Substituent Effects on the Preparations and Thermal Decarboxylations of β-Lactones Derived from the Cycloaddition of Dichloroketene with Monosubstituted Benzaldehydes[1]

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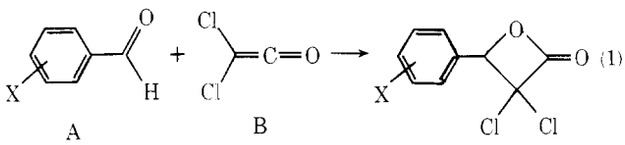
Cycloaddition reactions of dichloroketene and monosubstituted benzaldehydes gave 3,3-dichloro-4-aryloxetan-2-ones in isolated yields of approximately 20–80%. Benzaldehydes substituted with electron-withdrawing groups led to higher yields than benzaldehydes bearing electron-donating substituents. Thermolysis of these β-lactones gave the corresponding β,β-dichlorostyrenes in good yields. Electron-donating groups enhance the rate of decarboxylation. The kinetics of the process were determined for the parent phenyl system and its three monochloro derivatives; the elimination of carbon dioxide is a first-order reaction, probably proceeds in a concerted fashion, and involves a highly polarized transition state.

Part A

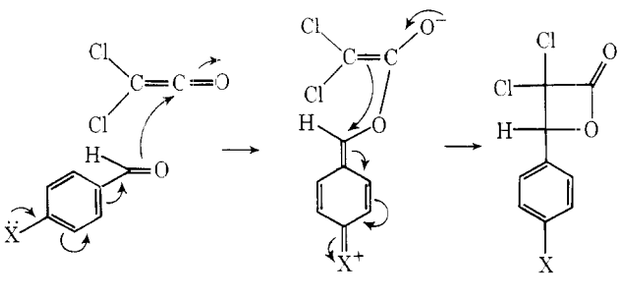
There is ample documentation that the reactions of diphenylketene with alkenes to produce cyclobutanone derivatives take place in a concerted fashion.[2] Furthermore, it has been demonstrated that diphenylketene behaves in an electrophilic manner [i.e., that it reacts from its lowest unoccupied molecular orbital (LUMO)].[2b] Similar conclusions have been invoked for cycloadditions involving dichloroketene and olefins.[2c,3] Another cycloaddition process characteristic of ketenes is the formation of 2-oxetanones (β-lactones) from reaction with aldehydes or ketones.[4,5] In connection with other investigations it was necessary to examine what effects, if any, substituents attached to the phenyl ring of benzaldehydes would have on the yields of the β-lactones produced in reactions with dichloroketene. In this report the interesting results of a study on the cycloadditions of dichloroketene with monosubstituted benzaldehydes (eq 1) are discussed.



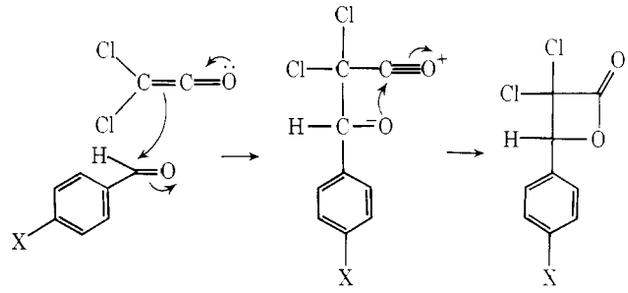
1a–16a

A priori, the substituent on the phenyl ring could influence the cycloaddition process in two ways, as illustrated in Schemes I and II.[6] In the former case (Scheme I), dichloroketene is electrophilic, and electron-donating groups (such as X = OCH_3) would be expected to lead to increased rates of cycloaddition compared to electron-withdrawing substituents (such as X = NO_2). In the latter case (Scheme II), dichloroketene is nucleophilic and electron-withdrawing groups should enhance the reactivity of cycloaddition. Of course, it is also possible that both types of effects could be operative, depending on the nature of the substituent or even that the substituents could have virtually no effect on the cycloaddition process. Interestingly, it has been reported that dichloroketene cycloadds readily to electron-poor aldehydes (such as chloral);[5a,b] yet, it does not react with electron-deficient alkenes (such as acrylonitrile) even though it undergoes cycloaddition very efficiently with electron-rich olefins (such as ethyl vinyl ether).[3a,d]

Scheme I



Scheme II



In Table I are assembled the identities and locations of the substituents attached to the phenyl ring, the important experimental parameters, and the yields of the β-lactones produced. The yields listed in Table I are *isolated yields of crude materials*. Because of the thermal lability of many of the β-lactones, some of the products were contaminated with small amounts of the corresponding β,β-dichlorostyrenes. Similarly, in some cases it was not possible to remove all of the unreacted starting aldehyde by the standard procedure of extraction with aqueous sodium bisulfite solution (probably because of unfavorable electronic effects impeding the formation of the aldehyde/bisulfite addition compound[7]). Fortunately, by integrating the peak areas associated with the NMR signals for the aldehyde formyl proton, the β,β-dichlorostyrene vinyl proton, and the β-lactone ring proton, the relative amounts of these components could be estimated and appropriate adjustments could be made to correct the yields of cycloaddition products. The β-lactones (all of which are oils at room temperature except for the nitrophenyl derivatives **8a–10a,** nitrile **11a,** and acetate **16a**) thus obtained were usually light yellow to golden orange in color (even after treatment with activated carbon). Attempts to purify the liquid cycloadducts by column chromatography using silica gel or by distillation at reduced pressure led to substantial amounts of contamination of the β-lactone by the corresponding β,β-dichlorostyrene as a result of concomitant decarboxylation. Therefore, the β-lactones were characterized by their spectral properties.[8] The infrared spectra showed strong signals at approximately 1860 cm^{-1}, which reflect a 25-cm^{-1} shift to higher frequency (because of the field effects of the adjacent

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Table I. Experimental Conditions and Results for the Preparation of β-Lactones from Monosubstituted Benzaldehydes and Dichloroketene[a]

Entry	Compd	Registry no.	X	Solvent[b]	Temp, °C	B/A[c]	$ZnCl_2$, equiv	Yield,[d] %
1	**1a**	22391-10-2	H	E	3	1	0	32
2	**1a**		H	E	3	1	0.5	30
3	**1a**		H	E	3	1	1	29
4	**1a**		H	E	3	1	1	35
5	**1a**		H	E	−78[e]	1	0	35
6	**1a**		H	E	24	2	0	41
7	**1a**		H	E	24	2	1	45
8	**1a**		H	E	24	2	1	55
9	**2a**	65086-06-8	2′-CH_3	E	3	1	1	19
10	**2a**		2′-CH_3	E	3	1	1	22
11	**2a**		2′-CH_3	E	24	2	0.25	37
12	**2a**		2′-CH_3	M	24	2	0.25	15
13	**3a**	65086-07-9	3′-CH_3	E	3	1	1	24
14	**3a**		3′-CH_3	E	3	1	1	26
15	**3a**		3′-CH_3	E	24	2	0.25	53
16	**3a**		3′-CH_3	P	24	2	0.25	34
17	**4a**	65086-08-0	4′-CH_3	E	3	1	1	26
18	**4a**		4′-CH_3	E	24	2	0.25	44
19	**4a**		4′-CH_3	B	24	2	0.25	33
20	**5a**	65086-09-1	2′-Cl	E	24	1	1	53
21	**5a**		2′-Cl	E	3	1	1	51
22	**6a**	65103-21-1	3′-Cl	E	24	1	1	59
23	**6a**		3′-Cl	E	3	1	1	59
24	**7a**	22391-11-3	4′-Cl	E	24	1	1	52
25	**7a**		4′-Cl	E	24	1	1	59
26	**8a**	65086-00-2	2′-NO_2	E/M	3	1	0	68
27	**8a**		2′-NO_2	E/M	3	1	0	85
28	**8a**		2′-NO_2	E/M	3	1	0.5	73
29	**8a**		2′-NO_2	E/M	3	1	1	73
30	**8a**		2′-NO_2	E/M	3	1	2	46
31	**9a**	65086-01-3	3′-NO_2	E/M	3	1	0	67
32	**9a**		3′-NO_2	E/M	3	1	0.5	65
33	**9a**		3′-NO_2	E/M	3	1	1	64
34	**9a**		3′-NO_2	E/M	3	1	1	71
35	**9a**		3′-NO_2	E/M	3	1	2	52
36	**10a**	65086-02-4	4′-NO_2	E/M	3	1	0.5	65
37	**11a**	65086-03-5	4′-CN	E/M	24	1	0.5	82
38	**12a**	65086-04-6	2′-OCH_3	E	3	1	0	0
39	**12a**		2′-OCH_3	E	3	1	1	0
40	**13a**		3′-OCH_3	E	3	1	0	38
41	**13a**	65086-05-7	3′-OCH_3	E	3	1	0.5	32
42	**14b**[f]		4′-OCH_3	E	24	1	1	23
43	**14b**[f]		4′-OCH_3	E	24	1[g]	1[g]	17
44	**15a**	65085-87-2	3′-$OCOCH_3$	E	3	1	0	36
45	**15a**		3′-$OCOCH_3$	E	3	1	0.5	44
46	**16a**	65085-88-3	4′-$OCOCH_3$	E	3	1	0	29

[a] See eq 1 for reaction. [b] E, ether; M, methylene chloride; P, pentane; B, benzene. [c] Molar ratio of dichloroketene precursor (dichloroacetyl chloride) to monosubstituted benzaldehyde. [d] Isolated yields of crude materials; adjusted to correct for the presence of small amounts of β,β-dichlorostyrenes and unreacted aldehydes; see text. [e] In this experiment the dichloroketene was generated at −78 °C *in the absence of benzaldehyde*, then filtered into a solution of benzaldehyde at −78 °C, and allowed to gradually warm to room temperature. [f] Only the β,β-dichlorostyrene was isolated; see eq 2. [g] In this experiment the dichloroketene was generated by the dechlorination of trichloroacetyl chloride with activated Zn.

dichloromethylene unit[9]) of the characteristic β-lactone carbonyl absorption frequency of about 1835 cm^{-1}.[4b] The ^1H NMR spectra displayed singlet absorption signals for the 2-oxetanone ring hydrogen attached to carbon 4 at 5.68–6.53 ppm, reflecting its benzylic nature and the effects of the adjacent oxy and dichloromethylene groups. The ^{13}C NMR spectra were also in accord with the β-lactone structures. The mass spectra showed relatively small signals for the molecular ions; the base peaks generally occurred at the isotopic cluster *m/e* 110, 112, 114 corresponding to the molecular ion of dichloroketene.[10] In addition to their spectral properties, β-lactones **8a–11a** and **16a** could be purified by recrystallization and, accordingly, were further characterized by consistent elemental analyses. Finally, each of the β-lactones was decarboxylated to provide the corresponding β,β-dichlorostyrenes (see eq 2) which were fully characterized.

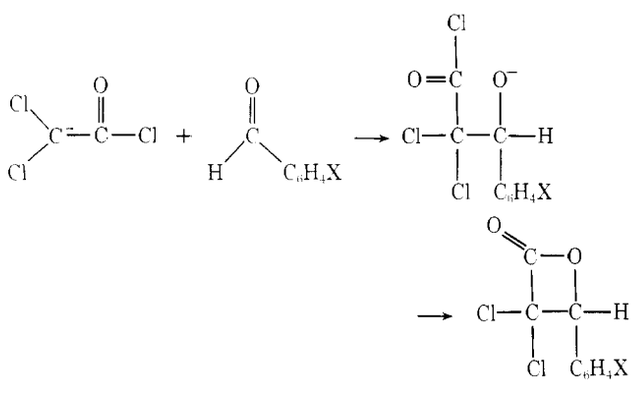
Inspection of the data in Table I clearly reveals that substituent effects are important. For the cycloadditions involving benzaldehyde it is seen that the yields of β-lactone ranged from 29 to 35% and that the presence of freshly fused zinc chloride had virtually no effect on the yield of the product (entries 1–5); the yield was increased somewhat by employing 2 equiv of the dichloroketene precursor (entries 6–8). Introduction of an electron-donating methyl group on the aromatic ring led to slightly reduced yields (19–26%) of the corresponding β-lactones relative to those obtained from benzaldehyde under comparable reaction conditions (entries 9, 10, 13, 14, and 17); again doubling the amount dichloloketene

resulted in higher yields of cycloadduct. Also, in the case of the tolualdehydes, it was found that ether is a better solvent than methylene chloride, pentane, or benzene (compare entires 11, 15, and 18 with 12, 16, and 19, respectively). With the electron-rich *p*-anisaldehyde the yield of the cycloaddition product (only the decarboxylated β,β-dichlorostyrene could be isolated; see Part B) was about 20% (entries 42 and 43). On the other hand, with *m*-anisaldehyde (which according to Hammett σ substituent constants should be slightly electron deficient relative to benzaldehyde[11]) the yield of β-lactone formation was 32–38% (entries 40 and 41). Results analogous to those obtained for the methoxybenzaldehydes were realized with the acetoxybenzaldehydes (entries 44–46). For the moderately electron-withdrawing chlorine substituents (entries 20–25) the yields of the corresponding isomeric β-lactones were significantly higher (51–59%) than those obtained with benzaldehyde. Yields of β-lactone products were further increased (64–85%) by the use of the strongly electron-withdrawing nitro or cyano functionalities (entries 26–37). In these cases it was necessary to utilize a mixed solvent system (ether/methylene chloride) in order to circumvent solubility problems encountered with ether alone. Again, it was observed that the presence of zinc chloride had little effect on the yields of β-lactones (except when 2 equiv were employed).

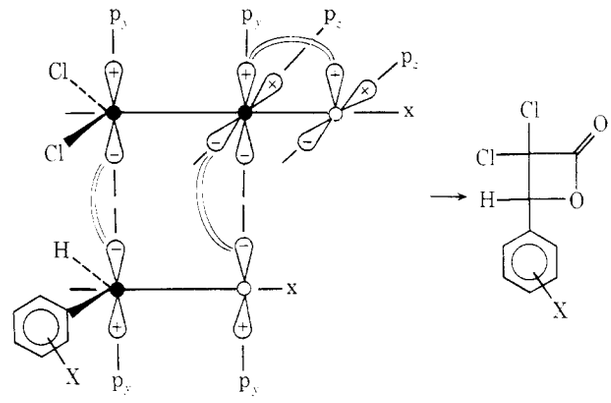
Clearly, the most striking feature of the data collected in Table I is the unmistakable trend that the *more electron withdrawing* the substituent on the benzaldehyde is, the *higher* the yield is for β-lactone formation. The observed reactivity trend is similar to that established for *nucleophilic* additions to carbonyl groups,[12] and suggests that the dichloroketene is behaving in a nucleophilic manner [i.e., the reaction takes place via the highest occupied molecular orbital (HOMO) of the dichloroketene and the lowest unoccupied molecular orbital (LUMO) of the monosubstituted benzaldehyde[13]]. Accordingly, the effects of the aryl substituents on the cycloaddition process are represented better by Scheme II than by Scheme I.[6]

A possible explanation for the interesting results obtained for the cycloaddition reactions tabulated in Table I is that dichloroketene is *not* the reactive species but rather that the chloroacetyldichloro carbanion initiates the cycloaddition process by nucleophilically attacking the aldehyde carbonyl group; subsequent or perhaps simultaneous displacement of the acyl chloride by the aldehyde oxygen would provide the β-lactone structure (Scheme III).[14] In order to test this interpretation, dichloroketene was generated at −78 °C *in the absence of benzaldehyde* by the addition of an ether solution of triethylamine to an ether solution of dichloroacetyl chloride, which resulted in the immediate precipitation of triethylamine hydrochloride; the dichloroketene solution was then filtered into a solution of benzaldehyde at −78 °C and the reaction mixture allowed to warm to room temperature. The 35% yield

Scheme III

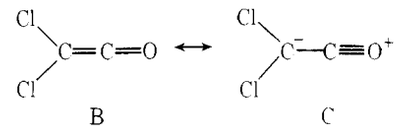


Scheme IV



of β-lactone **1a** from this experiment (Table I, entry 5) was essentially the same as the 32% yield (Table I, entry 1) of **1a** obtained when the reaction was carried out according to the general procedure (see the Experimental Section). Significantly, a nearly quantitative yield of the triethylamine hydrochloride by-product was isolated as the filtration residue. Therefore, it appears that dichloroketene is, in fact, the reactive intermediate in the cycloaddition process.

From the information presently available, it is not possible to ascertain whether the cycloadditions involving monosubstituted benzaldehydes and dichloroketene proceed in concerted or stepwise fashions. There is, of course, compelling evidence which indicates that the reactions between ketenes and double-bond-containing compounds to give four-membered cycloadducts take place in a concerted manner.[2,3,15] Of the two orbital symmetry-allowed processes (the $_{\pi}2_s + _{\pi}2_a$ process[15] and the $_{\pi}2_s + _{\pi}2_s + _{\pi}2_s$ process[2b]) currently relied upon to rationalize the results of ketene cycloadditions, the six-electron $_{\pi}2_s + _{\pi}2_s + _{\pi}2_s$ mechanism is particularly well suited to rationalize the remarkably sensitive substituent effects discovered in the present investigation. In this pictorial representation of the transition state (Scheme IV), an orbital containing a pair of nonbonding electrons from the ketene carbonyl oxygen overlaps with the p_y orbital of the central carbon of the ketene and imparts enhanced electron density to the terminal (chlorine-bearing) carbon of the ketene (thus providing the resonance hybrid C); overlap of the electron-rich



B C

p_y orbital of the terminal carbon of the ketene with the p_y orbital of the carbonyl carbon of the substituted benzaldehyde, followed immediately (or simultaneously if the process is absolutely concerted) by overlap of the p_y orbital of the carbonyl oxygen of the aldehyde with the p_z orbital of the central carbon of the ketene, leads to the β-lactone cycloadduct. The alternative $_{\pi}2_s + _{\pi}2_a$ concerted mechanism[15] cannot be ruled out; however, it would not appear to be able to account for the observed substituent effects in as satisfying a manner as the $_{\pi}2_s + _{\pi}2_s + _{\pi}2_s$ mechanism does.

Part B

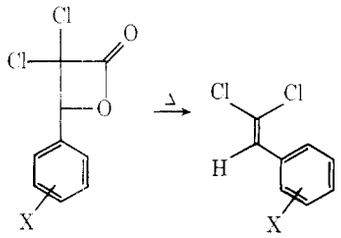
The thermally induced decarboxylation of a β-lactone is a very convenient and efficient synthetic method for the stereospecific introduction of a double bond in an organic molecule.[16] Previous studies have shown for 2-oxetanone itself that the thermal decomposition in the gas phase is a first-order reaction and produces *only* ethylene and carbon dioxide; in addition, the presence of nitric oxide has no effect on the reaction, implicating a nonradical pathway from reactant to

Table II. Experimental Conditions and Results for the Preparation of β,β-Dichlorostyrenes by the Decarboxylation of β-Lactones[a]

Compd	Registry no.	X	Temp, °C	Yield,[b] %	Bp, °C (Torr)	Mp, °C
1b	698-88-4	H	117	71	53–54 (0.25)[c]	
2b	65085-89-4	2′-CH_3	110	73	103–105 (2)	
3b	65085-90-7	3′-CH_3	95	78	117–125 (2)	
4b	4714-37-8	4′-CH_3	110	70	110–127 (2)[d]	35–37[e]
5b	56772-79-3	2′-Cl	165	69	63–64 (0.29)	
6b	65085-92-9	3′-Cl	168	66	69–70 (0.32)	
7b	5263-17-2	4′-Cl	165	78	71–72 (0.38)[f]	
8b	51991-50-5	2′-NO_2	120[g]	21		45–46
9b	65085-93-0	3′-NO_2	175[h]	73		53–55
10b	5281-22-1	4′-NO_2	175[h]	70		90–92[i]
11b	65085-94-1	4′-CN	175[h]	86		75–76
13b	65085-95-2	3′-OCH_3	87	74	156–158 (3)	
14b	41448-64-0	4′-OCH_3	24[j]	23	85–86 (0.50)[k]	27–29
15b	65085-97-4	3′-$OCOCH_3$	87	57		
16b	65085-91-8	4′-$OCOCH_3$	95	63		33–35

[a] See eq 2 for reaction. [b] Isolated yield (not optimized) of purified material. [c] Lit. ("Dictionary of Organic Compounds", 4th ed, Vol. 2, Oxford University Press, New York, N.Y., 1965, p 1000) 103–104 °C (15 Torr). [d] Lit.[20g] 110 °C (15 Torr). [e] Lit.[20a] 40–41 °C. [f] Lit.[20d] 138 °C (5 Torr). [g] In refluxing tetrachloroethylene. [h] In perchlorobuta-1,3-diene. [i] Lit.[20i] 93–94 °C. [j] Product isolated directly from the cycloaddition reaction (eq 1); see text. [k] Lit.[20l] 100 °C (12 Torr).

products.[17] Furthermore, for substrates wherein the stereochemistry of the reaction could be examined, it was found that the decarboxylations are stereospecific cis eliminations.[18] Finally, a few years ago, it was reported that halogenated 2-oxetanones are less susceptible toward decarboxylation than other 2-oxetanones.[19] In the present investigation it has been found that the nature and position of a substituent on the aromatic ring of a 3,3-dichloro-4-phenyloxetan-2-one exert substantial influence on the rate of decarboxylation (eq 2).



1a–16a 1b–16b (2)

As indicated in Part A, for the reaction involving *p*-methoxybenzaldehyde and dichloroketene, *only* the β,β-dichlorostyrene **14b** was isolated, demonstrating that the intermediate β-lactone **14a** is extremely susceptible toward decarboxylation, even at room temperature. On the other hand, it was found that for the *p*-nitrophenyl-substituted β-lactone **10a,** prolonged heating at 175–180 °C was necessary to carry out to completion the decarboxylative conversion to the desired β,β-dichlorostyrene **10b.** Clearly, substituent effects are very important for the reactions of eq 2. The other aryl-substituted β-lactones available in this study responded to thermal activation with decarboxylation performances within the limits mentioned above for **10a** and **14a** (Table II). In all cases (except for the *o*-nitrophenyl β-lactone **8a**) the decarboxylations proceeded smoothly and provided the β,β-dichlorostyrenes in good yields. The β,β-dichlorostyrenes were easily purified by distillation and/or chromatography, and their structures were established by a combination of spectral properties.[8,20]

Qualitatively, the following relative orders of susceptibility toward decarboxylation for the various families of isomeric substituents were found: *p*-$OCH_3 \gg m$-OCH_3; *p*-$CH_3 > m$-CH_3, *o*-CH_3; *p*-Cl > *m*-Cl, *o*-Cl; *p*-$NO_2 < m$-$NO_2 < o$-NO_2. Furthermore, it was qualitatively observed that *p*-$OCH_3 \gg$ *p*-$CH_3 >$ *p*-H > *p*-Cl $\gg$ *p*-NO_2.

In order to gain some quantitative insight on the nature of the substituent effects, the kinetics of the decarboxylation of the parent phenyl-substituted β-lactone **1a** and its three monochlorophenyl derivatives, **5a–7a**, were examined in detail. The rates of decarboxylation of these materials are of such magnitudes that they can be determined conveniently with NMR spectroscopy by measuring the disappearance of the singlet associated with the proton attached to carbon 4 of the β-lactone ring and the appearance of the singlet for the vinyl proton of the β,β-dichlorostyrene product. Fortunately, for **1a,b** and **5a,b–7a,b** the critical ^{1}H NMR signals were each easily recognizable and well separated from one another as well as from the signals for the aromatic protons. By employing this technique it was not necessary to employ an internal standard; furthermore, the small amounts of impurities present in the β-lactone starting materials did not interfere with the kinetic analyses. The experimental procedure utilized for the rate studies was adapted from the literature.[2b] The neat β-lactone, in an NMR tube, was placed in a constant temperature bath, heated for a definite period of time, placed in an ice water bath to quench the decarboxylation reaction, analyzed by recording the NMR spectrum and obtaining multiple integrations of the signals for the critical protons, and then returned to the constant temperature bath for further reaction.

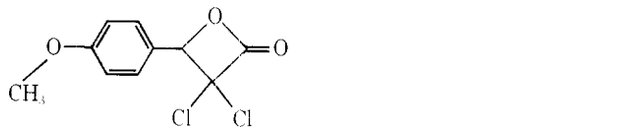
The results of the kinetics experiments are presented in Table III. The first-order rate constants were obtained from least-squares plots of the data. The thermodynamic properties (Table IV) of the decarboxylation reactions were calculated from the Arrhenius equation plots. A plot of the logarithms of the rate constants vs. σ^+ substituent constants[21] gave a least-squares line (r = 0.998) with a slope (ρ value) of −3.07.[22] The sign and magnitude of ρ indicate the accumulation of considerable positive character at the benzylic carbon in the transition state of the decarboxylation reaction; the fact that a linear correlation of the rate was obtained with σ^+ constants indicates that substituents can interact via resonance with the reactive site. These considerations are suggestive of a mechanistic interpretation like that shown in Scheme V (illustrated with the *p*-methoxyphenyl system). That the dipolar species **14c** is the transition state for the decarboxylation reaction is indicated by $\Delta S^{\ddagger}$ values (Table IV) which are virtually zero, consistent with a concerted unimolecular elimination process.[23] Furthermore, attempts to intercept the dipolar species **7c** with either electron-rich or electron-deficient olefins (*n*-

Table III. Rate Constants for the Decarboxylation of 3,3-Dichloro-4-phenyloxetan-2-one and Its Three Monochlorophenyl Derivatives at Various Temperatures[a,b]

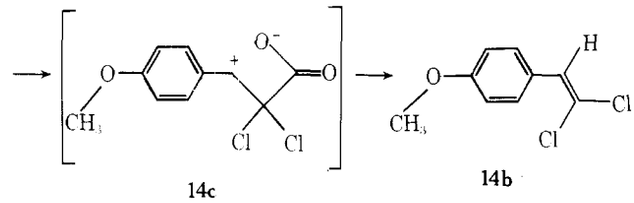
Compd	X	Temp, °C	$10^5 k$, s^{-1}	r[c]
1a	H	76	1.92	0.998
1a	H	82	3.06	0.998
1a	H	85	3.69	0.998
5a	2′-Cl	104	0.294[d]	0.997
5a	2′-Cl	130	2.81	0.997
5a	2′-Cl	144	7.61[e]	0.994
6a	3′-Cl	86	0.222[f]	0.991
6a	3′-Cl	104	1.03	0.997
6a	3′-Cl	130	7.61	1.000
7a	4′-Cl	72	1.29	0.999
7a	4′-Cl	86	2.52	0.997
7a	4′-Cl	88	2.74	1.000
7a	4′-Cl	98	6.00[g]	0.989

[a] See eq 2 for reaction. [b] The estimated precision for the rate constants is ±4% or better except as noted. [c] Correlation coefficient for least-squares plots of rate data. [d] The estimated precision is ±11%. [e] The estimated precision is ±6%. [f] The estimated precision is ±14%. [g] The estimated precision is ±9%.

Scheme V

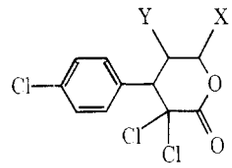


14a



14c 14b

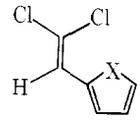
butyl vinyl ether or methyl acrylate, respectively) and produce the substituted valerolactones **17** were unsuccessful; *only* the



17a, X = H; Y = CO_2CH_3
b, X = OC_4H_9; Y = H

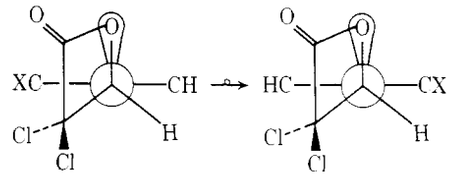
β,β-dichlorostyrene **7b** was produced in each experiment.[24,25]

In line with the facile decarboxylation of the *p*-methoxyphenyl β-lactone **14a** are the results for the cycloaddition reactions of dichloroketene with furfural or thiophene 2-carboxaldehyde. In each case *only* the decarboxylated materials **18b** and **19b** were isolated from the reaction mixtures, reflecting the electron-donating abilities via resonance of the heteroatoms. The low yields (9% for **18b** and 17% for **19b**) are also in accord with the electronic effects discussed previously in Part A.



18b, X = O
19b, X = S

The low relative rate of decarboxylation found for the *o*-chlorophenyl β-lactone is interesting. In order for the aromatic system to interact via resonance with the electron-deficient benzylic carbon and thus to facilitate the decarboxylation, the conformation of the β-lactone must approach that shown in Newman projection I (or its rotational isomer II). For the



I II

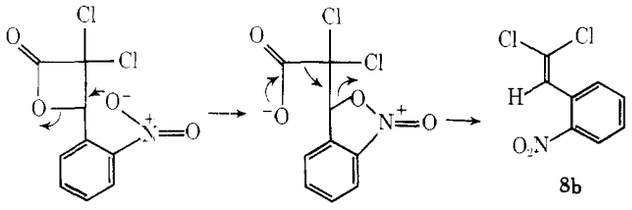
meta- and para-substituted substrates, X in formulas I and II is hydrogen; but for the ortho-substituted derivative, X is the substituent, and accordingly additional steric strain is imparted to the system. Apparently, this enhanced steric hindrance [between the substituent and either the dichloromethylene unit (I) or the β-lactone hydrogen (II)] is sufficiently great so as to drastically diminish any resonance stabilization of the transition state; only the electron-withdrawing inductive effect of the chlorine remains operative, and therefore the rates of decarboxylation of the *o*- and *m*-chlorophenyl-substituted β-lactones are quite similar. In contrast to the isomeric chlorophenyl-substituted β-lactones are the decarboxylations of the isomeric nitrophenyl derivatives. Both the *m*- and *p*-nitro systems **9a** and **10a** were totally unreactive when heated for several hours in refluxing tetrachloroethylene (bp 120 °C); on the other hand, the *o*-nitrophenyl compound **8a** underwent decarboxylation under these conditions. However, the decarboxylation of **8a** was not very clean and only a 21% yield of the β,β-dichlorostyrene **8b** was obtained; this result may be compared to the decarboxylations of **9a** and **10a** which took place smoothly in hexachlorobutadiene at 175–180 °C to give the β,β-dichlorostyrenes **9b** and **10b** in yields of 73 and 70%, respectively. It should also be noted that β-lactone **8a** decomposes to an intractable material merely upon standing (even in a freezer), while **9a** and **10a** are indefinitely stable at room temperature. Perhaps the proximity of the *o*-nitro group to the β-lactone is responsible for both its relatively facile decarboxylation to the β,β-dichlorostyrene

Table IV. Absolute and Relative Rates and Thermodynamic Values for the Decarboxylation of 3,3-Dichloro-4-phenyloxetan-2-one and Its Three Monochlorophenyl Derivatives at 100 °C[a,b]

Compd	X	$10^5 k$, s^{-1}	k_{rel}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol K)	r[c]
1a	H	10.4	50	17.4	5.07×10^{-4}	0.999
5a	2′-Cl	0.208	1	24.7	1.91×10^{-1}	0.999
6a	3′-Cl	0.647	3	17.1	3.09×10^{-2}	1.000
7a	4′-Cl	5.92	28	13.9	2.59×10^{-6}	0.982

[a] See eq 2 for reaction. [b] Values for the rate constants were extrapolated from the data presented in Table III. [c] Correlation coefficient for least-squares plots of the Arrhenius equation.

Scheme VI



8a 8b

(Scheme VI) and its spontaneous decomposition to uncharacterized materials.

Experimental Section

Materials. Benzaldehyde, *o*-, *m*-, and *p*-chlorobenzaldehyde, *o*-, *m*-, and *p*-tolualdehyde, and *o*-, *m*-, and *p*-anisaldehyde were commercially available and were distilled before use; *o*-, *m*-, and *p*-nitrobenzaldehyde and *p*-cyanobenzaldehyde were commercially available and were used without prior treatment; *m*- and *p*-acetoxybenzaldehyde were prepared and purified according to literature methods.[26] Dichloroacetyl chloride was commercially available and used as received.

General Comments. Melting points, obtained with a Thomas-Hoover capillary melting point apparatus, and boiling points are uncorrected. ^{1}H NMR spectra were obtained with a Varian Associates T-60 instrument employing deuteriochloroform solutions with internal tetramethylsilane (Me_4Si) as reference. ^{13}C NMR spectra were obtained with a Varian CFT-20 spectrometer utilizing ^{1}H decoupling at 80 MHz and simultaneous ^{13}C observation at 20 MHz; in all cases the solvent was deuteriochloroform with internal Me_4Si. Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer; liquid samples were measured as neat films, while solid materials were measured as approximately 10% solutions in chloroform. Mass spectra were obtained with a Du Pont CEC 21104 mass spectrometer operated at 70 eV and ambient source temperatures. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer. High-pressure liquid chromatography was performed with (1) a Waters Associates ALC-201 HPLC fitted with a 4 ft × 3/8 in. stainless steel column packed with Porasil-A using CH_2Cl_2 as solvent or (2) a Waters Associates Prep 500 system equipped with a PrepPak-500/silica column with 2:1 hexane/methylene chloride as the solvent system. Gas chromatographic analyses and collections were carried out with a Varian Aerograph 1520 instrument equipped with a 5 ft × 0.25 in. aluminum column packed with 20% SE-30 on Chromosorb W.

General Procedure for β-Lactone Preparation. To a 500-mL three-necked round-bottomed flask equipped with an addition funnel charged with 15.0 mL (10.89 g, 0.108 mol) of anhydrous triethylamine diluted to 50 mL with anhydrous diethyl ether, a mechanical stirrer, and a Claisen adapter fitted with a thermometer and an Allihn condenser whose efflux end was connected to a nitrogen bubbler was added 0.100 mol of aldehyde, 100 mL of anhydrous ether, a specified amount of fused $ZnCl_2$,[27] 100 mL of anhydrous diethyl ether, 10.0 mL (15.32 g, 0.104 mol) of dichloroacetyl chloride, and 20 mL of anhydrous diethyl ether. The temperature of the reaction mixture was maintained at 22–24 °C with a room temperature water bath or at 3–5 °C with an ice water bath. With vigorous stirring under a nitrogen atmosphere the triethylamine solution was discharged dropwise over an approximately 1-h period of time. When addition was complete, the mixture was stirred for an additional 1 h, after which time the reaction was processed by vacuum filtration, the residue was washed with diethyl ether, and the combined filtrate and washings were washed with water (1 × 50 mL), dried with anhydrous magnesium sulfate, and concentrated on a rotary evaporator to provide the crude product (contaminated with dichloroketene polymeric materials, unreacted aldehyde, and other minor unidentified impurities) which was treated with a total of 200 mL of pentane to remove polymeric materials. The resulting pentane solution was then washed with H_2O (1 × 50 mL), saturated aqueous sodium bisulfite solution (4 × 50 mL), H_2O (1 × 50 mL), and saturated aqueous sodium bicarbonate solution (2 × 50 mL), dried over anhydrous magnesium sulfate, stirred with activated carbon, and concentrated on a rotary evaporator to provide the desired β-lactone.

For the nitrophenyl and cyanophenyl systems the reaction solvent was 100 mL of methylene chloride and 175 mL of ether in order to circumvent the insolubility of the starting aldehyde in ether alone. In addition, in the processing of the β-lactones **8a–11a, 15a,** and **16a,** ether rather than pentane was used because of solubility considerations.

General Procedure for Decarboxylation of β-Lactones. In a round-bottomed flask equipped with a condenser and a magnetic stirring bar was placed an amount of a β-lactone. The flask was placed in a heated oil bath until NMR/IR spectra revealed that the reaction was complete. The β,β-dichlorostyrene was then isolated and purified by distillation or chromatography.

For the nitrophenyl and cyanophenyl systems the decarboxylations were carried out in chlorocarbon solvents (tetrachloroethylene for **8a** and perchlorobutadiene for **9a–11a**) since attempts to effect the reaction with the pure materials led only to intractable products.

Registry No.—18b, 65085-98-5; **19b,** 65085-96-3; benzaldehyde, 100-52-7; *o*-chlorobenzaldehyde, 89-98-5; *m*-chlorobenzaldehyde, 587-04-2; *p*-chlorobenzaldehyde, 104-88-1; *o*-tolualdehyde, 529-20-4; *m*-tolualdehyde, 620-23-5; *p*-tolualdehyde, 104-87-0; *o*-anisaldehyde, 135-02-4; *m*-anisaldehyde, 591-31-1; *p*-anisaldehyde, 123-11-5; *o*-nitrobenzaldehyde, 552-89-6; *m*-nitrobenzaldehyde, 99-61-6; *p*-nitrobenzaldehyde, 555-16-8; *p*-cyanobenzaldehyde, 105-07-7; *m*-acetoxybenzaldehyde, 34231-78-2; *p*-acetoxybenzaldehyde, 878-00-2; dichloroketene, 4591-28-0.

Supplementary Material Available: Spectral and analytical data for the β-lactones **1a–16a** and β,β-dichlorostyrenes **1b–16b** (12 pages). Ordering information is given on any current masthead page.

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Substituent Effects on Reductive Cleavage of *N*-Methylarenesulfonanilides. Cleavage by Sodium Anthracene and Electrochemically at the Vitreous Carbon Electrode

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The relative rates of cleavage of ten para-substituted *N*-methylbenzenesulfonanilides by sodium anthracene in tetrahydrofuran at 25 °C were determined. The rates of those with less electronegative substituents (*p*-dimethylamino through *p*-fluoro) give a moderately good correlation with σ constants, $\rho = 1.91$ ($r = 0.987$). More strongly electron-withdrawing substituents, however, result in a cleavage rate much slower than expected due to reduction of the substituent rather than of the sulfonyl group. Electrochemical reduction in acetonitrile solution at a vitreous carbon electrode proceeds via an irreversible two-electron process. The peak potentials of all the sulfonamides give an excellent correlation with σ^n constants, $\rho = 1.07$ V ($r = 0.995$). Whether this is an eec or ece process is discussed, as well as possible causes for the large differences between homogeneous and electrochemical reduction. A suggested value of σ^n for the *p*-methanesulfinyl group is +0.54.

Arenesulfonamides of secondary amines have been investigated in considerable detail with respect to their reductive cleavage reactions.[2-6] Manousek, Exner, and Zuman showed that 4-cyanobenzenesulfonamide undergoes electrochemical cleavage in aqueous solution at the carbon–sulfur bond (eq 1),[5] while Cottrell and Mann observed only S–N cleavage in

$$ArSO_2NH_2 + 2e + H^+ \rightarrow ArH + {}^-SO_2NH_2 \xrightarrow{H_2O} HSO_3^- + NH_3 \quad (1)$$

electrochemical reduction of several arenesulfonamides in acetonitrile.[4] They proposed an irreversible, two-electron reduction followed by rapid cleavage to two anions (eq 2).

$$ArSO_2NR_2 \xrightarrow{2e} ArSO_2NR_2^{2-} \rightarrow ArSO_2^- + {}^-NR_2 \quad (2)$$

Asirvatham and Hawley noted that Cottrell and Mann's results could also be explained by either the *ece* mechanism shown in eq 3, where the nitrogen- or oxygen-centered radical

$$ArSO_2NR_2 \xrightarrow{e} (ArSO_2NR_2)^{-\cdot} \longrightarrow \begin{cases} ArSO_2^- + \cdot NR_2 \\ \text{or } ArSO_2\cdot + {}^-NR_2 \xrightarrow{e} ArSO_2^- + {}^-NR_2 \end{cases} \quad (3)$$

would be rapidly reduced at a potential less cathodic than that of the initial reduction, or by a rate-determining disproportionation process (eq 4).[5] Either of these processes would

$$2(ArSO_2NR_2)^{-\cdot} \xrightarrow{slow} ArSO_2NR_2^{2-} + ArSO_2NR_2 \xrightarrow{fast} ArSO_2^- + {}^-NR_2 \quad (4)$$

account for the products and n values reported.[4] The only arenesulfonamide of a secondary amine (*N*,*N*-dimethylnitrobenzenesulfonamide) examined by Asirvatham and Hawley, however, underwent reversible, stepwise reduction, yielding the corresponding dianion.[5] Cleavage to amine was not reported.[5]

Kovacs and Ghatak reported that sodium–liquid ammonia reduction of tosylamides leads primarily to C–S cleavage, similar to the results of Manousek et al.,[5] but with a minor pathway involving S–N cleavage.[2] From their data it was not possible to ascertain more information on the mechanism of cleavage. One might expect that reduction of arenesulfonamides with arene anion radicals in ether solvents might proceed in a fashion similar to that in liquid ammonia, but our earlier work using sodium biphenyl, naphthalene, and anthracene in tetrahydrofuran (THF) and dimethoxyethane (DME) showed only the occurrence of S–N cleavage.[3] In addition though we found that the selectivity of cleavage of arenesulfonamides in competition experiments was quite different for sodium anthracene vs. sodium naphthalene.[3] This observation rules out a disproportionation mechanism similar to eq 4 and would be best explained by a mechanism similar to eq 3, where the initial electron transfer is rate determining. Further study of the relative reactivities of different sulfonamides toward sodium anthracene, which would have been useful in refining the cleavage mechanism, was hampered by poor reproducibility.

In this work we wish to present a study of the relative rates of cleavage of a series of *N*-methylarenesulfonanilides by sodium anthracene in THF, a cyclic voltammetric study of the redox behavior of the same series of sulfonamides using the vitreous carbon electrode in acetonitrile, and a discussion of the similarities and differences of these two types of reduction.

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