*Anal.* Calcd for *p*-toluidine product (**18**): C, 57.12; H, 4.26; N, 7.40; Cl, 31.22. Found: C, 56.53; H, 4.08; N, 7.33; Cl, 32.05.

**Reaction of 1 with Dimethylamine.**—A 250-ml portion of a saturated (10 *M*) solution of dimethylamine in isopropyl alcohol was slowly added to a well-stirred solution of 28.8 g (0.08 mol) of **1** in 250 ml of tetrahydrofuran. The reaction mixture was evaporated to dryness and treated with methylene chloride. The mixture was filtered and the filtrate was evaporated to afford a solid which was crystallized from chloroform–hexane to yield pale yellow crystals, mp 166–167°, of *N,N,N',N'*-tetramethyl-2-dimethylamino-3,3-dichloro-4-dichloromethylenecyclobutenylcarboxamidinium chloride (**16**): $\lambda_{max}$ 273 mμ (ε 25,300), 372 (6100); ir (KBr) 3.42 (CH), 5.86 (C═C), 6.15 μ (C═C, amidinium); nmr ($CDCl_3$) τ 6.51 (s, 6 H), 6.61 (s, 3 H), 6.71 (s, 6 H), 6.74 (s, 3 H); nmr ($D_2O$) τ 6.60 (s, 3 H), 6.74 (s, 6 H), 6.84 (s, 6 H), 6.96 (s, 3 H); mass spectrum (70 eV) *m/e* 329.

*Anal.* Calcd for $C_{12}H_{18}N_3Cl_5 \cdot H_2O$: C, 36.07; H, 5.05; N, 10.52. Found: C, 35.93; H, 4.96; N, 10.58.

**Reaction of 1 with Phenylhydrazine.**—A solution of 6.05 g (56.0 mmol) of phenylhydrazine in 200 ml of tetrahydrofuran was added dropwise, under a stream of nitrogen, over a period of 2 hr, to a well-stirred solution of 5.0 g (14 mmol) of **1** in 200 ml of tetrahydrofuran. The precipitate which deposited (phenylhydrazine hydrochloride) was removed by filtration. The filtrate was concentrated and chromatographed on Silicar CC-7. Elution was performed with increasing concentrations of chloroform in carbon tetrachloride. Isolated from the column were orange crystals, mp 130°, of 2-phenyl-3,4-(3,3-dichloro-4-dichloromethylene)cyclobuteno-5-chloropyrazole (**22**): $\lambda_{max}$ 240 mμ (ε 6200), 420 (5200); ir (KBr), 5.92 (C═C), 6.20 (C═C), 6.58 μ (pyrazole); mass spectrum (70 eV) *m/e* 352.

*Anal.* Calcd for $C_{12}H_5N_2Cl_5$: C, 40.56; H, 1.42; N, 7.90; Cl, 50.01. Found: C, 40.76; H, 1.26; N, 8.04; Cl, 50.02.

**Reaction of 1 with Excess Phenylhydrazine.**—A solution of 13.0 g (120 mmol) of phenylhydrazine in 200 ml of ethyl ether was added dropwise, under a stream of nitrogen, over a period of 2 hr, to a well-stirred solution of 7.12 g (20 mmol) of **1** in 200 ml of ethyl ether. The precipitate was filtered, washed with water to remove phenylhydrazine hydrochloride, and crystallized from carbon tetrachloride–hexane to yield orange crystals, mp 158° of **23**, ir (KBr) 2.90, 3.00, 6.24, 6.64, 8.02, 8.48, 13.35, and 14.58 μ.

*Anal.* Calcd for $C_{18}H_{12}N_4Cl_4$: C, 50.73; H, 2.84; N, 13.15; Cl, 33.28. Found: C, 50.57; H, 3.07; N, 13.02; Cl, 32.93.

**Registry No.**—**1**, 1680-65-5; **8**, 38400-90-7; **9**, 38400-91-8; **10**, 38400-92-9; **11**, 38400-93-0; **12**, 38400-94-1; **13**, 38400-95-2; **14**, 38400-96-3; **15**, 38400-97-4; **16**, 38400-98-5; **17**, 38400-99-6; **20**, 38583-52-7; **21**, 38401-00-2; **21** (HCl), 38401-03-5; **22**, 38401-01-3; **23**, 38401-02-4; ammonia, 7664-41-7; isopropylamine, 75-31-0; aniline, 62-53-3; dimethylamine, 124-40-3; phenylhydrazine, 100-63-0.

**Acknowledgment.**—Robert Shapiro is the holder of a Public Health Service Career Development Award from the National Institute of General Medical Sciences.

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# Effect of Geometry and Substituents on the Electrochemical Reduction of Dibenzoylethylenes and Dibenzoylcyclopropanes

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*Received August 24, 1972*

The electrochemical reduction of the geometric isomers of dibenzoylethylene, dibenzoylstyrene, dibenzoylstilbene, dibenzoylcyclopropane, dibenzoylphenylcyclopropane, and dibenzoyldiphenylcyclopropane has been investigated by polarographic and cyclic voltammetric techniques. The polarographic waves were complicated by maxima; hence discussion and conclusions are based on the cyclic voltammetric results. The *cis*- and *trans*-dibenzoylethylenes show a remarkable 267-mV difference in ease of reduction. The dibenzoylethylenes become more difficult to reduce upon successive addition of phenyl groups. The difference between reduction of the geometric isomers of the dibenzoylethylenes reverses from the trans reducing at the more positive potential for dibenzoylethylene to the cis reducing at the more positive potential for dibenzoylstilbene. No discernible trends are observed for the dibenzoylcyclopropanes. The effects of structural changes on reduction potential are discussed.

Chemical reduction of dibenzoylethylenes has been extensively studied by Lutz and coworkers;[2,3] however, the analogous dibenzoylcyclopropanes have received considerably less attention.[4] The reduction of *cis*- and *trans*-dibenzoylethylene by a variety of reducing agents has not shown a demonstrable difference in ease of reduction of these isomers;[3] however, the marked liability of the cis isomer under the reaction conditions suggests that the relative ease of reduction of the cis isomer has not been assessed.[2b,3] On the other hand, preferential and facile reduction of *cis*- over *trans*-dibenzoylstilbene has been observed with $NaBH_4$, $LiAlH_4$, $PCl_3$, and aluminum isopropoxide.[2b,5] These results have been explained in terms of a "cis-group effect" which presumably arises in part as a result of dipole–dipole interactions of the proximate carbonyl groups and in part from reductions in π-orbital overlap in the cis isomer due to steric crowding. In contradistinction to the above reagents, Zn–HOAc, $SnCl_2$–HOAc–HCl, and sodium hydrosulfite reduce both isomers with apparently comparable ease.[2b,3a] Such differences do not appear to have been reported in the cyclopropane systems. Quantitative assessment of the relative ease of reduction by electrochemical methods should add to the understanding of the reduction of these unsaturated ketones.

There have been only a limited number of investigations comparing the effect of geometry on ease of electrochemical reduction for stereoisomers. *cis*- and *trans*-

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[1] This work represents a partial fulfillment of the requirements for the B.S. degree by W. F. W.

[2] (a) W. M. Hankins, R. E. Lutz, E. L. Anderson, M. G. Hankins, and D. W. Boykin, Jr., *J. Org. Chem.*, **35**, 2934 (1970); (b) R. E. Lutz and W. J. Welstead, Jr., *J. Amer. Chem. Soc.*, **85**, 755 (1963); (c) C. K. Dien and R. E. Lutz, *J. Org. Chem.*, **21**, 1492 (1956); (d) R. E. Lutz and M. G. Reese, *J. Amer. Chem. Soc.*, **81**, 127 (1959).

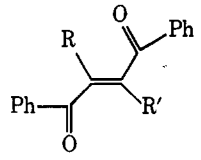
[3] (a) R. E. Lutz and C. R. Bauer, *ibid.*, **73**, 3456 (1951); (b) R. E. Lutz and J. S. Gillespie, Jr., *ibid.*, **72**, 344 (1950).

[4] (a) J. B. Conant and R. E. Lutz, *ibid.*, **49**, 1083 (1927); (b) E. P. Kohler and W. N. Jones, *ibid.*, **41**, 1249 (1919).

[5] R. E. Lutz, C. R. Bauer, R. G. Lutz, and J. S. Gillespie, *J. Org. Chem.*, **20**, 218 (1955).

Table I

$E_{1/2}$ (−V) Values at the Dropping Mercury Electrode (DME)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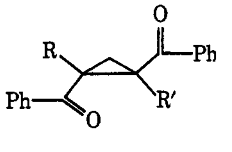
3

| | 2 | | | 3 | | |
|---|---|---|---|---|---|---|
| R, R′ | trans[a] | cis[a] | Δ[b] | trans[a] | cis[a] | Δ[b] |
| H, H | 0.87 (959-28-4) | 1.11 (959-27-3) | 0.24 | 1.43 (38400-84-9) | 1.49 (3238-03-7) | 0.06 |
| H, Ph | 1.20 (34880-76-7) | 1.18 (13249-75-7) | −0.02 | 1.45 (30698-22-7) | 1.48 (30698-21-6) | 0.03 |
| Ph, Ph | 1.18 (10496-80-7) | 1.19 (6313-26-4) | 0.01 | 1.51 (38400-88-3) | 1.44 (38400-89-4) | −0.08 |

[a] Registry numbers are given in parentheses. [b] $\Delta = E_{1/2}(\text{cis}) - E_{1/2}(\text{trans})$.

stilbene have been reduced electrochemically in DMF[6] and $CH_3CN$;[7] the $E_{1/2}$ values were −2.07 V cis and −2.08 V trans in DMF and −1.87 V cis and −1.73 V trans in $CH_3CN$. It appears that in this system there is little difference in the ease of reduction of the isomers. A study of fumaric and maleic acid and their esters in pyridine showed that the trans isomers were reduced at slightly more positive potentials.[8] On the other hand, fumaronitrile is reduced at a more negative value than maleonitrile, and *trans*-crotononitrile is reduced at a more negative value than *cis*-crotononitrile in aqueous media.[9] The easier reduction of these cis isomers was attributed to adsorption on the electrode.[9] The reduction of *cis*- and *trans*-dibenzoylethylenes in aqueous media shows that the trans isomer is more readily reduced than the cis isomer, $E_{1/2}$(trans) −0.46 V and $E_{1/2}$(cis) − 0.75 V.[10a,b]

As part of a continuing investigation[11] of the nonaqueous electrochemistry of $\alpha,\beta$-unsaturated ketones, we have measured the polarographic half-wave potentials and the $E_{p/2}$ values from cyclic voltammetry for three sets of isomeric dibenzoylethylenes and dibenzoylcyclopropanes in an attempt to quantitatively assess the differences in ease of reduction in these systems. The geometric sets we have examined were also selected in order to assess the effect on reduction of systematic addition of phenyl groups to the double bond and the cyclopropane ring in these 1,4-diketone systems.

## Results

**Polarography.**—The reduction of *trans*-dibenzoylethylene at the dropping mercury electrode in DMF exhibited two well-defined waves and exhibited no maxima. A plot of the log $[i/(id - i)]$ *vs.* $E$ for the first wave yielded a straight line with a slope equaling 0.059, indicating that the reduction is a one-electron process. The presence of a stable free radical was confirmed by esr.[12] The polarograms for most of the other compounds studied were complicated by maxima. A typical example of the maxima problems encountered is shown in Figure 1. In an attempt to eliminate the polarographic maxima phenomena, limited studies altering various electrochemical parameters were undertaken. Changing the solvent to DMSO, altering the supporting electrolyte from TEAP to tetrabutylammonium iodide, and limited investigations employing the surfactants Triton-X and gelatin did not appreciably alter the appearance of the polarographic waves. Because of these problems the $E_{1/2}$ data presented in Table I are, doubtlessly, only rough estimates of the relative reduction half-wave potentials of these compounds; nevertheless, they may be used in a qualitative manner. Since it was the original objective of this investigation to accurately measure the $E_{1/2}$ values for the geometric isomers, an alternate method for assessing their reduction potentials was sought.

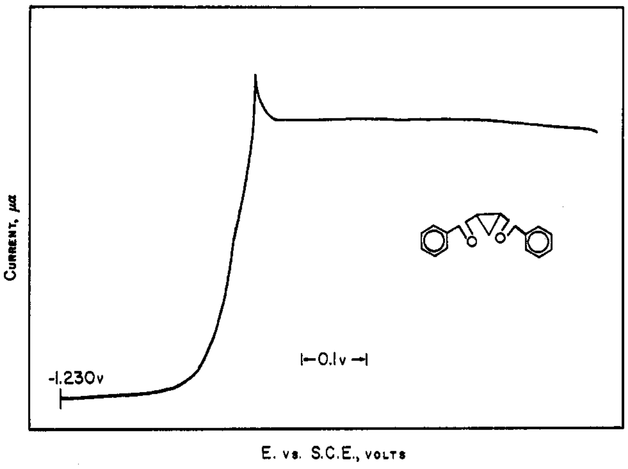

Figure 1.—Polarogram of *cis*-dibenzoylcyclopropane.

**Cyclic Voltammetry.** In spite of the fact that frequently the data obtained by linear sweep voltammetry at the hanging drop electrode (HDE) are less accurate than those obtained at the DME, the measurement is far less time consuming. The half-peak potential ($E_{p/2}$) while not directly relatable to the formal reduction potential, unless the exact electrode mechanism is known, is nevertheless experimentally a most useful measurement of the relative ease of oxidation or reduction. Also, additional information about reactive intermediates and chemical follow-up reactions is often obtained by reversing the voltage scan (cyclic voltammetry) and observing the oxidation of the reduction product(s) which has accumulated at the station-

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(6) S. Wawzonek, E. W. Blaha, R. Berkey, and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955).

(7) P. G. Grodzka and P. J. Elving, *ibid.*, **225**, 231 (1963).

(8) R. Takahashi and P. Elving, *Electrochim. Acta*, **12**, 213 (1967).

(9) S. K. Smirov, I. G. Sevast'yanov, A. P. Tomilov, L. A. Fedorova, and O. G. Strukov, *Zh. Org. Khim.*, **5**, 1392 (1969); *Chem. Abstr.*, **71**, 108455d (1969).

(10) (a) H. Keller, R. Pasternak, and H. V. Halban, *Helv. Chim. Acta*, **29**, 512 (1946). (b) R. Pasternak, *ibid.*, **31**, 753 (1948). (c) *Cf.* reduction of *trans*-dibenzoylethylene in DMF: R. H. Phillip, Jr., R. L. Flurry, and R. A. Day, Jr., *J. Electrochem. Soc.*, **111**, 328 (1964).

(11) M. L. Ash, F. L. O'Brien, and D. W. Boykin, Jr., *J. Org. Chem.*, **37**, 106 (1972).

(12) F. L. O'Brien, unpublished results.

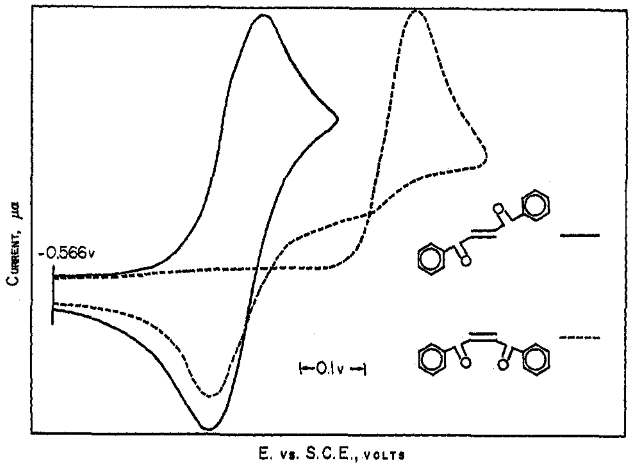

Figure 2.—Cyclic voltammograms of *cis*- and *trans*-dibenzoylethylene.

ary electrode. The magnitude of the anodic response for reversible electron transfer, followed by an irreversible chemical reaction, is directly relatable to the half-life of the product of electron transfer (*e.g.*, the anion radical).[13a,b] It is expected by analogy with other α,β-unsaturated ketones[13c] that this type of process is important here.

Frequently, when polarographic maxima occur, adsorption peaks are observed at the HDE, which may be accompanied by a significant shift in the potential for the normal reduction wave. Only one compound, *trans*-dibenzoylstyrene, of the 12 studied exhibited a current-voltage curve with adsorption peaks. The values for $E_{p/2}$ for the six sets of geometric pairs are listed in Table II.

TABLE II

$E_{p/2}$ (−V) VALUES AT THE HDE

| | 2 | | | 3 | | |
|---|---|---|---|---|---|---|
| R, R′ | trans | cis | Δ[a] | trans | cis | Δ[a] |
| H, H | 0.89 | 1.15 | 0.27 | 1.43 | 1.50 | 0.07 |
| H, Ph | 1.19 | 1.19 | 0.00 | 1.46 | 1.48 | 0.02 |
| Ph, Ph | 1.22 | 1.19 | −0.03 | 1.45 | 1.50 | 0.05 |

[a] $\Delta = E_{p/2}(\text{cis}) - E_{p/2}(\text{trans})$.

## Discussion

There is a good qualitative parallel between the reduction potential values obtained by the two different electrochemical methods employed. The only serious discrepencies between the techniques are for the diphenyldibenzoylethylene and -cyclopropane pairs. In spite of this general agreement, this discussion will assume, owing to uncertainty in the DME values caused by maxima problems, that the data obtained by the HDE techniques are more reliable.

**Dibenzoylethylenes.**—Examination of the $E_{p/2}$ values for the dibenzoylethylene series reveals interesting trends. First, it is observed that for both cis and trans isomers, albeit not so pronounced in the cis series, the successive addition of a phenyl group to the ethylene carbon results in a successive shift in $E_{p/2}$ to a more negative value. However, the addition of the second phenyl group does not produce as large an effect as the first, and, therefore, a simple incremental effect of addition of a phenyl group is not observed. It is evident in this series that the inductive effect of the added phenyl group is not playing a predominate role in determining the $E_{p/2}$ values. The negative shift suggests that the important influence on the ease of reduction by the addition of a phenyl group to this system is to decrease stability of the presumed intermediate anion radical, which should be brought about by a decrease in coplanarity as a result of increased steric crowding.

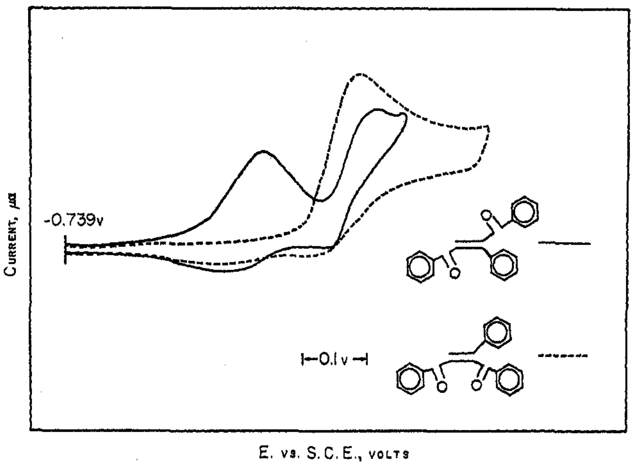

Figure 3.—Cyclic voltammograms of *cis*- and *trans*-dibenzoylstyrene.

The second interesting trend is seen by considering the effect on the Δ values [$\Delta = E_{p/2}(\text{cis}) - E_{p/2}(\text{trans})$] for the isomer with successive addition of a phenyl group to the parent system. The trans isomer of dibenzoylethylene is reduced in DMF at 267 mV less negatively than the cis isomer, which is of the same order of magnitude of the difference in aqueous media,[10a,b] an isomeric difference in ease of reduction which is without precedent! The addition of a single phenyl group to the parent system, forming the dibenzoylstyrene system, results in a leveling out of the differences between the isomers as shown by a Δ value of −5 mV. And finally, the addition of two phenyl groups to the system, to form the dibenzoylstilbene system, produced a reversal of the ease of the reduction. The cis isomer is reduced at a potential 32 mV less negative than the trans. In a series of geometric nitriles in which the cis isomers were reduced at more positive potentials than the trans isomers, the reversal was attributed to absorption phenomenon and intermoleculcar interactions.[9] No complicating maxima are seen in the current-voltage curves for *cis*- and *trans*-dibenzoylstilbene (see Figure 4). One plausible explanation for this reversal could be that in the dibenzoylstilbene case a special influence may be operative which stablizes the anion radical for *cis*-dibenzoylstilbene and therefore could account for the easier reduction of the cis than the trans isomer (*vide infra*).

Anodic sweep of the cyclic voltammograms of each isomer of the geometric sets provides additional information concerning the stability of the anion radicals produced on reduction. In Figure 2, for the dibenzoylethylene pair, it can be seen for the trans isomer

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(13) (a) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964); (b) E. R. Brown and R. F. Large in "Techniques of Chemistry, Physical Methods of Chemistry," *Vol. I, Part IIA*, A. Weissberger and B. W. Rossiter, Ed., Wiley-Interscience, New York, N. Y., 1971, Chapter 6; (c) J. P. Zimmer, J. A. Richards, J. C. Turner, and D. H. Evans, *Anal. Chem.*, **43**, 1000 (1971).

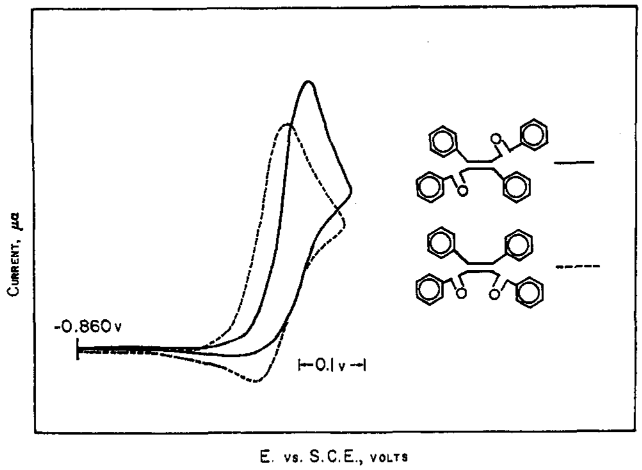


Figure 4.—Cyclic voltammograms of *cis*- and *trans*-dibenzoylstilbene.

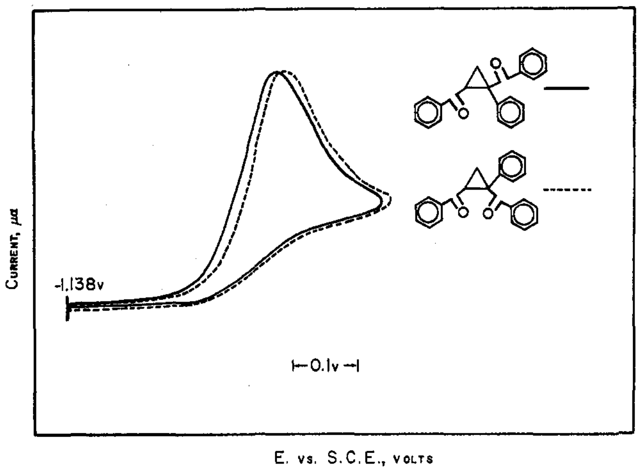
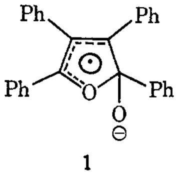


Figure 5.—Cyclic voltammograms of *cis*- and *trans*-phenyldibenzoylcyclopropane.

that reduction produces a relatively stable radical, whose esr signal has been observed[12] and which can be reoxidized at the expected potential. On the other hand, the absence of the reverse anodic wave suggests that the radical anion produced by reduction of the cis isomer is unstable and does not survive to be reoxidized. However, an oxidation wave is observed at the potential coinciding with that of the presumed trans anion radical, strongly suggesting that the *cis*-dibenzoylethylene anion radical is rapidly converted to the trans anion radical.

The cyclic voltammograms for the isomers of dibenzoylstyrene (Figure 3) are not as distinctive as the preceding ones. However, owing to the absence of significant anodic waves for both isomers, it can be deduced that the half-lives of the anion radicals are short with respect to *trans*-dibenzoylethylene. The large symmetrical peak at *ca.* 0.2 V anodic of the main reduction wave of the trans is due to adsorption.

The existence of a distinct anodic wave in the case of the cis isomer in the cyclic voltammograms of the dibenzoylstilbenes (Figure 4) indicates that the anion radical of the cis isomer is considerably longer lived than its trans isomer. $E_{p/2}$ values as well as increased lifetime of the intermediate (anion radical) produced on reduction of *cis*-dibenzoylstilbene exemplify the differences between the dibenzoylethylene and dibenzoylstilbene systems. These observations could be explained in terms of the appearance of a significant inductive effect arising from the phenyl or benzoyl groups due to diminution of coplanarity of the groups for the cis isomer relative to trans due to steric crowding. However, it was noted above that the shift of $\Delta$ upon addition of phenyl groups was in the wrong direction for the inductive effect to make a significant contribution. On the other hand, an attractive alternative interpretation is that, because of the proximity of the carbonyl groups in the cis isomer, a cyclic delocalized anion (such as **1**) is the stable intermediate. Similar intermediates have been proposed previously by Lutz to account for "cis-group effects" on chemical reduction in these systems.[2] Obviously, **1** could not result from the trans isomer without rotation around the 2,3 carbon bond, although the energy barriers to such rotation in analogous systems are known to be low;[14] the distinct differences between the cyclic voltammograms for the isomers suggest this is not occurring to an appreciable extent. The intervention of an intermediate of the type **1** is particularily attractive since it has been shown that in the mild chemical reduction of 2,3-disubstituted *cis*-dibenzoylethylenes dihydrofuran intermediates can be isolated.[2a]



**1**

**Dibenzoylcyclopropanes.**—The results from the electrochemical reduction of the cyclopropane diketones were of particular interest in view of the continuing comparisons of the chemistry of cyclopropanes and ethylenes.[15] In this study, however, the double bond properties of cyclopropane were not as apparent as have been noted in other systems.

The $E_{p/2}$ data show that the trans isomers of the three cyclopropane pairs are reduced at lower potentials than their corresponding cis isomers. Such an observation is in accord with increased stabilization of intermediate radical anions [and/or the transition state(s) leading to same] due to greater delocalization in the trans isomer compared to the cis. Such delocalization no doubt involves the cyclopropane ring to some extent. It is clear from the cyclic voltammetry that compared to the ethylenes the cyclopropane anion radicals are relatively unstable. In contrast to the ethylene series, no oxidation wave was observed for any cyclopropane studied. Cyclic voltammograms typical of the cyclopropane series are shown in Figure 5. In further contrast to the ethylene series, no discernible trends in $E_{p/2}$ values (Table II) were observed upon successive addition of phenyl groups to the dibenzylcyclopropane system.

## Experimental Section

**Chemicals.**—The preparation of the dibenzoylethylenes and the dibenzoylcyclopropanes has been reported.[2-5,16] Each com-

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[14] H. H. Freedman, V. R. Sandel, and B. P. Thill, *J. Amer. Chem. Soc.*, **89**, 1762 (1967).

[15] (a) M. Charton in "The Chemistry of the Alkenes," Vol. 2, J. Zabicky, Ed., Interscience, New York, N. Y., 1970, p 511 ff; (b) A. B. Turner, R. E. Lutz, N. S. McFarlane, and D. W. Boykin, Jr., *J. Org. Chem.*, **36**, 1107 (1971).

[16] C. R. Taylor, Ph.D. Dissertation, University of Virginia, 1970.

pound was recrystallized from ethanol to a constant melting point and dried *in vacuo*. The purification of dimethylformamide and tetraethylammonium perchlorate has been previously described.[11]

**Instrumentation and Procedures.**—The three-electrode potentiostat of conventional design, the polarographic cell, the capillary constant, and the general electrochemical procedures have been reported previously.[11] The signal generator used for polarography and cyclic voltammetry consisted of an Analog Devices Model 119 operational amplifier connected in the typical voltage integrator circuit. The desired rates of voltage change were obtained by selection of appropriate values for the input resistor and feedback capacitor. Sweep reversal was affected manually by reversal of the integrator input voltage. The polarographic scan rate was 0.06 V/min, and for cyclic voltammetry the scan rate for potential measurement was 2.5 V/min. The hanging drop electrode was constructed in the usual manner by sealing a piece of platinum wire into soft glass tubing, polishing the end, and etching the exposed platinum with aqua regia. The recessed platinum contact was then plated with mercury at the beginning of each day. For each measurement two new drops of mercury from the DME were transfered to the HDE *via* a small glass spoon that was added to the polarographic cell.

The reported $E_{p/2}$ values are the average of at least three measurements per day on at least 2 different days. Most values agreed to within 5 mV or less with 13 mV the largest single deviation observed. Polarographic $E_{1/2}$ values were approximated graphically.

**Acknowledgment.**—We thank Professor R. E. Lutz and his coworkers for generous samples of the compounds used in this investigation.

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# Chemistry of Difluorocyclopropenes. Application to the Synthesis of Steroidal Allenes

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The synthesis of a number of trisubstituted allenyl steroids is reported. Reaction of *N*-(2-chloro-1,1,2-trifluoroethyl)diethylamine on difluorocyclopropenylcarbinols is shown to be a convenient route to trifluoromethylallenes. Chlorotrifluorotriethylamine reacts stereoselectively with cyclopropenonylcarbinols to provide allenic acid fluorides in high yield. Allenic acid fluorides are easily converted into β-keto esters. The structure and stereochemistry of the novel steroidal allenes are based on their chemical and spectroscopic properties.

Some time ago, we developed an interest in incorporating allene functionality into the steroid molecule. When this work was undertaken there had been no reports of allene-substituted steroids. However, several related publications have appeared in the more recent literature.[2,3] This report summarizes our findings related to the synthesis of novel 3- and 17-substituted allenyl steroids.[4]

Addition of difluorocarbene, generated by pyrolysis of the sodium salt of chlorodifluoroacetic acid[5] to the triple bond of the diacetate **1b**, readily obtained from **1a**,[4a] afforded the difluorocyclopropene derivative **2a**. Conversion of **2a** to its 17-monoacetate **2c** was achieved by sodium methoxide hydrolysis to **2b**, followed by partial acetylation. Reaction of the 3β-hydroxy compound **2c** with *N*-(2-chloro-1,1,2-trifluoroethyl)diethylamine (fluoramine) in dry methylene chloride[6] provided a mixture of three substances, which were separated by preparative thin layer chromatography (tlc). The major compound was the 3β-fluoro steroid **2d** (25%), the formation of which could be expected from previous experience with this reagent.[6d] A second substance obtained in 15% yield did not have any fluorine in the molecule, but showed ultraviolet (uv) absorption at 244 nm, a strong carbonyl band in the ir at 1820 cm$^{-1}$, and two olefinic protons in the nuclear magnetic resonance (nmr) spectrum, one of them substantially deshielded (see Experimental Section). These properties are consistent with structure **3a**, which presumably results from dehydration[6] of the 3β alcohol **2c**, followed by hydrolysis of the difluorocyclopropene to give the conjugated cyclopropenone **3a**, because of traces of water. The vinylic proton resonating at 8.11 ppm corresponds to the cyclopropenone proton,[7] while the doublet centered at 6.66 ppm is due to the vinylic hydrogen at C-2. The facile hydrolysis of a conjugated difluorocyclopropene to a conjugated cyclopropenone has been observed previously.[8] Additionally, a compound isomeric with **2d** was isolated in 3% yield. As in the case of **2d**, its mass spectrum exhibited a molecular ion at *m/e* 410, suggesting the presence of three fluorines in the molecule. The strong ir band at 1970

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