an unstable compound which could not be purified by distillation or gas-liquid partition chromatography. The crude reaction product was reduced with 1.5 g of lithium aluminum deuteride[57] according to previously reported conditions[59] (except that the reaction mixture was heated under reflux for 4 days) to yield 750 mg of a crude product which was purified by gas-liquid partition chromatography on a 10 ft × 0.25 in. stainless steel column packed with 5% SE-30 on Chromosorb W with a He flow rate of 75 cc/min at 100°. The infrared spectrum was identical with unlabeled hexanol and the mass spectrum showed that the product, 5,5-d_2-2-hexanol, had an isotopic composition of 99% d_2 and 1% d_1. Oxidation of this labeled alcohol according to the conditions of Djerassi, *et al.*,[61] and purification of the product by gas-liquid partition chromatography (conditions identical with those used for the isolation of 5,5-d_2-2-hexanol) yielded 600 mg of 5,5-d_2-2-hexanone (IIb).

Acknowledgment. We wish to thank Professors J. I. Brauman, J. L. Beauchamp, and F. Kaplan for numerous valuable comments; Mr. J. Garcia for technical assistance and maintenance of the instrument; Mr. A. M. Babcock for drawing the figures; and Mr. G. Eadon for reading the manuscript.

(61) C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

Relative Rates of Cleavage by Alkoxide Ions of Diphenylcyclopropenone and of Diphenylthiirene 1,1-Dioxide

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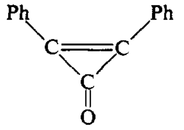
Abstract: The rates of reaction of diphenylcyclopropenone (**1**) with sodium methoxide in methanol, sodium ethoxide in ethanol, and sodium isopropoxide in isopropyl alcohol have been determined at several temperatures. A comparable study has been made with diphenylthiirene 1,1-dioxide (**2**). In each instance the relative rates were in the order, NaOMe:NaOEt:NaO-*i*-Pr ≅ 1:2:6. The ratio of rates for **2** to **1** was *ca.* 5000 to 1. This striking reversal of the usual much more facile attack of base on the carbonyl group than on the sulfonyl group is attributed to a marked conjugative stabilization of **1** as contrasted to a slight conjugative stabilization of **2**.

The extensive investigations of Breslow and his coworkers on cyclopropenone,[2a] its mono- and dialkyl derivatives, and its diphenyl derivative (**1**)[2b] have clearly established that the cyclopropenone system has considerable conjugative stabilization. The much greater thermal stability of diphenylthiirene 1,1-dioxide (**2**)[3,4] as compared to its saturated analogs, *cis*- and *trans*-2,3-diphenylthiirane 1,1-dioxides,[4] suggested that this might be true also for thiirene 1,1-dioxides, although much less information concerning this series is available.[5] It appeared to be of interest to compare the rates of cleavage of **1** and **2** with alkoxide ions. Ordinarily attack at the carbonyl group by hydroxide or alkoxide ions is much more facile than attack at the sulfonyl group. We wanted to see whether this would be true also for systems **1** and **2**.



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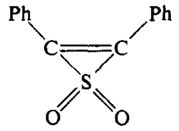

2

Table I. Kinetic Data for the Reactions of Diphenylcyclopropenone (**1**) with Sodium Alkoxides in Alcohol Solvents

Alkoxide (concn, M)	T,°C	k, M^{-1} sec$^{-1\,a}$	E_a, kcal/mol	ΔS^*, eu
NaOMe (0.03116)	10	9.59×10^{-3}	14	−21
NaOMe (0.03116)	25	3.46×10^{-2}		
NaOMe (0.08628)	25	$(3.72 \times 10^{-2})^b$		
NaOMe (0.03116)	40	1.07×10^{-1}		
NaOEt (0.01390)	10	1.55×10^{-2}	17	−9
NaOEt (0.01390)	25	6.83×10^{-2}		
NaOEt (0.01422)	40	2.74×10^{-1}		
NaO-*i*-Pr (0.02495)	10	6.90×10^{-2}	14	−16
NaO-*i*-Pr (0.02495)	25	2.70×10^{-1}		
NaO-*i*-Pr (0.02495)	40	7.88×10^{-1}		

[a] Average of three or more runs; individual runs on the same day were reproducible to within ±5%, but the over-all reproducibility was closer to ±10%. [b] When corrected for a small positive salt effect (determined in separate runs with added salt) the order of the reaction in base is calculated to be 1.04.

Results

Diphenylcyclopropenone (**1**) is known to hydrolyze rapidly in aqueous sodium hydroxide to give a high yield of *cis*-2,3-diphenylpropenoic acid.[2b] In 95% ethanol at 24° the half-life of this reaction with 0.1 N base was found to be about 5 min.[2b] In the present study **1** was observed to give high yields (95%) of the methyl, ethyl, and isopropyl esters of *cis*-2,3-diphenylpropenoic acid when treated with the appropriate sodium alkoxide in the corresponding alcohol. Rate constants for these reactions were determined spectrophotometrically by following the rate of disappearance of the band at 296 mμ, characteristic of diphenylcyclopropenone, in the presence of excess standard base. The results are summarized in Table I.

The reaction of sodium methoxide in methanol with diphenylthiirene 1,1-dioxide (**2**) at 0° has been found to give methyl *cis*-2,3-diphenylethenesulfonate (75%) and diphenylacetylene (16%); similar results were obtained

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(1) National Science Foundation Undergraduate Research Participant, Summer, 1966.

(2) (a) R. Breslow and G. Ryan, *J, Amer. Chem. Soc.*, **89**, 3072 (1967), and references cited therein; (b) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1320 (1965).

(3) L. A. Carpino and L. V. McAdams, III, *ibid.*, **87**, 5804 (1965).

(4) F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *ibid.*, **90**, 429 (1968).

(5) Only one additional compound in this series appears to have been prepared to date, see L. A. Carpino and R. H. Rynbrandt, *ibid.*, **88**, 5682 (1966).

Table II. Kinetic Data for the Reaction of Diphenylthiirene 1,1-Dioxide (**2**) with Sodium Alkoxides in Alcohol Solvents

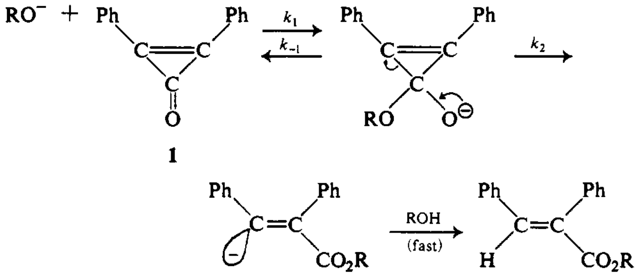
Alkoxide	T,°C	k, M^{-1} sec^{-1}	E_a, kcal/mol	ΔS, eu
NaOMe[a]	25	1.8×10^2	10	−16
NaOEt	3.6	7.7×10^1		
	24.6	3.4×10^2	11	−10
NaO-*i*-Pr	3.6	1.6×10^2		
	24.6	9.3×10^2	14	−1

[a] Taken from ref 6.

with potassium *t*-butoxide.[6] The kinetic study reported previously with sodium methoxide[6] has now been extended to sodium ethoxide in ethanol and to sodium isopropoxide in isopropyl alcohol (Table II).

Discussion

As discussed elsewhere,[6] retention of configuration in formation of the esters from **1** and **2** in reactions with alkoxides in alcohols is not surprising in view of the high rate of protonation anticipated for the intermediate carbanions. By analogy with other carbonyl reactions the reactions with **1** can be formulated as shown.



Addition to the carbonyl group of **1** will, of course, destroy the aromaticity of the system. Therefore, the rate in the addition step (k_1) would be expected to be slow and the reversal of this step (k_{-1}), which restores the aromatic system, would be expected to be very fast. It is likely, then, that a preequilibrium will be established ($k_{-1} > k_2$). The position of the equilibrium will be sensitive to the degree of aromaticity of **1**, and the rate will depend, therefore, on this degree of aromaticity. It is possible, although less likely, that $k_2 > k_{-1}$; under these circumstances preequilibrium will not be established and k_1 will be rate determining. But here too the rate will reflect the degree of aromaticity in **1**.

Comparable mechanisms for the reaction of RO⁻ with **2** can be written, but here there is no analogy to draw on. Adduct formation could occur in this instance without destroying the inherent aromaticity of the thiirene 1,1-dioxide ring system, if such exists. The rate would still probably reflect the inherent aromaticity of the system, however, since the rate of decomposition of the adduct would be rate determining. Alternatively, RO⁻ might attack sulfur with a direct (SN2-like) displacement of the carbanion. The rate of this reaction should also be a reflection of the aromaticity inherent in **2**.

As should now be apparent, little detailed information concerning the mechanisms of the reactions of **1** and **2** with alkoxide ions is available at present, but most, if not all, mechanisms suggest that there should be a relationship between aromaticity and rate of cleavage. One bit of evidence suggesting that the mechanisms are not greatly different for **1** and **2** is the close similarity in the rate response for each as the alkoxide is changed from MeO⁻ to EtO⁻ to *i*-PrO⁻. The rate constant for **1** is nearly doubled in going from sodium methoxide to the more strongly basic sodium ethoxide, and the latter value is more than tripled in going to the still more basic sodium isopropoxide. Nearly parallel changes in rate constants with increasing basic character of the alkoxide occur with **2**. The rates for **2** are uniformly about 5000 times greater than those for **1** with corresponding bases. For the reactions of **2** the activation energy increases with increased alkoxide basicity; The rates increase, despite this adverse factor, due to a sharply more positive activation entropy term. For the reactions of **1** the rate increases with increased alkoxide basicity are again attributable to favorable activation entropies, but here the progression of activation parameters is not orderly.

The rate constants given in Tables I and II are most meaningful when compared with those for the reactions of open-chain analogs (Table III).

Examination of Table III shows that in the hydroxide ion catalyzed hydrolysis of phenyl acetate attack by hydroxide ion is about five powers of ten greater than attack by hydroxide ion on sulfur in phenyl *p*-toluenesulfonate under comparable conditions.[7] It is remarkable indeed to find that with **1** and **2** the relative rates of attack at the carbonyl group and sulfonyl group have been *reversed*. Now attack at sulfur occurs about 5×10^3 faster than at the carbonyl group. If we assume that **1** and **2** have about equal strain energies and that the difference in rates reflects a difference in ground-state energies the over-all rate change of 5×10^8 would correspond to a change in free energies of about 12 kcal/mol. This then constitutes a crude estimate of the conjugative stabilization in the cyclopropenone system, assuming that the thiirene 1,1-dioxide system possesses little or no conjugative stabilization. This estimate is probably on the low side since conjugative stabilization of the thiirene 1,1-dioxide system would not be expected to be zero,[8] although it should be considerably less than that of the cyclopropenone system.[9] It is noteworthy that the rate of reaction of **2** with methoxide ion is much faster than that of its saturated analog.[4] This suggests that the increased strain resulting from incorporation of the C=C bond into the thiirane 1,1-dioxide system

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[6] F. G. Bordwell, J. M. Williams, Jr., and B. B. Jarvis, *J. Org. Chem.*, **33**, 2026 (1968).

[7] C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, 1872 (1951), have shown by isotopic studies that attack of hydroxide occurs on sulfur rather than on carbon of the phenyl group.

[8] From measurements of dissociation constants the σ^- constants for p-CH$_3$SO$_2$ have been shown to be +0.82 for thiophenols, +0.98 for phenols, and +1.13 for anilinium ions, as compared to $\sigma = +0.72$ for benzoic acids, F. G. Bordwell and H. M. Anderson, *J. Amer. Chem. Soc.*, **75**, 6019 (1953). This clearly establishes the ability of the sulfone grouping to enter into conjugation with electron-donor groups. The evidence for conjugation with a C=C bond is less clearcut, but there is no reason to expect it to be nonexistent.

[9] The lesser conjugative ability of the sulfone group is clearly indicated by the fact that methyl sulfone appears to be a weaker acid than acetone by about five pK_a units [F. G. Bordwell, R. H. Imes, and E. C. Steiner, *ibid.*, **89**, 3905 (1967)] despite the much greater inductive effect on the sulfonyl group.

Table III. Comparisons of Rate Constants for **1** and **2** with Those of Related Carbonyl and Sulfonyl Compounds

Compound	T,°C	Base	Solvent	k, M^{-1} sec^{-1}	k (rel)
p-$CH_3C_6H_4SO_2OC_6H_5$	25	HO^-	H_2O	$(4.9 \times 10^{-5})^a$	1.0
$CH_3CO_2C_6H_5$	30	HO^-	H_2O	5.3^b	1×10^5
$CH_3COCMe_2COCH_3$	25	HO^-	H_2O	$(1.1 \times 10^{-1})^c$	2×10^3
Diphenylcyclopropenone (**1**)	25	MeO^-	MeOH	3.5×10^{-2}	7×10^2
Diphenylthiirene 1,1-dioxide (**2**)	25	MeO^-	MeOH	1.8×10^2	4×10^6

[a] O. R. Zaborsky and E. T. Kaiser, *J. Amer. Chem. Soc.*, **87**, 3084 (1965). [b] In 1 *M* LiCl solution, T. C. Bruice, A. Donzel, R. W. Huffman, and A. R. Butler, *ibid.*, **89**, 2106 (1967). [c] Extrapolated from the data of R. G. Pearson and E. A. Mayerle, *ibid.*, **73**, 926 (1951).

is more decisive with respect to affecting the reactivity of **2** toward methoxide ion than is the conjugative stabilization provided thereby. The opposite is no doubt true for **1**. Although no quantitative data are available as yet, the qualitative data indicate that alkyl-substituted cyclopropanones are very readily attacked by methoxide ion.[10] On the other hand, dialkylcyclopropenones are much less susceptible to alkaline hydrolysis than is the diphenyl derivative,[11] and would appear to be much less reactive than tetramethylcyclopropanone.[10] It is also of interest to note that the cleavage of **1** by methoxide ion is actually slower than that of 3,3-dimethyl-2,4-pentanedione by hydroxide ion (Table III). (The latter is an acyclic analog in which the basicity of the carbanion liberated on cleavage is probably within a few orders of magnitude of that formed from **1** and in which the carbonyl group is more shielded from attack.) The fact that this hindered, unstrained molecule is cleaved more rapidly than the highly strained **1** attests once again to the high degree of conjugative stabilization in the latter.[2]

Experimental Section

Alkyl *cis*-2,3-Diphenylpropenoates from Diphenylcyclopropenone (1). A solution of 0.5 g (9.72 mmol) of sodium methoxide in 200 ml of methanol was added slowly with stirring to 1 g (4.82 mmol) of **1**.[2b,12] After stirring for 2 hr the solution was neutralized with dilute hydrochloric acid and concentrated *in vacuo* to 5 ml. Dilution with water and extraction with ether yielded, after drying and concentrating, 90% methyl 2,3-diphenylpropenoate, mp 75–76° (lit.[13] mp 75–76°). The uv, ir, and nmr spectra of this ester, as well as the ethyl and isopropyl esters, were consistent with those reported or those expected.

Comparable yields of ethyl *cis*-2,3-diphenylpropenoate, bp 163–165° (lit.[14] bp 163–165°), and of isopropyl *cis*-2,3-diphenylpropenoate, mp 65–70°, were obtained in the same manner. An analytical sample of the latter was prepared by crystallization from aqueous ethanol; mp 70.5–71°; $\lambda_{\max}^{\text{EtOH}}$ 284 mμ (log $\varepsilon_{\max}$ 4.19); $\lambda_{\max}^{\text{KBr}}$ 3.35, 5.88, 6.15, 6.68, 6.90, 7.25, 8.00, 8.15, 14.10, and 14.50 μ; nmr ($CDCl_3$) 1.25 (d, 6 H), 5.20 (m, 1 H), 7.30 (d, 10 H), and 7.90 (s, 1 H). *Anal.*[15] Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81; O, 12.01. Found: C, 80.89; H, 6.75; O, 12.55.

Kinetic Measurements. The rate constants for the reactions of **1** were determined by following its rate of disappearance at 296 mμ (the absorbance of **1** is about threefold greater than that of the product esters at this wavelength) in solutions containing about a 200-fold excess of standard base. Pseudo-first-order rate constants were obtained by multiplying the slope of the line obtained from a plot of log $(A_t - A_\infty)$ *vs.* t by 2.302. The second-order constants recorded in Tables I and II were obtained by dividing the pseudo-first-order constants by the base concentration. A similar procedure was used for **2** except that the measurements were made at 320.5 mμ.[6]

Acknowledgment. We wish to thank Dr. E. B. Hoyt, Jr., for valuable assistance and advice and the National Science Foundation for financial support.

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(10) N. J. Turro and W. B. Hammond, *J. Amer. Chem. Soc.* **87**, 3258 (1965).

(11) R. A. Breslow and R. Peterson, *ibid.*, **82**, 4426 (1960); R. A. Breslow, L. J. Altman, A. Krebs, E. Mohaesi, I. Murata, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1326 (1965).

(12) *Warning!* Diphenylcyclopropenone appears to produce rashes. Care should be taken to avoid contact with the skin.

(13) J. F. Codington and E. Mosettig, *J. Org. Chem.*, **17**,, 1027 (1952); G. Drefahl, G. Heublein, and G. Telztaff, *J. Prakt. Chem.*, **23**, [5] 318 (1964).

(14) W. Reppe, *Ann.*, **582**, 1 (1953); G. P. Mueller and F. L. MacArtor, *J. Amer. Chem. Soc.*, **76**, 4621 (1954).

(15) Micro-Tech Laboratories, Skokie, Ill.