 ± 5.7, −6.3 ± 5.8, and −8.1 ± 1.7 eu. The activation parameters for decomposition of the diazo compounds are interpreted in terms of an increasing dipole moment in the transition state relative to ground state. Product formation from carbene intermediate is viewed in terms of a competition of a singlet oxygen abstraction reaction with intersystem crossing to triplet.

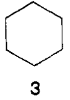
Although there have been a number of interesting studies on the nature of vinylcarbenes,[1] there remain questions concerning the effects of conjugation on the stability and reactivity of vinylcarbene intermediates. An interesting series to illustrate the nature of conjugated carbenes, we thought, might well be the series carbena-2,5-cyclohexadiene (**1**), carbena-2-cyclohexene (**2**), and carbenacyclohexane (**3**), the cyclic framework serving the useful purpose of preventing the intramolecular insertion into the double bond to produce a cyclopropene moiety due to strain considerations. A priori, one might expect on the basis of simple qualitative MO theory that the electrophilicity of the carbene center in the singlet would increase as the delocalization of the π system is decreased from a four electron five orbital system to a two electron three orbital system to a completely localized system (**1** to **3**).



1



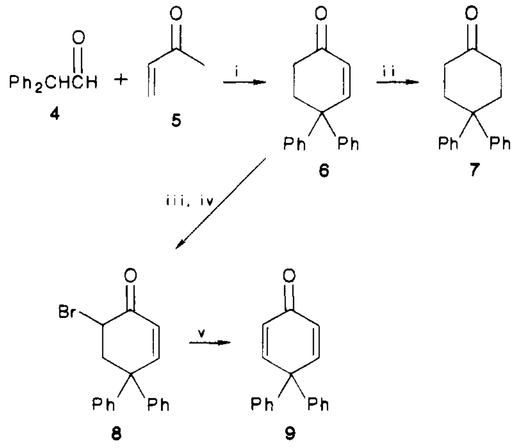
2



3

If one considers the present state of knowledge of the nature of carbocation intermediates in organic chemistry, it is clear that measurement of rates of solvolytic reactions and characterization of reaction pathways through identification of products have been preeminent as investigative modes of analysis.[2] Use of both modes of analysis in carbene studies has been rare due to the lack of a generally useful method for analysis of the rate of carbene formation that would play the same role as tosylate solvolysis has in carbocation chemistry. It appeared to us that the decomposition of the lithium salts of tosylhydrazones

Scheme I[a]



[a] i = 3 M KOH/ether; ii = H_2, Pd/C; iii = $CH_3CO_2C(CH_3)$=CH_2, *p*-TsOH; iv = Br_2/CCl_4; v = Li_2CO_3, LiBr, DMF.

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(1) (a) Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 6695. (b) Inagaki, S.; Iwase, K.; Goto, N. *J. Org. Chem.* **1986**, *51*, 362. (c) Honjou, N.; Pacansky, J.; Yoshimine, M. *J. Am. Chem. Soc.* **1984**, *106*, 5361. (d) Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* **1978**, *100*, 1333. (e) Davis, J. H.; Goddard, W. A. III; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 2427. (f) Hoffmann, R.; Zeiss, G. D.; VanDine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485. (g) Steinmetz, M. G.; Mayes, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 2111. (h) Kostikov, R.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1528.

(2) Olah, G.; Schleyer, P. R. *Carbonium Ions*; Wiley: New York, 1968–76; 5 volumes.

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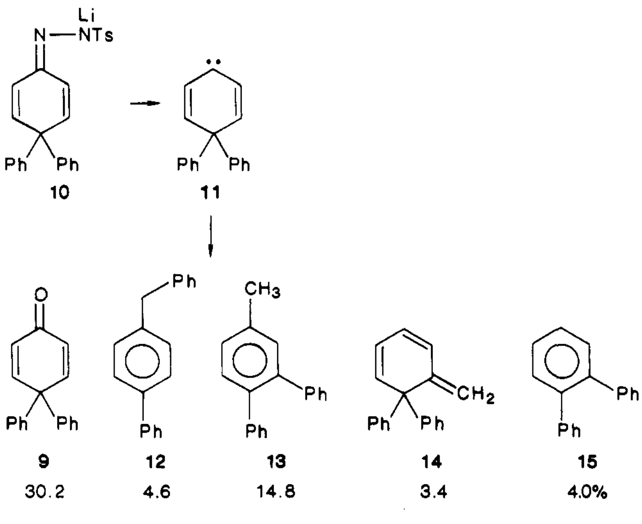
Scheme II

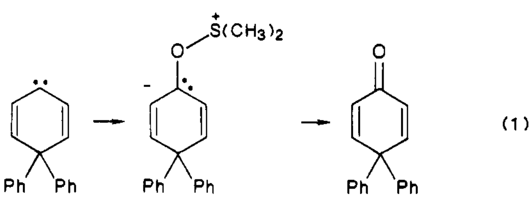


could be handled in a manner that would provide the necessary rates of diazo compound to carbene decomposition as well as a convenient method for product generation and analysis.

As an experimentally convenient model system for the carbena-2,5-cyclohexadienyl series, the 4,4-diphenyl derivatives were prepared by using synthetic methods developed by Zimmerman and co-workers[3] for the preparation of parent ketones **6** and **9** to prepare **6**, **7**, and **9** (Scheme I).

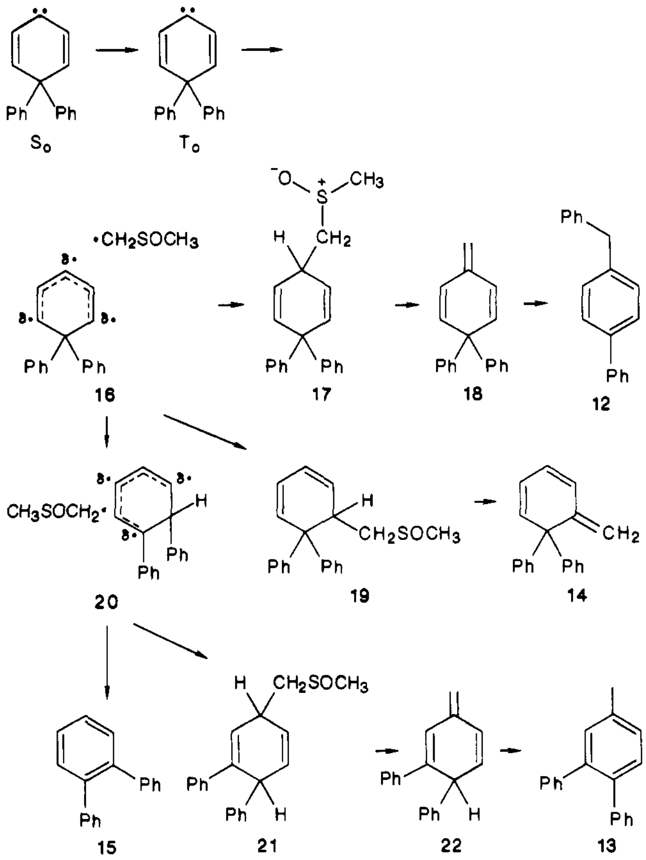
Treatment of 4,4-diphenyl-2,5-cyclohexadienone (**9**) with 1 equiv of tosylhydrazine in warm ethanol converted it to the desired tosylhydrazone, which was treated with methyllithium in THF to produce the desired starting material, tosylhydrazone lithium salt (**10**). Tosylhydrazone **10** decomposed smoothly in dry dimethyl sulfoxide at 110 °C to generate the products illustrated in Scheme II. Parent 4,4-diphenyl-2,5-cyclohexadienone (**9**), *p*-benzylbiphenyl (**12**), 3,4-diphenyltoluene (**13**), and *o*-terphenyl (**15**) were identified by spectral comparison with authentic standards, while **14** was assigned the 6,6-diphenyl-1-methylene-2,4-cyclohexadiene structure on the basis of the absorption for exo-methylene, δ 4.72 (1 H, shielded by one of the phenyls of the adjacent geminal diphenyl grouping) and 5.40 (1 H), four cyclohexene hydrogens at 5.8–6.3, and geminal diphenyl grouping (sharp singlet at 7.22 Hz, 10 H).

The formation of 4,4-diphenyl-2,5-cyclohexadienone seems most reasonably ascribed to reaction of singlet carbene with the electron-rich oxygen center of dimethyl sulfoxide to form a zwitterion, which then eliminates dimethyl sulfide (eq 1). The remaining hydrocarbon products, **12–15**, are most likely formed subsequent to intersystem crossing to triplet carbene, which, in turn, abstracts hydrogen from the solvent to form radical pair **16**. Radical pair **16** may couple either at the center carbon or end carbon of the symmetrical delocalized cyclohexadienyl species. Coupling at the central carbon generates sulfoxide **17**, which might be expected to eliminate under the reaction conditions[4] to form 4,4-diphenyl-1-methylene-2,5-cyclohexadiene (**18**). A 1,5-phenyl shift produces product *p*-benzylbiphenyl (**12**). Alternatively, radical coupling at the end of the cyclohexadienyl system produces sulfoxide **19**, which undergoes pyrolytic elimination to generate triene **14**. An alternative to radical coupling of radical pair **16** is 1,2-phenyl migration generating radical pair **20**. Hydrogen transfer within this radical pair leads to *o*-terphenyl (**15**), while coupling generates sulfoxide **21**, which undergoes elimination to triene **22**, which in turn undergoes a 1,5-hydrogen shift to produce 3,4-diphenyltoluene (Scheme III).



(1)

Scheme III



The work of Hart and DeVrieze suggests that the 1,5-phenyl shift of **18** to form *p*-benzylbiphenyl (**12**) might proceed by homolytic fission and an intermolecular process analogous to that which they have proposed for the rearrangement of hexamethyl triene **23** (eq 2 and 3). This fission was observed at 165 °C in decalin or 150 °C in cumene.[5] Similar fissions have been observed in the case of the closely related diphenylcyclohexadienyl radical **24**, generated by hydrogen abstraction from parent hydrocarbon (or by the pyrolysis of the dimer of **24**),[6] in our previous study of 4,4-diphenylcyclohexadienylidene (**11**)[7] (eq 4), generated in a dry salt pyrolysis reaction, and possibly in the reversible attack of *o*-(α-naphthyl)phenyl upon benzene.[8] An interesting question for consideration

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[3] Zimmerman, H. E.; Hackett, P.; Juers, D. F.; McCall, J. M.; Schröder, B. *J. Am. Chem. Soc.* **1971**, *93*, 3653.

[4] (a) Kice, J. L.; Campbell, J. D. *J. Org. Chem.* **1967**, *32*, 1631. (b) Emerson, D. W.; Craig, A. P.; Potts, I. W., Jr. *J. Org. Chem.* **1967**, *32*, 102.

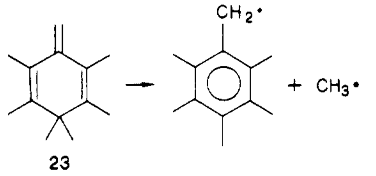
[5] Hart, H.; DeVrieze, J. D. *Tetrahedron Lett.* **1968**, 4257.

[6] (a) Perkins, M. J.; Ward, P. *Tetrahedron Lett.* **1971**, 2379. (b) Atkinson, D. J.; Perkins, M. J.; Ward, P. *J. Chem. Soc. C* **1971**, 3240.

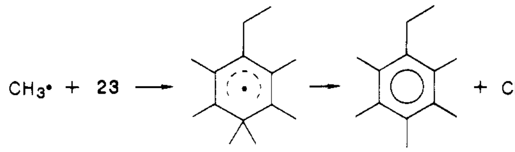
[7] Freeman, P. K.; Swenson, K. E. *Tetrahedron* **1982**, *24*, 3737.

[8] Henderson, W. A., Jr.; Lopresti, R.; Zweig, A. *J. Am. Chem. Soc.* **1969**, *91*, 6049.

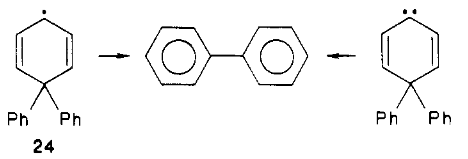
is why triene **14** survives and triene **18** rearranges under the reaction conditions. An examination of framework molecular models provides a convincing illustration of the lack of planarity of the two benzene rings in the *o*-phenylbenzyl radical (**25**), whereas there is no inhibition of coplanarity in the case of the *p*-phenylbenzyl radical, so that resonance stabilization of the incipient phenylbenzyl radical in the homolytic fission of triene **14** is not as completely developed as with triene **18**. Finally, it is interesting to note that no *p*-terphenyl is generated either from singlet or triplet 4,4-diphenylcarbena-2,5-cyclohexadiene in contrast to the outcome for dry salt pyrolysis of **10**, which does generate biphenyl and *p*-terphenyl.[7]



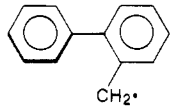
(2)



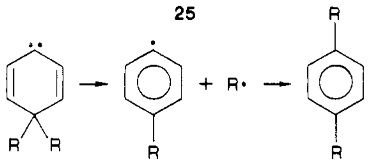
(3)



(4)



25

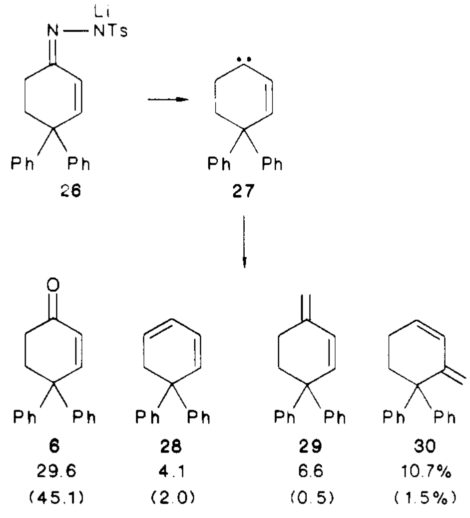


(5)

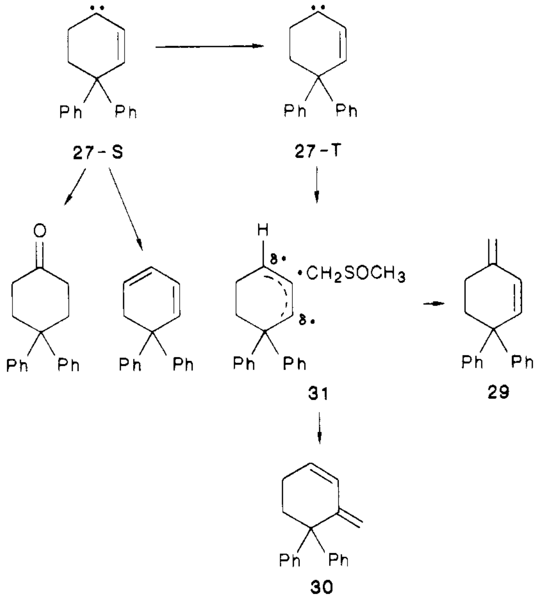
Thus, a 1,4-phenyl shift analogous to the 1,4-alkyl shifts observed by Jones and co-workers[9] (illustrated in eq 5) is not operative. This difference seems most reasonably ascribed to the rapid reactions of 4,4-diphenylcyclohexadienylidene singlet and triplet with solvent and to the milder reaction conditions. The dry salt pyrolysis was carried out over a temperature range of 118–185 °C.[8]

The second carbene precursor, **26**, was prepared from ketone **6** in an analogous manner to that employed for the preparation of lithium tosylhydrazone salt **10**. The generation of bivalent carbene intermediate **27** was carried out by heating the lithium salt of the tosylhydrazone (**26**) in dry dimethyl sulfoxide at 110–125 °C. The product array includes parent ketone (**6**), 5,5-diphenyl-1,3-cyclohexadiene (**28**) (^{1}H NMR absorption for an allylic methylene doublet at δ 2.85 with four cyclohexene protons at 5.80–6.30 and the gem diphenyl at 7.15), and the closely related dienes **29** and **30** in the percent yields listed in Scheme IV without parentheses. 4,4-Diphenyl-1-methylene-2-cyclohexene (**29**) exhibits a normal absorption for the exo-methylene at δ 4.70–4.75 (multiplet), an isolated cyclohexene etheno unit at 6.01, 6.32 (a pair of doublets, J = 10 Hz), allylic methylene at 2.25 and homoallylic at 2.05, and the gem diphenyl at 7.10 in the ^{1}H NMR spectrum, while conjugation is revealed in the ultraviolet (λ_{max} = 232 nm, ϵ = 22 000; phenylcyclohexane provides ϵ = 260 at λ = 232 nm). 6,6-Diphenyl-1-methylene-2-cyclohexene (**30**) exhibits a shielded exo-methylene hydrogen at δ 4.35, a normal exo-methylene at 5.15, two cyclohexene protons at 5.55–5.80 (m) and 6.30 (d, J = 8 Hz), allylic methylene at 2.50, homoallylic methylene at 1.90, and geminal diphenyls at 7.15 in the ^{1}H NMR spectrum, while conjugation is again revealed in the ultraviolet spectrum (λ_{max} = 232 nm, ϵ = 20 490).

Scheme IV



Scheme V



In the case of 4,4-diphenyl-2-carbenacyclohexene (**27**), the mechanistic picture is similar to that of carbenacyclohexadiene **11** with the initially formed singlet (**27-S**) abstracting an oxygen from dimethyl sulfoxide and undergoing a 1,2-hydride shift (a known singlet process[10]) in competition with intersystem crossing to triplet (**27-T**).

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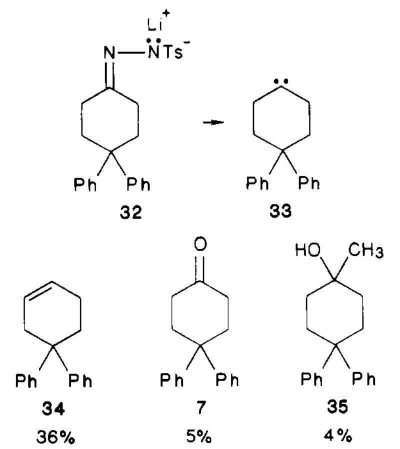
[9] (a) Berdick, T. E.; Levin, R. H.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 5087. (b) Wolf, A. D.; Kane, V. V.; Levin, R. H.; Jones, M., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 1680. (c) Kane, V. V.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2643. (d) Jones, M., Jr. *Acc. Chem. Res.* **1974**, *7*, 415.

[10] (a) Freeman, P. K.; Hardy, T. A.; Balyeat, J. R.; Wescott, L. D., Jr. *J. Org. Chem.* **1977**, *42*, 3356. (b) Sohn, M. B.; Jones, M., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 8280. (c) Moritani, I.; Yamanoto, Y.; Murahashi, S.-I. *Tetrahedron Lett.* **1968**, 5697. (d) Jones, M., Jr.; Ando, W. *J. Am. Chem. Soc.* **1968**, *90*, 2200.

Scheme VI

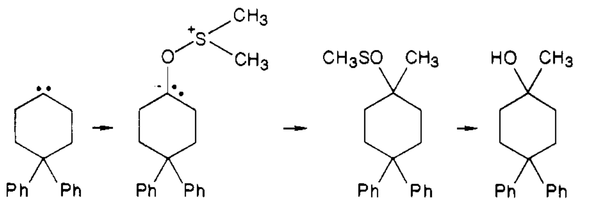


The triplet carbene species then abstracts hydrogen from the solvent to generate radical pair **31**, which, in turn, couples and eliminates in processes analogous to those described above for carbenacyclohexadiene **11** (Scheme V).

The photolysis of the lithium salt of the tosylhydrazone of 4,4-diphenyl-2-cyclohexenone (**26**) provides an interesting contrast to the thermolysis of **26**. Photolysis of lithium salt **26** in dimethyl sulfoxide using a medium-pressure 450-W mercury lamp and a Pyrex filter produced the same four products, but in rather different ratios (the percent yields are provided in parentheses in Scheme IV). The products ascribed to singlet-state processes above are enhanced (**6** and **28**), while the triplet state products (dienes **29** and **30**) are just detectable. These sharp differences may be due the participation of an excited state singlet or excited state diazo compound as product-determining intermediate. This situation is strikingly similar to that observed by M. Jones and co-workers in their study of the reactions of the 4,4-dimethylcyclohexadienylidene intermediate.[11]

The synthesis of the third carbene precursor, the lithium salt of the tosylhydrazone of ketone **7** (**32**), was readily achieved. Thermolysis of **32** in dimethyl sulfoxide at 110–125 °C generated 4,4-diphenylcyclohexene (**34**, 36%), parent ketone (**7**, 5%), and 1-methyl-4,4-diphenylcyclohexanol (**35**, 4%) (Scheme VI).

4,4-Diphenylcyclohexene is the result of 1,2-hydride shift in the singlet carbene precursor, and formation of parent ketone **7** is analogous to the singlet oxygen abstractions from solvent observed for carbenes **11** and **27**. The pathway leading to tertiary alcohol **35** is less certain, but a mechanism involving homolysis and formation of a radical pair and a methyl shift to a tertiary sulfenate, analogous to the Stevens rearrangement,[12] is conceivable (eq 6).



(6)

One can consider the product distributions for each intermediate in terms of the competition between electrophilic attack upon the solvent [k_s(DMSO)] and intersystem crossing (k_{isc}) (Scheme VII). On the basis of our initial qualitative Hückel MO analysis, it was anticipated that the electrophilicity of the singlet bivalent intermediate would increase in the order **11** < **27** < **33**, the four electron, five orbital π-system **11** exhibiting reaction characteristics reflecting greater electron density at the carbene carbon compared with **27**, a two electron three orbital system, which should exhibit greater electron density at the carbene carbon than the localized intermediate **33**, which is in agreement with the rate ratios observed.

Scheme VII

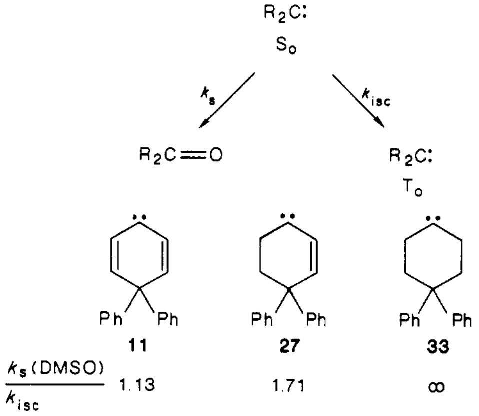
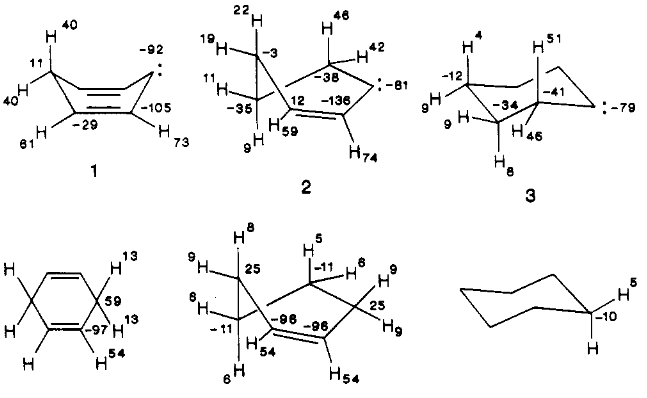


Chart I. MNDO Charge Densities on Model Carbenes (in thousandths)



However, MNDO MO calculations[13] on the related model systems carbenacyclohexadiene (**1**), carbenacyclohexene (**2**), and carbenacyclohexane (**3**) do not reflect our initial intuitive view as closely as might have been anticipated (Chart I). The electron densities at the carbena carbons of carbenacyclohexane and carbenacyclohexene are essentially the same with the charge density a little greater for carbenacyclohexadiene.

The replacement of a CH_2 unit in cyclohexane by a carbena carbon apparently results in hyperconjugative electron donation to the carbena carbon, which is not entirely countered by back-electron donation of the filled sp^2 orbital on the carbena carbon. In 2-carbenacyclohexene one can compare the charge density pattern with the parent hydrocarbon cyclohexene. Since the methylene group at C-4 in 2-carbenacyclohexene very nearly has the same charge density as the corresponding methylene in cyclohexene, it is noteworthy that the substitution of a carbena carbon for a methylene at C-3 in cyclohexene results in the ethano moiety donating 34 thousandths, while the vinylene group donates 93 thousandths of an electronic charge to the carbene center. That the vinylene

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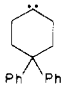
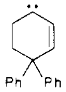
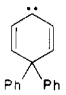
[11] (a) Chambers, G. R.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4516. (b) Chang, K.-T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082. (c) Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072.

[12] Olsen, R. K.; Currie, J. O. In *The Chemistry of the Thiol Group*; Patai, S., Ed.; Wiley: New York, 1974; Part 2, pp 561–566.

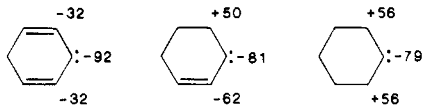
[13] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

Table I. Summary of the Kinetic Results

	k_2, h^{-1}				E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/mol	$\Delta G^{\ddagger}$ kcal/mol
	110 °C	115 °C	120 °C	125 °C				
	8.22	11.2	18.7	27.4	23.9 ±2.2	23.1 ±2.2	-10.7 ±5.7	27.2 ±3.1
	197	266	443	633	23.2 ±2.2	22.4 ±2.2	-6.3 ±5.8	24.8 ±3.1
	363	566^a	933^a	1210	22.0 ±0.6	21.2 ±0.6	-8.1 ±1.7	24.2 ±0.9

^{a} Values interpolated from an Arrhenius plot.

Chart II. MNDO Resultant Charges (in thousandths)

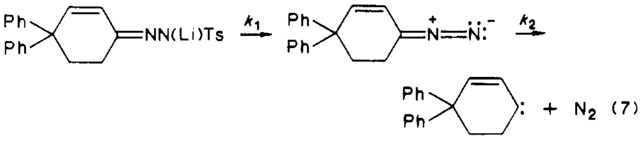


1 2 3

unit is more effective than an ethano unit in transmitting electron density to the carbene center is reinforced by comparing carbenacyclohexane and carbenacyclohexadiene with their parent hydrocarbons (Chart I). Since in each case the C-4 methylene retains very nearly the same charge in the transition from parent to carbene, the charge density patterns reveal that the ethano units in carbenacyclohexane donate 39 thousandths and the vinylene units in carbenacyclohexadiene donate 86 thousandths of an electronic charge to the carbene center.

If one considers in addition to the charge densities on the carbene carbons, the resultant charges on the α CH_2 (or CH) units, we have the patterns portrayed in Chart II. It is clear that the charge dipole interactions in the singlet oxygen abstraction reaction dictated by this pattern would provide a reactivity sequence **3** > **2** > **1** and thus **33** > **27** > **11**. If the interaction of the carbene LUMO and dimethyl sulfoxide HOMO is an important contributing factor, this trend would be reinforced as the p_z coefficients of the carbene carbons of the LUMO's of **3**, **2**, and **1** are 0.92, 0.66, and 0.60, respectively.

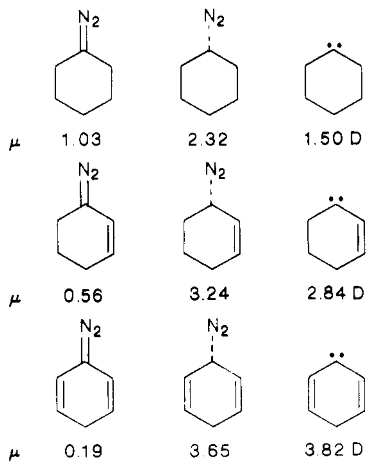
With the product analyses complete, we focused our attention on an analysis of the rates of carbene generation. A reconsideration of the carbene generation method employing the pyrolysis of the lithium salt (e.g. **26**) reveals that the process involves two consecutive first-order steps (eq 7). Our interest is in the carbene-forming step, step 2, the rate constant for which can be determined by measuring the volume of nitrogen evolved with time and fitting the data to the integrated rate expression (eq 8) by using a nonlinear least-squares curve fitting program (PCNONLIN). The kinetic results are summarized in Table I.

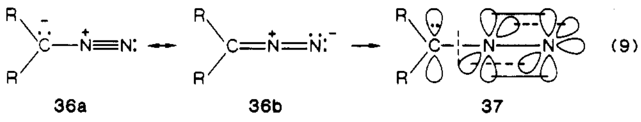


$$[N_2] = \frac{(TH)_0}{k_2 - k_1}\left[k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})\right] \quad (8)$$

The rate constants at each temperature suggest that increased conjugation stabilizes the carbene singlet more than the ground state diazo compound; however, the differences are not dramatic. The activation parameters (E_a, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$) are the same within experimental error. The entropies of activation are also the same and, interestingly, are negative. At first consideration, the negative entropies of activation for the fragmentation of a neutral diazo compound to two neutral fragments, the carbene and nitrogen, are a surprise. However, if one considers that the magnitude of the overlap integral for 2p π interaction falls off much more rapidly than sp^2 σ overlap,[14] carbene generation may involve the transformation of a ground state, in which the two resonance forms (**36a** and **36b**) contribute nearly equally, to a transition state (**37**) in which there is a considerable amount of disconnection of the p π system with substantial sp^2 σ bonding (contribution of form **36a** predominant eq 9). This would provide an increase in the dipole moment.

Chart III. MNDO Dipole Moments for Reactants, Transition States, and Products





36a **36b** **37**

MNDO calculations of the dipole moment for the starting diazo compound, transition state, and carbene are presented in Chart III, which support the hypothesis that there is a dipole moment increase and thus increased solvent orientation as the ground state is converted to transition state.

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[14] Roberts, J. D. *Notes on Molecular Orbital Calculations*; Benjamin: New York, 1961; pp 29-30.

Experimental Section

General Procedures. Melting points were determined using a Büchi melting point apparatus and are uncorrected. Boiling points are also uncorrected. Infrared spectra were recorded on either a Perkin-Elmer 727B or a Perkin-Elmer 621 grating spectrophotometer. Proton NMR spectra were run with a Varian Associates EM-360 (60 MHz) or FT-80 (80 MHz) spectrometer, while ^{13}C NMR spectra were measured with a FT-80 spectrometer at 20 MHz. Mass spectra were obtained on a Varian-Matt CH-7 mass spectrometer; GC–mass spectral runs were carried out on a Finnigan 4023 mass spectrometer equipped with a Finnigan 9610 gas chromatograph. High-resolution mass spectra were run by the University of Oregon Chemistry Department. Elemental analyses were obtained from Mic Anal Organic Microanalysis, Tucson, AZ. Vapor-phase chromatography analyses were performed with a Varian 3700 gas chromatograph employing a flame ionization detector for quantitative analyses or a thermal conductivity detector for preparative GC. The following columns were utilized: (A) 10 ft × 0.25 in. aluminum column containing 7% OV-101 on Chrom-W-AW, 100–120 mesh; (B) 12 ft × 0.25 in. copper column containing 10% Apiezon-L on Chrom-W-AW, 60–80 mesh.

Preparation of 4,4-Diphenyl-2-cyclohexenone Tosylhydrazone. To a 100-mL round-bottom flask, fitted with a reflux condenser and a magnetic stirrer, was added a solution containing 5.0 g (0.020 mol) of 4,4-diphenylcyclohex-2-en-1-one (**6**)[3] in 40.0 mL of absolute ethanol. The solution was heated to 50 °C. Tosylhydrazine (3.72 g, 0.020 mol) in 20.0 mL of absolute ethanol was also heated to 50 °C and then added to the enone **6**. The reaction mixture was stirred at 60 °C for 1 h and then for 2 h at room temperature, during which time white crystals precipitated out. The crystals were collected with a Büchner funnel and then were recrystallized from ethanol and water, yielding 6.5 g (0.0156 mol, 78%) of white crystals of the desired tosylhydrazone. Its NMR, IR, and mass spectra are consistent with data in the literature.[15] The product has a mp of 191–192 °C and the following spectral characteristics: NMR (80 MHz, CDCl$_3$) δ 2.20 (m, 4 H), 2.40 (s, 3 H, benzylic protons), 6.25–6.60 (d of d, J = 10 Hz, 2 H, vinylic protons), 7.05–7.30 (12 H, aromatic protons + two tosyl aromatic protons), 7.75 (d, 3 H, two tosyl aromatic protons superimposed over the NH proton signal); IR 3220 (NH stretch, strong), 3050 (medium), 2920 (medium), 1650 (C=N stretch, medium), 1580 (C=C stretch, strong), 1420 (medium), 1330 (SO$_2$ asym, medium), 1160 (SO$_2$, sym, medium), 1060 (weak), 925 (weak), 820 (strong), 710, 720 (strong), 695 (strong), 670 cm^{-1} (strong); chemical ionization mass spectra calcd MW 416.55; found 415 (negative ion) and 417 (positive ion); m/e (negative ion) 311, 155; m/e (positive ion) 402, 261, 248, 234, 233, 232, 157, 139, 91.

Preparation of 4,4-Diphenyl-2,5-cyclohexadienone Tosylhydrazone. To a 50-mL round-bottom flask fitted with a magnetic stirrer and a reflux condenser was added 2.5 g (0.0102 mol) of 4,4-diphenyl-2,5-cyclohexadienone[3] in 25.0 mL of ethanol. The mixture was heated to 50 °C to dissolve the dienone. Tosylhydrazine (1.90 g, 0.0102 mol) dissolved in 10.0 mL of ethanol and heated to 50 °C was added to the dienone solution, and the reaction mixture was stirred at 60 °C for 3 h, at which time the product started to precipitate. The reaction was then cooled in an ice bath and filtered through a Büchner funnel. The collected crystals were recrystallized from methanol, yielding 2.7 g (0.0065 mol, 64%) of the desired tosylhydrazone, mp 140–141 °C (lit.[8] mp 140–141 °C). The product has the following spectroscopic characteristics, which are consistent with the proposed structure: NMR (80 MHz, CDCl$_3$) δ 2.40 (s, 3 H, benzylic protons), 6.33 (d, J = 4 Hz, 2 H, vinylic protons), 6.80 (s, 2 H, vinylic protons), 7.20 (m, 12 H, aromatic protons), 7.90 (d, J = 8 Hz, tosyl aromatic protons, 2 H); IR (Nujol mull) 3250 (medium), 1650 (C=N stretch, weak), 1620 (C=C stretch), 1595 (strong), 1490 (strong), 1450 (strong), 1400 (weak), 1340 (weak), 1230 (strong), 1050 (weak), 920 (weak), 860 (strong), 820 (weak), 710 cm^{-1} (strong).

Preparation of 4,4-Diphenylcyclohexanone. 4,4-Diphenylcyclohex-2-en-1-one (3.00 g, 0.0121 mol) was added to a 250-mL centrifuge bottle fitted with an inlet for hydrogen gas and as outlet for releasing the pressure. To the above ketone were added 150 mL of 1:1 benzene/absolute ethanol and 0.750 g of 10% Pd/C (0.100 g of catalyst per 20 mL of solvent (96)). A stirring bar was added, and the reaction mixture was stirred for 24 h at room temperature under 20 psi. Then the reaction mixture was filtered through a Büchner funnel twice. The clear solution was evaporated with a rotary evaporator, leaving behind white crystals, which were recrystallized from 95% ethanol, yielding 2.95 g (0.0120 mol, 99%) of product, mp 135.5–136.5 °C; NMR δ 2.4–2.6 (symmetrical multiplet, 8 H, cyclohexyl protons), 7.10–7.30 (m, 10 H, aromatic protons); IR 3050 (strong), 2920 (strong), 1710 (C=O stretch, medium), 1270 (strong), 1210 (strong), 1120 (medium), 770, 710 cm^{-1}. Anal. Calcd for C$_{18}$H$_{18}$O: C, 86.64; H, 7.20. Found: C, 86.21; H, 7.53.

Preparation of 4,4-Diphenylcyclohexanone Tosylhydrazone. To a 50-mL round-bottom flask, fitted with a reflux condenser and a magnetic stirrer, was added 2.95 g (0.0120 mol) of 4,4-diphenylcyclohexanone in 20 mL of absolute ethanol. The mixture was heated to 60 °C in order to dissolve all of the ketone, and then 2.24 g (0.0120 mol) of tosylhydrazine dissolved in 20 mL of absolute ethanol was added. The solution was stirred for 2 h at 60 °C and 2 h at room temperature, at which time the product started to precipitate. The reaction mixture was then filtered through a Büchner funnel. The white crystals were recrystallized from DMSO and 95% ethanol, yielding 4.52 g (0.0108 mol, 90%) of the desired tosylhydrazone, mp 170–171 °C. The product has the following spectroscopic characteristics, which are consistent with the proposed structure: ^{1}H NMR (DMSO-d_6) δ 7.6–7.75 (d, 3 H, two tosyl aromatic protons superimposed over the NH proton signal), 7.1–7.4 (m, 12 H, aromatic protons), 2.3 (s, 3 H, benzylic), 2.3 (s, 8 H); IR (Nujol mull) 3230 (strong, sec N—H stretch), 2920, 1650 (medium, C=N stretch), 1600 (C=C stretch, strong), 1495 (strong), 1325 (medium O=S=O), 1160 (O=S=O, symmetric, strong), 1020 (medium), 930 (medium), 950 (medium), 820 (strong), 770 (strong), 710 (strong), 670 cm^{-1} (strong); chemical ionization mass spectra calcd MW 418.54, found 417 (negative ion) and 419 (positive ion); m/e (negative ion) 417, 311, 157, 156; (positive ion) 419, 291, 265, 235, 233, 185, 172, 157, 139, 79.

Conversion of the Tosylhydrazones into Their Lithium Salts. The same procedure was used for each tosylhydrazone in forming the lithium salt. Methyllithium was used as the base, and it was standardized with diphenylacetic acid according to the procedure of Fron and Caclawski.[16] Into a 50-mL round-bottom flask, fitted with a nitrogen inlet and outlet, were placed 0.5 g of diphenylacetic acid and 10.0 mL of dry THF. Then the methyllithium was added dropwise with a syringe until the solution turned a pale yellow color, indicating the initial formation of the dianionic species, i.e., the endpoint.

The conversion of the tosylhydrazone to its lithium salt was accomplished as follows. To a three-neck round-bottom flask, fitted with a reflux condenser, a rubber septum, and a dropping funnel containing dry THF, were added 3.0 g of the tosylhydrazone and 50 mL of THF. The mixture was stirred at room temperature until all of the tosylhydrazone dissolved, and then with a syringe, an equimolar amount of methyllithium was added dropwise. More THF was added from the dropping funnel as needed. After the addition of the methyllithium was completed, the mixture was stirred at room temperature for another 2 h; then the solvent was evaporated using a rotary evaporator, and the residue was placed under high vacuum, giving the lithium salt in 95–98% yield.

Pyrolysis of the Tosylhydrazone Lithium Salts. To a 25-mL round-bottom flask fitted with a screw cap and an outlet connected to a gas measuring burette was added 5.00 mL of dry DMSO with a syringe. The cap was closed immediately. The temperature of the silicone oil bath was increased and controlled by a thermostat; only after the oil had heated and equilibrated to the desired temperature was a constant amount (0.45 g, 0.0011 mol) of the tosylhydrazone salt added to the hot round-bottom flask. The screw cap was closed immediately. After a few seconds bubbles of nitrogen gas evolved, displacing the diethyl phthalate in the burette. The fixed amount of 0.0011 mol of the lithium salt was used for each of the three tosylhydrazone salts at all temperatures throughout the experimental work. In most cases,

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(15) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 8749.

(16) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

the temperatures used for the decomposition ranged from 110 to 125 °C. In some cases, however, lower temperatures had to be used for the very reactive tosylhydrazone salts, such as **10**, in order to slow down the evolving nitrogen so as to assure more accurate readings.

Each of the reaction mixtures obtained from the pyrolysis of the three tosylhydrazone lithium salts, **10**, **26** and **32**, was worked up by adding 50 mL of saturated sodium chloride solution to the DMSO solution and then extracting with 3 × 40 mL of ethyl ether. The ether layers were combined and extracted with 3 × 40 mL of saturated sodium chloride solution and then dried over magnesium sulfate. After a few hours, the mixture was filtered, and the ether was distilled off with a rotary evaporator, yielding a dark red oil, which was analyzed by gas chromatography.

Identification of the Pyrolysis Products of 4,4-Diphenyl-2,5-cyclohexadienone Tosylhydrazone Lithium Salt. The recovered oil was analyzed on a programmable GC (Varian 3700) with column B. The GC settings were as follows: detector temperature, 280 °C; injector temperature, 280 °C; column temperature programmed from 160 to 240 °C at 2 °C/min, He pressure, 36 psi. All yields were determined with dodecane as the internal standard. The first peak, which had a retention time of 40 min, was identified as *o*-terphenyl, **15** (4.0% yield). The mass spectrum obtained from the GC–mass spectral analysis matches the mass spectrum of an authentic sample. Also, the mass and ^{1}H NMR spectra of the corresponding fraction isolated by preparative GC match those of an authentic sample.

The second peak, which had a retention time of 46 min, was identified as 1-methylene-6,6-diphenyl-2,4-cyclohexadiene, **14** (3.4% yield). The following spectroscopic data were obtained for the corresponding fraction isolated by preparative GC: high-resolution MS, m/e calcd for $C_{19}H_{16}$ 244.125, found 244.125; ^{1}H NMR ($CDCl_3$) δ 4.72 (s, 1 H, shielded methylene proton), 5.4 (s, 1 H, methylene proton), 5.8–6.3 (m, 4 H, cyclohexadiene protons), 7.15–7.35 (10 H, aromatic); IR (neat) 3040 (strong), 3030 (strong), 1650 (strong), 1600 (medium), 1590 (medium), 1470 (medium), 1450 (medium), 920 (medium), 770 (strong), 740 (medium), 710 cm^{-1} (medium).

The third peak, which had a retention time of 47 min, was identified as 3,4-diphenyltoluene, **13** (83) (14.8% yield). The following spectroscopic data were obtained for the corresponding fraction isolated by preparative GC: MS, m/e 244; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3 H, methyl), 6.92–7.24 (13 H, aromatic); ^{13}C NMR ipso carbons δ 141.48, 141.65, 140.41, 137.78, 137.04, 131.32, 130.53, 129.85; two overlapping carbons 128.18 and 127.79; two overlapping carbons 126.34 and 126.21; 21.03; IR 3020 (strong), 3040 (weak), 2940 (strong), 1490 (strong), 1440 (strong), 1070 (strong), 1010 (strong), 910 (medium), 820 (medium), 780 (broad), 730, 700 cm^{-1}.

The fourth peak, which had a retention time of 59 min, was identified as the starting ketone, **9** (30.2% yield). The GC retention time and the mass and ^{1}H NMR spectra of the corresponding isolated fraction match those of the authentic sample.

The fifth peak, which had a retention time of 72 min, was identified as *p*-benzylbiphenyl, **12** (4.6% yield). The melting point of the corresponding fraction isolated by preparative GC was 84 °C (lit. mp 85 °C) and the NMR spectrum matched that in the literature.[17] The following spectroscopic data were obtained: MS, m/e 244; ^{1}H NMR δ 3.95 (s, 2 H, benzylic), 7.10–7.50 (aromatic, 14 H); ^{13}C NMR δ 140.89, 140.13, 138.91, 128.87, 128.63, 128.42, 127.79, 126.90, 126.56, 126.48, 126.28, 126.05, 41.48; IR (neat) 3020 (weak), 2920 (weak), 1595 (strong), 1585 (medium), 1495 (medium), 1485 (strong), 1450 (strong), 1445 (strong), 1440 (strong), 1410 (strong), 1110, 1075, 1010 (strong), 910 (strong), 860 (strong), 760 (strong), 730, 700 (strong), 615 cm^{-1} (strong).

Identification of the Pyrolysis Products of 4,4-Diphenyl-2-cyclohexenone Tosylhydrazone Lithium Salt. The recovered oil was analyzed by gas chromatography with column A. The GC settings were as follows: detector temperature, 280 °C; injector temperature, 280 °C; oven temperature programmed from 160 to 240 °C at 4 °C/min; He pressure, 36 psi. All yields were determined with dodecane as the internal standard.

The first peak, which had a retention time of 16 min, was identified as 5,5-diphenyl-1,3-cyclohexadiene, **28** (4.10% yield). The following spectroscopic data were obtained for the isolated diene **28**: high-resolution MS, m/e calcd for $C_{18}H_{16}$ 232.125, found 232.124; ^{1}H NMR ($CDCl_3$) δ 2.85 (d, 2 H, J = 4 Hz), 5.80–6.30 (m, 4 H), 7.15 (s, 10 H, aromatic protons).

The second peak, which had a retention time of 18 min, was identified as methylene-6,6-diphenyl-2-cyclohexene, **30** (10.7% yield). The following spectroscopic data were obtained for **30** after isolation by preparative GC: high-resolution MS, m/e calcd for $C_{19}H_{18}$ 246.141, found 246.141; ^{1}H NMR ($CDCl_3$) δ 1.90 (m, 2 H), 2.50 (t, J = 6 Hz, 2 H), 4.35 (s, 1 H, one methylene proton, shielded), 5.15 (s, 1 H, one methylene proton), 5.55–5.80 (m, 1 H), 6.30 (d, J = 8 Hz, 1 H), 7.15 (10 H, aromatic); ^{13}C NMR δ 23.86, 34.50, 52.90, 116.76, 126.04, 127.66, 128.82, 129.46, 130.31, 145.84, 149.21; IR (Nujol mull) 3060 (strong), 3040 (strong), 2940 (weak), 1630 (strong, exo-methylene =C—H stretch), 1595 (C=C stretch), 1490 (strong), 1155, 1185 (strong), 1040 (strong), 1030 (strong), 900 (strong), 780 (strong), 700 (strong), 635 cm^{-1} (strong); UV λ_{max} 232 nm, ϵ 20 490.

The third peak, which had a retention time of 18 min, was identified as 1-methylene-4,4-diphenyl-2-cyclohexene, **29** (6.60% yield). The following spectroscopic data were obtained for the isolated diene **29**: high-resolution MS, m/e calcd for $C_{19}H_{18}$ 246.141, found 246.139; ^{1}H NMR ($CDCl_3$) δ 2.25 (2 H), 2.05 (2 H), 4.70–4.75 (multiplet, exo-methylene, 2 H), 6.01, 6.32 (a pair of doublets, J = 10 Hz, 2 H), 7.10 (s, 10 H, aromatic); IR (neat) 3040–3060 (strong), 2940 (strong), 1670 (weak), 1595, 1490, 1155 (strong), 1185 (strong), 1010 (strong), 905 (weak), 730 (weak), 700 (medium), 650 cm^{-1} (strong); UV λ_{max} 232 nm, ϵ 22 000.

The fourth peak, which had a retention time of 23 min, was identified as the starting ketone, 4,4-diphenyl-2-cyclohexenone, **6** (29.6% yield). The GC retention time and NMR, IR, and mass spectra of the isolated substance match those of an authentic standard.

Identification of the Pyrolysis Products of 4,4-Diphenylcyclohexanone Tosylhydrazone Lithium Salt. The recovered oil was analyzed by gas chromatography with column B. The GC settings were as follows: detector temperature 280 °C, injector temperature 280 °C, oven temperature programmed from 140 to 240 °C at 4 °C/min. The He pressure was 36 psi.

The first peak, which had a retention time of 40 min, was identified as 4,4-diphenylcyclohexene, **34** (48% yield). A mp of 62–63 °C and the following spectroscopic data were obtained for isolated **34**: high-resolution MS, m/e calcd for $C_{18}H_{18}$ 234.141, found 234.142; ^{1}H NMR ($CDCl_3$) δ 1.75 (m, 2 H), 2.30 (t, J = 5 Hz, 2 H), 2.60 (s, 2 H), 5.70 (m, 2 H), 7.10–7.25 (10 H, aromatic protons); IR (neat) 3040 (medium), 2920 (medium), 1650 (medium), 1600 (medium), 1470 (medium), 910 (medium), 765 (medium), 735 (medium), 705 cm^{-1} (medium).

The second peak, which had a retention time of 58 min, was identified as 1-methyl-4,4-diphenylcyclohexanol, **35** (5.4% yield). A mp of 98–99 °C and the following spectroscopic data were obtained for isolated **35**: high-resolution MS, m/e calcd for $C_{19}H_{22}O$ 266.167, found 266.167; ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 3 H), 1.60–1.70 (m, 5 H, four cyclohexyl protons + overlapping alcoholic proton), 2.30–2.40 (m, 4 H, four cyclohexyl protons; pattern of signal identical to the one at 1.60–1.70), 7.10–7.30 (10 H, aromatic); IR (neat) 3300–3400 (broad), 3040 (medium), 1590 (medium), 1445 (medium), 1100 (weak), 1010 (medium), 980 (medium), 910 (medium), 750 (weak), 700 (strong), 2920 cm^{-1} (medium).

The third peak, which had a retention time of 62 min, was identified as the starting ketone, **7** (6.0% yield). The gas chromatographic retention time and the ^{1}H NMR, IR, and mass spectra correspond to those of the starting ketone.

Photolysis of 4,4-Diphenyl-2-cyclohexenone Tosylhydrazone Lithium Salt. To a quartz tube, connected to a nitrogen monitoring apparatus, were added 0.45 g (0.0011 mol) of the tosylhydrazone lithium salt **26** (λ_{max} = 320 nm) and 5.0 mL of freshly distilled DMSO. The solution was degassed and photolyzed for 5 days with a 450-W medium-pressure Hanovia lamp and a Pyrex filter. The reaction was monitored by the evolution of nitrogen bubbles. After the reaction was completed, the reaction mixture was treated with 50 mL of saturated sodium chloride and extracted with 2 × 40 mL of ethyl ether. The ether layers were combined and dried over $MgSO_4$. After a few hours

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(17) *The Sadtler Standard Spectra*; Sadtler Research Laboratory: Philadelphia, 1974; Vol. 4, no. 2261.

the mixture was filtered, and the ether was distilled off using a rotary evaporator, yielding a dark red oil. The oil was analyzed by gas chromatography, showing the same four products that had been found in the pyrolysis of tosylhydrazone lithium salt **26**, but in totally different yields: 5,5-diphenyl-1,3-cyclohexadiene, **28** (2.0%), 1-methylene-6,6-diphenyl-2-cyclohexene, **30** (1.5%), 1-methylene-4,4-diphenyl-2-cyclohexene, **29** (0.5%), and 4,4-diphenyl-2-cyclohexenone, **6** (45.1%).

Determination of k_1. Since eq 8 is a symmetrical equation it was necessary to determine k_1 in an independent manner. This was accomplished by measurement of the loss of starting tosylhydrazone salt with an HPLC analysis. To a 25-mL round-bottom flask fitted with a rubber septum and an outlet connected to a measuring burette were added constant amounts (0.45 g, 0.0011 mol) of the tosylhydrazone lithium salt and of the internal standard *N*,*N*-dimethyl-*p*-tolylsulfonamide (0.22 g, 0.0011 mol) dissolved in 5.00 mL of freshly distilled DMSO. The mixture was heated at 125 °C, and five 0.5-mL aliquots were taken at different time intervals. The aliquots were quenched in cold empty test tubes set in an ice bath (the test tubes were not left in the ice bath too long since DMSO freezes at about 20 °C). Then 0.5 mL of 10% acetic acid in DMSO was added in order to convert the tosylhydrazone lithium salt back to its tosylhydrazone, since the latter is much easier to analyze on the HPLC.

The five aliquots were analyzed with HPLC and a reverse-phase column (Zorbax) and the following conditions: eluting solvent 60% CH_3CN and 40% H_2O; UV 250 and 260 nm for tosylhydrazones corresponding to **26** and **32**, respectively. The following retention times were obtained: internal standard 3 min, tosylhydrazone corresponding to **26** 10 min, and tosylhydrazone corresponding to **32**, 8 min. The rate constant, k_1, for decomposition of **26** is 5.0 h^{-1} at 125 °C, which compares well with the slow step k_1 from the curve fitting analysis (k_1 = 3.85 h^{-1} at 125 °C), while the rate constant k_1 for the decomposition of **32** is 6.50 h^{-1}, which compares well with the slow step k_1 from the curve fitting analysis (k_1 = 6.39 h^{-1} at 125 °C).

Nucleophilic Ring-Opening Reactions of Morpholin-2-ones. A Resolution of *dl*-(Secondary-alkyl)amines

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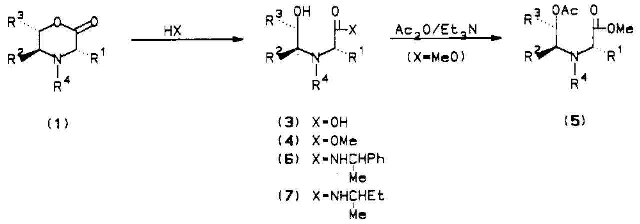
The alcoholysis of morpholin-2-ones yielded an equilibrium mixture of morpholin-2-one and the corresponding hydroxy ester. The equilibrium constants for the methanolysis of several substituted morpholin-2-ones were determined. Treatment of optically active morpholin-2-ones with (secondary-alkyl)amines resulted in stereoselective ring opening to afford hydroxy amides with up to 30% de. Hydrolysis of one such hydroxy amide regenerated the optically active (secondary-alkyl)amine and the morpholin-2-one.

Introduction

In our investigations of stereoselective reactions of amides, we have reported on the asymmetrically induced reduction of α-keto amides.[1] Although the aminolysis of α-amino acid esters seems to be an important methodology for the formation of amide bonds in peptide synthesis, there are few reports on the stereoselective aminolysis of esters. The reaction conditions generally employed in the aminolysis of esters are sufficiently severe to racemize the optically active α carbon of α-amino acid derivatives. Acyclic α-amino acid esters are sterically labile and should be less effective in asymmetric induction than their conformationally more stable cyclic analogues.

Scheme I



(1)

(3) X=OH
(4) X=OMe
(6) X=NHCHPh(Me)
(7) X=NHCHEt(Me)

(5)

a: $R^1=R^2=R^3=H$, $R^4=PhCH_2$
b: $R^1=R^2=R^3=H$, $R^4=Me$
c: $R^1=Me$, $R^2=R^3=H$, $R^4=PhCH_2$
d: $R^1=R^3=H$, $R^2=Me$, $R^4=PhCH_2$
e: $R^1=R^2=H$, $R^3=Me$, $R^4=PhCH_2$
f: $R^1=i\text{-}Bu$, $R^2=R^3=H$, $R^4=PhCH_2$
g: $R^1=i\text{-}Pr$, $R^2=R^3=H$, $R^4=PhCH_2$

Table I. pH Dependence of the Hydrolysis of 4-Benzylmorpholin-2-one (1a) (25 °C)

	pH[a]					
	4.3	5.2	6.5	7.3	8.3	9.4
k ($\times 10^{-4}$ s^{-1})	4.9	1.8	0.98	0.79	1.6	3.0

[a] Represents the initial pH of the reaction mixture.

We have recently prepared optically active morpholin-2-ones **1** either from 2-amino alcohols and α-bromo esters or from α-amino acids and 1,2-dibromoethane.[2] In general, these cyclic esters are about 100 times more reactive than acyclic esters in such nucleophilic substitution reactions as alcoholysis and aminolysis.[3] We wished to compare nucleophilic ring-opening reactions such as hydrolysis, alcoholysis, and aminolysis of these cyclic α-amino acid esters with the same reactions of a carbocyclic lactone. Furthermore, we wished to investigate **1** as a model for asymmetric induction on amide bond formation from α-amino acid esters by aminolysis. Since α-lactones form equilibrium mixtures with their ring-opening products on hydrolysis and alcoholysis,[4] 2-[(2-hydroxyethyl)amino]acetic acid and its homologues should be easily cyclized into morpholin-2-ones. Accordingly, the aminolysis of **1** followed by hydrolysis should provide a kinetic resolution of amines. There have been a few reports on the kinetic resolution of amino acids by (*S*)-α-amino acid esters in the presence of condensing agents,[5] with moderate stereose-

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[1] Kashima, C.; Harada, K.; Omote, Y. *J. Chem. Soc., Perkin Trans. 1*, **1987**, 1495.

[2] Kashima, C.; Harada, K. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1521.

[3] Huisgen, R.; Ott, H. *Tetrahedron* **1959**, *6*, 253.

[4] Brown, H. C.; Keblys, K. A. *J. Org. Chem.* **1966**, *31*, 485.

0022-3263/89/1954-0789$01.50/0