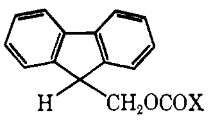
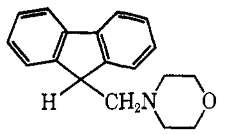


3a, X = Cl
b, X = N_3



4

or complex polypeptides, the FMOC group is stable under conditions involved in the removal of most of the commonly used protective groups such as hydrogen bromide or chloride in various organic solvents, trifluoroacetic acid, and catalytic hydrogenolysis over palladium–carbon. Cleavage by-products (monomeric or polymeric dibenzofulvene (**2**) or an amine–dibenzofulvene adduct such as **4**) depend on both reaction conditions and the reagent used and in all cases are easily separated from the desired amine. As an example, a solution of FMOC-glycine (**1**, R = CH_2CO_2H), mp 174–176°, in liquid ammonia is allowed to stand for 10–12 hr, the ammonia evaporated, and the residue treated with ether to remove **2**. The residue is treated with water to remove a trace of dibenzofulvene polymer and evaporation gives glycine in quantitative yield. Similarly a solution of FMOC-aniline (**1**, R = C_6H_5), mp 189–190°, in morpholine is allowed to stand at room temperature for 25 min, diluted with water, filtered to remove adduct **4**, mp 172.5–174° (95%), and extracted with ether to give aniline (96%). If ethanolamine is substituted for morpholine as solvent and cleavage reagent the by-product is **2** rather than an analog of **4**. Authentic **2** was shown to react with morpholine to give **4**.

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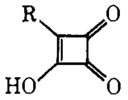
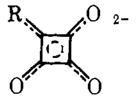
Methylhydroxycyclobutenedione

Sir:

We wish to report the synthesis of methylhydroxycyclobutenedione (**1**), the first simple homolog of hydroxycyclobutenedione (**2**). On the basis of previous work on the phenyl analog,[1] **1** was expected to be a strong monoprotic acid. In addition, abstraction of another proton by base would lead to a new species (**3**) isoelectronic with the aromatic squarate anion (**4**).[2] Simple Hückel calculations performed on **3** suggest that a substantial amount of the stability exhibited by **4** should also be found in **3**.[3] In this report we wish to communicate the synthesis of **1** and the formation of **3** under relatively mild conditions.

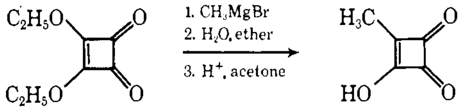


1, R = CH_3
2, R = H



3, R = CH_2
4, R = O

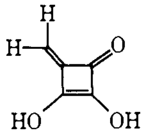
Treatment of diethoxycyclobutenedione[2a] (4.7 g, 27.6 mmol) with methyl magnesium bromide (2.95 *M*, 32 mmol) in ether at −78° followed by hydrolysis and extraction afforded a residue which was treated with an aqueous acid–acetone mixture and allowed to evaporate. Trituration with ether afforded **1** (1.34 g, 44%) as colorless crystals after sublimation and recrystallization;[4] mp 162–164° (acetone–heptane); nmr (acetone-d_6, TMS) τ 1.98 (0.99 H, s), 7.82 (3 H, s); ν_{max} (Nujol) 2650–2150 (broad), 1800, 1725, 1540, 1070, 755 cm^{-1}; λ_{max} (H_2O) 260 (ϵ 11,000), 230 mμ (24,000).



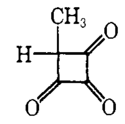
1

Anal. Calcd for $C_5H_4O_3$: C, 53.58; H, 3.60; mol wt, 112. Found: C, 53.70; H, 3.48; *m/e*, 112, neut equiv, 115.

The presence of only two resonances in the nmr spectrum of **1** coupled with the absence of any appreciable amount of H/D exchange in the methyl group (acetone-d_6, D_2O, HCl) precludes the presence of tautomer **1b**. Keto–enol tautomers such as **1c** in rapid equilibrium with **1**, however, cannot be ruled out at present.

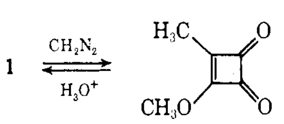


1b



1c

Treatment of **1** (720 mg, 6.43 mmol) with excess diazomethane afforded the crystalline methyl ether derivative **5** (680 mg, 84%); mp 49–51°; ν_{max} (Nujol) 1820, 1800, 1760 cm^{-1}; λ_{max} (CH_3OH) 228 mμ (ϵ 17,000); nmr ($CDCl_3$, TMS) τ 5.53 (2.96 H, s), 7.75 (3 H, s). Acid-catalyzed hydrolysis of **5** gave back **1** (90%). The mass spectrum of **5** consisted of four major



5

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(1) E. J. Smutny and J. D. Roberts, *J. Amer. Chem. Soc.*, 77, 3420 (1955); E. J. Smutny, M. C. Caserio, and J. D. Roberts, *ibid.*, **82**, 1793 (1960).

(2) (a) G. Maahs and P. Hegenberg, *Angew. Chem., Int. Ed. Engl.*, **5**, 888 (1966); (b) R. West, H. Y. Niu, D. L. Powell, and M. V. Evans, *J. Amer. Chem. Soc.*, **82**, 6204 (1960); (c) R. West and D. L. Powell, *ibid.*, **85**, 2577 (1963); (d) M. Ito and R. West, *ibid.*, **85**, 2580 (1963); (e) R. West and H. Y. Niu in "Non-Benzenoid Aromatics," Vol. I, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1969, pp 311–345.

(3) Using Coulomb and resonance integrals of $\alpha + \beta$ and 0.8β for oxygen,[2e] these calculations indicate that about 80% of the delocalization of **4** would be retained by **3**.

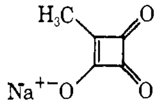
(4) A small amount of dimethylcyclobutenedione was also isolated from the ether-soluble portion (dinitrophenylhydrazone derivative, mp 204° (lit. 205–208° dec)): A. T. Blomquist and R. A. Vierling, *Tetrahedron Lett.*, **19**, 655 (1961).

fragment ions, loss of CO, C_2H_3O, C_2O_2, and C_3O_2, similar to that observed for other oxocarbons.[5]

Anal. Calcd for $C_6H_6O_3$: C, 57.14; H, 4.80; mol wt, 126. Found: C, 57.11; H, 4.71; mol wt, 129 ($CHCl_3$); *m/e*, 126.

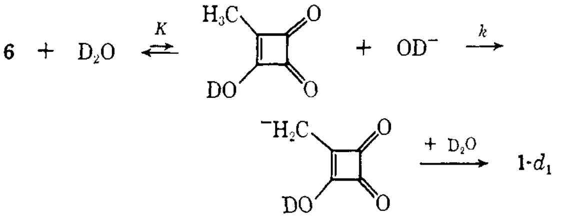
The p*K* of **1** was found to be 0.69 ± 0.03 by measurement of the pH of 0.147, 0.207, and 0.433 *M* aqueous solutions. In comparison, phenylhydroxycyclobutenedione (pK = 0.37) is about twice as strong an acid as **1**. This result is consistent with the relative stabilizing effects of the two groups.

Neutralization of **1** afforded the crystalline salt **6**



6

(>90%); mp ≥270°; ν_{max} (Nujol) 1790, 1700, 1580, and 1065 cm^{-1}; nmr (D_2O, $(CH_2OH)_2$) τ 7.97 (s). When dissolved in a solution of deuterium oxide–sodium deuterioxide, **6** rapidly underwent H/D exchange as evidenced by a decrease in the methyl resonance at τ 7.97. The pseudo-first-order rate constant for exchange divided by the deuterioxide ion concentration is approximately $3 \times 10^{-3}\ M^{-1}\ sec^{-1}$ (31°).[6] A mechanism involving a hydrolysis step prior to exchange requires exchange to proceed independent of added deuterioxide concentration (eq 1). In contrast



(1)

$$\begin{aligned} \text{rate}_{(\text{H/D ex})} &= kK[\mathbf{6}] \\ &= k_{\text{obsd}}[\mathbf{6}] \\ K &= K_w/K_a \end{aligned}$$

the mechanism shown in eq 2 demands the presence of

$$\mathbf{6} + OD^- \xrightarrow{k} \mathbf{3} + D_2O \longrightarrow \mathbf{6}\text{-}d_1 + OD^- \qquad (2)$$

$$\begin{aligned} \text{rate}_{(\text{H/D ex})} &= k[\mathbf{6}][OD^-] \\ &= k_{\text{obsd}}[\mathbf{6}] \end{aligned}$$

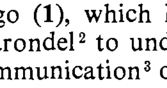
added base. The kinetic data shown in Table I allow a distinction between these two possibilities. These data demonstrate the requirement of added base for exchange and an independence of the calculated second-order rate constant (k_{obsd}/[NaOD]) on the added deuterioxide concentration. The observed first-order dependence on deuterioxide ion (Table I) requires the exchange process to proceed through a dianion intermediate (eq 2). Although the structure of the dianion may be subject to question, **3** is probably a reasonable representation.[7]

Table I[a,b]

[**6**][c]	$k_{obsd} \times 10^4$,[d] sec^{-1}	[NaOD][e]	$k_{obsd} \times 10^3$/[NaOD], $M^{-1}\ sec^{-1}$
Ca. 0.9	No exchange[6]	0.00	
0.7	1.27	0.038	3.3
1.1	3.89	0.138	2.8
0.9	5.25	0.186	2.8
0.9	7.90	0.249	3.2

[a] Temperature, 31°. [b] Rates were measured by nmr integration of the methyl resonance of **6** as a function of time. [c] Moles/liter. [d] k_{obsd}'s are pseudo-first-order rate constants obtained from single runs carried out to approximately three half-lives by plotting ln [**6**] as a function of time. [e] Added sodium deuterioxide.

The facile exchange observed in **6** suggests that H/D exchange might serve as a delicate probe in determining the relative stabilities of the π systems in the similar three-, five-, and six-membered ring analogs (**7**, *n* = 0, 2, 3) and other related systems.[2e] Unfortunately these compounds are not yet available.



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Acknowledgments. We thank the Research Corporation for partial financial support of this work and Professor R. Winter for stimulating discussions.

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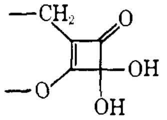
[5] S. Skujins, J. Delderfield, and G. A. Webb, *Tetrahedron*, **24**, 4805 (1968).

[6] **1** could be recovered in excess of 80% after complete exchange. The methyl group was found to contain 2.8 D/molecule (mass spectroscopy). No exchange could be detected in the absence of added base.

[7] In a very similar system, 3-hydroxy-2,4-dimethylcyclobutenone (pK_a 2.8),[8] no appreciable base-catalyzed H/D exchange was observed (K_2CO_3, D_2O) in the methyl group.[9] This suggests intermediates such as i are not involved in the exchange process.



i

[8] R. B. Woodward and G. Small, Jr., *J. Amer. Chem. Soc.*, **72**, 1297 (1950).

[9] D. Farnum, T. Heybey, and B. Webster, *ibid.*, **86**, 673 (1964).

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Photochromic Indigoids. II.[1] Absorption Spectra and Quantum Yields for the Photoisomerization of Selenoindigo

Sir:

As part of an investigation of the photochemical cis–trans isomerization of indigoid dyes, we have examined selenoindigo (**1**), which has been reported by Pummerer and Marondel[2] to undergo photoisomerization. A recent communication[3] of the absorption spectra and quantum yields for the photoisomerization of *trans-* and *cis*-oxindigo (**2**) prompts us to report our results for **1**.

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[1] Paper I in this series: J. Blanc and D. L. Ross, *J. Phys. Chem.*, **72**, 2817 (1968).

[2] R. Pummerer and G. Marondel, *Chem. Ber.*, **93**, 2834 (1960).

[3] H. Güsten, *Chem. Commun.*, 133 (1969).