

**Figure 2.** Fluorescence emission spectra: (a) fluoranthene in polystyrene film (excitation at 337 nm); (b) perylene deposited in vacuo from a cold vapor on polystyrene (coverage, 1.6 ng/cm<sup>2</sup>; excitation at 390 nm); (c) fluoranthene in polystyrene with perylene overlay at 9.1 ng/cm<sup>2</sup> (curve 1 is emission excited at 337 nm; curve 2 shows direct excitation of perylene surface layer which emits 478 nm); (d) system in c with 20-Å gold overlay added (intensity scale is the same as c; curves 1 and 2 correspond to those in c).

Both are virtually identical with the spectra for isolated molecules in xylene solution. In particular, there is no evidence for crystalline association of perylene molecules.

Figure 2c shows the effect of the overlayer. When perylene is present, it dominates the emission spectrum, despite its being outnumbered in the example by 180:1 and despite the fact that the sample is excited in a region where perylene receives only 1% of the total excitation. The excitation spectrum for emission at 478 nm matches that of fluoranthene from 300 to 380 nm.

The intensities of the fluoranthene and perylene emission components were evaluated individually from digitized spectra. A least-squares method yielded the optimal linear combination of the pure component spectra. Perylene always quenched the fluoranthene component. For PS thicknesses of 2700 Å, the effect ranged from 9 to 30%, depending on the perylene load, which lay in the range of 1–9 ng/cm<sup>2</sup>.

These observations imply that the surface layer is being fed by energy absorbed in the fluoranthene/PS zone, and the degree of quenching by the perylene suggests that absorbers possibly as far as ~500 Å from the outer surface serve as antennas for the perylene sites. The readiest explanation involves energy migration by exciton diffusion among fluoranthene chromophores<sup>6–8</sup> until the exciton approaches the perylene plane sufficiently closely to be harvested, presumably by Förster's transfer,<sup>8,9</sup> into a perylene trap. Surface trapping effects like these have been used to evaluate exciton diffusion lengths in single molecular crystals,<sup>10,11</sup> but we are not aware of other studies involving thin films of any type.

At least two complications could apply to our results: (1) diffusion of perylene molecules into the bulk PS to produce homogeneous trapping centers, and (2) the presence of a sur-

face excess of fluoranthene so that ~20% quenching could be effected within a short range of the traps.

The first issue was explored in experiments involving overlays of gold deposited by evaporation at nominal thicknesses of 20 Å. One such system is shown in Figure 1b. Figure 2d shows that the placement of the gold selectively removed the perylene components from the luminescence spectra of the assembly. Analysis revealed that about half of the perylene molecules were lost during the deposition of the gold. Apparently they were etched by the hot impinging gold atoms. Selective total quenching of the remaining perylene indicates that it is adjacent to the gold, and not homogeneously distributed in the polystyrene. Ageing of the system over an 8-day period did not cause a reappearance of the perylene luminescence components. These experiments suggest that the structural integrity of the device is preserved over our experimental time scale, and that the perylene is indeed a surface trapping center.

A surface excess is more difficult to detect, and we are presently unable to comment further about this possibility. Experiments bearing on the issue are now underway.

The results presented here have two particularly noteworthy aspects. The first is the possible range over which energy may be harvested. A collection distance of several hundred ångströms is surprisingly large for a system of dispersed, randomly oriented chromophores. Its magnitude, if verified by additional experimentation, suggests that effective antenna systems might be created without special alignments or extremely high concentrations of the chromophores.<sup>7</sup> A second notable point concerns access to the traps. The real contribution of thin-film techniques to this problem is in the creation of trapping centers that are accessible in a way which permits the assembly of additional apparatus for utilization of the trapped energy.

**Acknowledgment.** We are grateful to the National Science Foundation for supporting this work under Grants MPS-75-05361 and CHE-78-00584.

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Received July 28, 1978

## [2 + 2] Cycloadditions of Tetraalkoxyethylenes with Ketenes: a General Route to 2-Substituted 1-Hydroxycyclobut-1-ene-3,4-diones<sup>1</sup>

Sir:

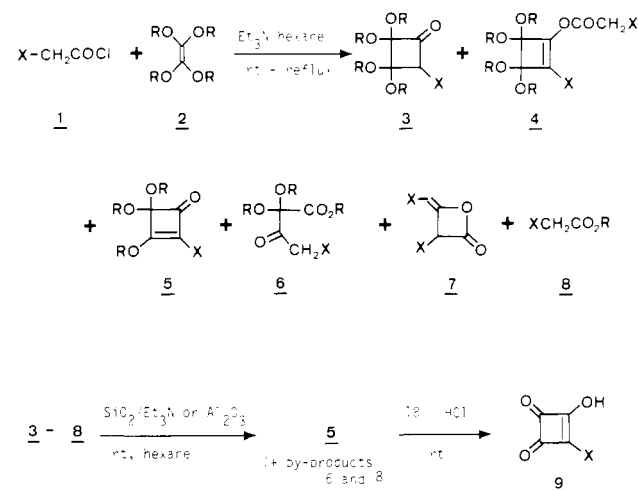
The parent acid **9** (X = H), 1-hydroxycyclobut-1-ene-3,4-dione (semisquaric acid), was reported several years ago.<sup>2</sup> Interest in **9** has increased since the discovery by Cole et al.<sup>3</sup> of potassium and sodium salts of **9** as fungal metabolites with plant growth regulating properties. These salts were named

**Table I.** Yields and Properties of Cyclobutenones **5** and 2-Substituted 1-Hydroxycyclobut-1-ene-3,4-diones **9**

1, X	2, R	% yield <sup>a</sup>	<b>5</b> bp, °C (mm)	% yield	<b>9</b> mp, °C <sup>b,c</sup>	pK <sub>a</sub> values of <b>9</b> <sup>d</sup>
CH <sub>3</sub>	Et	55		83	160–161 <sup>e</sup>	+0.20 ± 0.1
CH(CH <sub>3</sub> ) <sub>2</sub>	Et	81		92	84–86	
C(CH <sub>3</sub> ) <sub>3</sub>	Me	83	44.5–45.5 <sup>f</sup>	93	121–122	+0.28 ± 0.05
(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	Et	78		94	33–35	
cyclohexyl	Et	75		83	105.5–107	
benzyl	Et	85	110 (0.01) <sup>g</sup>	92	155–156	
CH=CCl <sub>2</sub> <sup>h</sup>	Et	62		58	188	–1.0 ± 0.05
CH <sub>2</sub> COOCH <sub>3</sub>	Me	34	87–91 (0.01)	73	156–157 <sup>i</sup>	
C <sub>6</sub> H <sub>5</sub>	Et	60	115 (0.015) <sup>g</sup>	65	207–208 <sup>j</sup>	–0.22 ± 0.1 <sup>k</sup>
4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Et	78	<i>l</i>	86	220 <sup>m</sup>	
4-ClC <sub>6</sub> H <sub>4</sub>	Et	71		68	227–228	–0.32 ± 0.05

<sup>a</sup> Total isolated yields calculated on **2** after distillation or crystallization or, where no boiling point or melting point are indicated, after treatment of crude reaction mixture with SiO<sub>2</sub>/Et<sub>3</sub>N system or Al<sub>2</sub>O<sub>3</sub>. <sup>b</sup> Compounds **9** were recrystallized from diethyl ether–hexane. All compounds **5** and **9** have consistent IR, UV, and NMR spectral data. <sup>c</sup> All compounds **9** except **9** (X = CMe<sub>3</sub>) melt with decomposition. <sup>d</sup> For method of determination, see ref 4 and 10a. Since the pK<sub>a</sub> value cited in ref 10a for **9** (X = Me) (+0.24 ± 0.1) could be exactly reproduced, the pK<sub>a</sub> values given in this table and in ref 10a are directly comparable. <sup>e</sup> Reference 7a: mp 162–164 °C. <sup>f</sup> Melting point (from hexane); IR (neat) 1755, 1632 cm<sup>–1</sup>; UV (MeOH) 232 nm (ε 14 520), 302 (150); NMR (CDCl<sub>3</sub>) δ 1.16 (s, 9 H), 3.47 (s, 6 H), 4.03 (s, 3 H). <sup>g</sup> In Kugelrohr. <sup>h</sup> See note 11. <sup>i</sup> **9** (X = COOH). <sup>j</sup> Reference 7b: mp 208–211 °C. <sup>k</sup> Reference 10a. <sup>l</sup> Oil; IR (neat) 1755, 1642, 1610 cm<sup>–1</sup>; isolated after Al<sub>2</sub>O<sub>3</sub> treatment of crude reaction mixture, containing mainly **4** (R = Et; X = 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>) (mp 96 °C; IR (neat) 1772, 1614, 1518 cm<sup>–1</sup>). <sup>m</sup> Reference 7c: mp 205–207 °C.

moniliformin.<sup>3</sup> We have recently reported practical large-scale preparations of **9** (X = H).<sup>4</sup> In this paper, we describe the smooth [2 + 2] cycloadditions of a number of monosubstituted, in situ prepared ketenes with readily available tetraalkoxyethylenes **2**<sup>4,5</sup> as a general and versatile synthetic method for cyclobutane derivatives **3–5**, which can be very simply hydrolyzed to 2-substituted 1-hydroxycyclobut-1-ene-3,4-diones **9** (i.e., alkyl, vinyl, and aryl moniliformins).<sup>6</sup> So far, only a few compounds **9** are available by specific routes.<sup>7</sup>



Typically, acyl chloride **1** was added to a solution of tetraalkoxyethylene **2** and triethylamine in hexane until **2** completely disappeared (TLC or GC).<sup>8</sup> After removal of the ammonium salts, a complex mixture of products was usually obtained, consisting of the “true” [2 + 2] cycloadduct **3**, its enol ester **4**, and its alcohol-elimination product **5** as main products, accompanied by small amounts of byproducts **6–8**. The composition of the crude reaction mixture varied considerably depending on the ketene used. As a specific example, the [2 + 2] cycloaddition of tetramethoxyethylene to isopropylketene, which was formed in situ for 3-methylbutanoic acid chloride, afforded nearly pure **3** (X = CHMe<sub>2</sub>) in 92% yield: bp 65–66 °C (0.04 mm); IR (neat) 1796 cm<sup>–1</sup>; NMR (CDCl<sub>3</sub>) δ 0.9–1.4 (m, 6 CH<sub>3</sub>), 1.9–2.4 (m, 1 H), 2.65 (d, *J* = 8 Hz, H–C(2)), 3.3–3.9 ppm (m, 4 OCH<sub>2</sub>).

The reaction of in situ formed arylketenes with **2** (R = Et) is also noteworthy. Spontaneous alcohol elimination **3** → **5**

occurs even under mild reaction conditions (room temperature). The reaction mixture consists then mainly of the “push-pull” cyclobutenones **5**.

The crude reaction mixture may be directly hydrolyzed to **9** by 18% hydrochloric acid at 60 °C. This procedure takes advantage of the pronounced tendency of **9** to crystallize, thus allowing removal of the oily byproducts such as **6** and **8** after hydrolysis by simple washing with hexane. The acidic byproducts (e.g., from **4** or **7**), however, sometimes render the isolation of **9** in pure form difficult. Moreover, the acid hydrolysis of **3** is accompanied to some extent by acid-assisted heterolytic ring cleavage,<sup>4</sup> especially where X is a bulky substituent, thus lowering the yields of **9** after direct hydrolysis of the crude reaction mixtures.

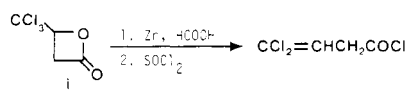
To overcome such isolation problems, we preferred to pretreat the hexane solution of the crude reaction mixture with a 15-fold weight excess of silica gel–3% triethylamine system<sup>4</sup> or basic alumina<sup>9</sup> at room temperature. This procedure converted **3** and **4** smoothly to **5**. Afterward, **5** was eluted by excess of hexane, while all polar byproducts were retained. This operation, followed by distillation, afforded cyclobutenones **5** (Table I), which were contaminated usually by small amounts (2–15%) of neutral byproducts **6**. **5** could now be hydrolyzed in high yields (Table I) to hydroxycyclobutenediones **9** by 18% HCl at room temperature. In contrast to **3**, no cleavage of **5** to ring-opened products was observed during the acid hydrolysis.

All compounds **9** are strong vinylogous acids with very low pK<sub>a</sub> values (Table I). Among them, 2-(2',2'-dichlorovinyl)-1-hydroxycyclobut-1-ene-3,4-dione represents the strongest oxo carbon acid (pK<sub>a</sub> = –1.0 ± 0.05) measured so far.<sup>4,10</sup> The reactivity of **9** is similar of that of moniliformin (**9**, X = H):<sup>4</sup> self-catalyzed esterification leads to esters; treatment with (COCl)<sub>2</sub>–trace of DMF affords stable chlorides,<sup>12</sup> from which amides and thioesters can be prepared in the usual way.<sup>7c</sup> In the <sup>13</sup>C NMR spectrum of **9**, only three ring carbons are detectable owing to rapid proton transfer, which can not be suppressed either by steric hindrance (**9**, X = CMe<sub>3</sub>) or by intramolecular hydrogen bonding (**9**, X = CH<sub>2</sub>COOH) even at low temperatures (–95 °C, acetone-*d*<sub>6</sub>).<sup>13</sup>

**Acknowledgment.** I thank Dr. H.-R. Blattmann for measurement of pK<sub>a</sub> values, Dr. H. Sauter for his help with NMR problems, Dr. H.-P. Fisher for valuable discussions of the practical utilization of **9**, and Dr. J. G. Dingwall for helpful comments on the manuscript.

## References and Notes

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- (11) **1** ( $\text{X} = \text{CH}=\text{CCl}_2$ ) (bp 48-54 °C (11 mm)) was prepared from the readily available (D. Borrmann and R. Wengler (to Bayer AG), German Patent 1 214 211 (1962); H. Ohse, R. Palm, and H. Cherdron, *Monatsh. Chem.*, **98**, 2138 (1967)) ketene chloral  $[2+2]$  cycloadduct **i** in 90% overall yield as shown.



- (12) E.g., chlorides of **9** with  $\text{X} = \text{cyclohexyl}$ , bp 100 °C (0.1 mm); with  $\text{X} = \text{CH}=\text{CCl}_2$ , mp 90.5-91 °C; with  $\text{X} = 4\text{-CH}_3\text{OC}_6\text{H}_4$ , mp 122-123 °C; and with  $\text{X} = 4\text{-ClC}_6\text{H}_4$ , mp 142-142.5 °C.
- (13) Similar  $^{13}\text{C}$  NMR signal averaging was observed for squaric acid (**9**,  $\text{X} = \text{OH}$ ) (W. Städeli, H. Hollenstein, and W. von Philipsborn, *Helv. Chim. Acta*, **60**, 948 (1977)), as well as for moniliformin (**9**,  $\text{X} = \text{H}$ ) (H.-D. Scharf, H. Frauenrath, and W. Pinske, *Chem. Ber.*, **111**, 168 (1978)).

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Received September 13, 1978

### Hypovalent Radicals. 3.<sup>1</sup> Chemical Reductions of Certain Diazo Compounds to Carbene Anion Radicals—Formation of (Fluorenylidene) disodium, a Carbene Dianion

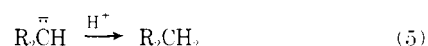
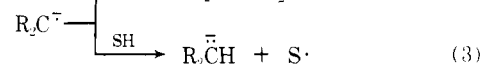
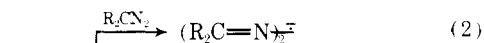
Sir:

We wish to report preliminary results of chemical reductions of diphenyldiazomethane ( $\text{Ph}_2\text{CN}_2$ ) and 9-diazo fluorene ( $\text{FIN}_2$ ) which demonstrate that coupling of diaryl carbene anion radicals occurs under certain conditions. Other results

establish that the 9-fluorenyl anion ( $\text{FIH}^-$ ) nucleophilically adds to the terminal nitrogen of  $\text{FIN}_2$ . This suggests that a similar addition of the carbene anion radical to the diazo compound is involved in azine anion radical formation, a principal reaction channel for  $\text{Ar}_2\text{C}^-$  produced in these and electrochemical experiments.<sup>1,2</sup> The further reduction of fluorenylidene anion radical ( $\text{FI}^\cdot$ ) by sodium naphthalene ( $\text{Na}^+\text{Naph}^-$ ) in THF to the carbene dianion, (fluorenylidene)-disodium ( $\text{FI}^{2-}\text{Na}^+$ ), is proposed to account for acid quenching studies on these reductions of  $\text{FIN}_2$ .

We have examined the reductions of  $\text{Ph}_2\text{CN}_2$  and  $\text{FIN}_2$  with  $\text{Na}^+\text{Naph}^-$  in THF by slow (1 h) dropwise addition and rapid (~5-s addition time) syringe injection of the diazo compounds to excess reducing agent. The reactions were quenched by adding water shortly after the additions were complete. The conditions and products of these chemical reductions are listed in Table I. Benzophenone ( $(\text{Ph}_2\text{C}=\text{N})_2$ ) and fluorenone azines ( $(\text{FI}=\text{N})_2$ ) are reduced by excess  $\text{Na}^+\text{Naph}^-$  in THF quantitatively to the corresponding primary amines.<sup>3</sup>

In expt 1 and 2 (Table I) involving slow additions of  $\text{Ph}_2\text{CN}_2$  to the reducing medium ( $\text{Na}^+\text{Naph}^-$ , THF), we observed a small increase in the amount of diphenylmethane ( $\text{Ph}_2\text{CH}_2$ ) produced by increasing the  $[\text{Na}^+\text{Naph}^-]/[\text{Ph}_2\text{CN}_2]$  ratio from 4 to 10. The low yield (17%) of  $\text{Ph}_2\text{CH}_2$  (expt 2) was in contrast to the reduction  $\text{FIN}_2$  under the same conditions (expt 4) where 40% fluorene ( $\text{FIH}_2$ ) was obtained. The yields of the hydrocarbon products,  $\text{Ph}_2\text{CH}_2$  and  $\text{FIH}_2$ , were attenuated when the THF solution of the diazo compound was syringe injected (addition time ~10 s) into the reducing medium (expt 3 and 5, Table I). The sequence of reactions considered to be in accord with this data is shown as eq 1-5.



The variations in the product yields of both the hydrocarbon and amine as a function of the method of addition of the diazo compound to the reduction medium show that one of the reaction channels of the carbene anion radical involves coupling with the diazo compound. That this reaction *could* occur on the terminal nitrogen of the diazo compound was demonstrated in the following way. One equivalent of  $\text{FIN}_2$  in THF was syringe injected into a THF solution of the 9-fluorenyl anion

**Table I.** Conditions and Products for the Chemical Reductions of Diazo Compounds  $\text{Ph}_2\text{CN}_2$  and  $\text{FIN}_2$

expt no.	substrate (mmol)	rate of addition	solvent	reducing agent (mmol)	products (% yields) <sup>a,b</sup>
1	$\text{Ph}_2\text{CN}_2$ (15.7)	slow <sup>c</sup>	THF <sup>d</sup>	$\text{Na}^+\text{Naph}^-$ (62.8)	$\text{Ph}_2\text{CH}_2$ (13), $\text{Ph}_2\text{CHNH}_2$ (84)
2	$\text{Ph}_2\text{CN}_2$ (15.8)	slow <sup>c</sup>	THF <sup>d</sup>	$\text{Na}^+\text{Naph}^-$ (159)	$\text{Ph}_2\text{CH}_2$ (17), $\text{Ph}_2\text{CHNH}_2$ (85)
3	$\text{Ph}_2\text{CN}_2$ (10.4)	fast <sup>e</sup>	THF <sup>f</sup>	$\text{Na}^+\text{Naph}^-$ (52.2)	$\text{Ph}_2\text{CH}_2$ (4), $\text{Ph}_2\text{CHNH}_2$ (92)
4	$\text{FIN}_2$ (15.6)	slow <sup>c</sup>	THF <sup>d</sup>	$\text{Na}^+\text{Naph}^-$ (157)	$\text{FIH}_2$ (40), $\text{FIHNH}_2$ (53)
5	$\text{FIN}_2$ (11.3)	fast <sup>e</sup>	THF <sup>f</sup>	$\text{Na}^+\text{Naph}^-$ (112)	$\text{FIH}_2$ (12), $\text{FIHNH}_2$ (88)
6	$\text{FIN}_2$ (10.2)	fast <sup>e</sup>	$\text{NH}_3$ <sup>g</sup>	Na (10.2)	$(\text{FI}=\text{N})_2$ (79), $\text{FI}=\text{O}$ (6), $\text{FI}=\text{FI}$ (4), $\text{FIH}-\text{HFI}$ (4)

<sup>a</sup> % yields are generally better than  $\pm 2\%$  in duplicate experiments. Yields of amines are corrected for known losses in the workup procedures.

<sup>c</sup> Slow, dropwise addition of  $\text{R}_2\text{CN}_2$  to reducing solution. <sup>d</sup>  $\text{Na}^+\text{Naph}^-$  in 400 mL of THF ( $-10^\circ\text{C}$ ),  $\text{R}_2\text{CN}_2$  in 100 mL of THF;  $\text{H}_2\text{O}$  quench.

<sup>e</sup> Rapid syringe injection of  $\text{R}_2\text{CN}_2$  to reducing solution. <sup>f</sup>  $\text{Na}^+\text{Naph}^-$  in 200 mL of THF ( $-10^\circ\text{C}$ ),  $\text{R}_2\text{CN}_2$  in 10 mL of THF;  $\text{H}_2\text{O}$  quench.

<sup>g</sup> 100 mL of  $\text{NH}_3(\text{l})$ ,  $\text{FIN}_2$  in 10 mL of THF; reaction quenched with  $\text{NH}_4\text{Cl}$ .