

plateau between 40 and 50% perchloric acid, and finally near 60% acid abruptly begins to increase again. We ascribe this complex profile to the interplay of the two mechanistic pathways available for hydrolysis of enol acetates. For the *cis* isomer **2**, below 59% perchloric acid, the predominant mode of hydrolysis is the normal ester pathway; above this acidity, the majority of the hydrolysis proceeds by way of olefin protonation.

For calculation of the predicted rate for hydrolysis by the normal ester mechanism, the following procedure was used. Yates and McClelland¹¹ have observed that many esters show a very similar rate-acidity profile in the middle range of sulfuric acid concentration, with eq 1 describing the behavior of the ester, with $m \cong 0.62$ and $r \cong 2$. Lane, Cheung, and Dorsey,¹²

$$\log k + mH_0 = r \log a_{H_2O} + \text{constant} \quad (1)$$

in a particularly careful study of the behavior of ethyl acetate, show that $m = 0.645$ and $r = 2$. To calculate the expected rate for normal ester hydrolysis for *cis*- α -acetoxystilbene (**2**) we have used eq 2, with data for the activity of water from Robinson and Baker¹³ with

$$\log (\text{rate}_{\text{ester}})_{\text{cis}} = -0.62H_0 + 2 \log a_{H_2O} - 4.65 \quad (2)$$

the constant term (-4.65) chosen to give a predicted rate in agreement with experiment at the lower acidities ($H_0 \cong -1.5$). In the most concentrated acid solution a very small correction for protonation of the ester has been made assuming pK_{BH^+} of -7.00 . For the predicted rate of reaction by way of olefin protonation, eq 3 was used¹⁴ with the constant term (-8.22) chosen to match the observed rates in 63% sulfuric acid ($H_0 = -5.9$).

$$\log (\text{rate}_{\text{olef}})_{\text{cis}} = -H_0 - 8.22 \quad (3)$$

Calculated rates for the *trans* isomer are obtained in a similar fashion, using eq 4 and 5, with the constant terms chosen as above.

$$\log (\text{rate}_{\text{ester}})_{\text{trans}} = -0.62H_0 + 2 \log a_{H_2O} - 5.51 \quad (4)$$

$$\log (\text{rate}_{\text{olef}})_{\text{trans}} = -H_0 - 8.82 \quad (5)$$

Finally it should be noted that the rates of olefin protonation for *cis*-stilbene⁷ and for *cis*- α -acetoxystilbene are very similar.

Experimental Section¹⁵

α -Acetoxystilbenes.—The procedure of House and Trost⁸ was followed. Ten grams of desoxybenzoin was dissolved in 150 ml of carbon tetrachloride and 51 g of acetic anhydride was added with stirring. After the dropwise addition of 0.5 ml of 70% perchloric acid, stirring was continued for 2.5 hr. The reaction mixture was washed thoroughly with aqueous sodium bicarbonate solution, the carbon tetrachloride layer was dried over anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator. The crude residue contained approximately 60% *trans*- α -acetoxystilbene, 10% *cis*- α -acetoxystilbene, and 30% desoxybenzoin as determined from the nmr spectrum.

The crude reaction mixture was dissolved in a minimum amount of diethyl ether and pentane was added to 500 ml. Upon cool-

ing, 4.7 g of *trans*- α -acetoxystilbene was collected as pale yellow crystals.¹⁶ Recrystallization from pentane gave colorless needles: mp 100.0–101.5° (lit. 100.5–101.0°); uv max 287 m μ (ϵ 27,400, ethanol); ir (CCl₄) 1764 cm⁻¹; nmr (CCl₄) δ 7.14–7.50 (m, 10 H), 6.55 (s, 1 H), 2.26 (s, 3 H).

Anal. Calcd for C₁₆H₁₄O₂: C, 80.65; H, 5.92. Found: C, 80.65; H, 5.98.

The mother liquors from the crystallization of the *trans* isomer were concentrated, and the *cis* isomer was separated from desoxybenzoin and remaining *trans* isomer by glpc on a 5 ft \times 0.25 in. 20% SE-30 column. *cis*- α -Acetoxystilbene was obtained as a viscous oil: uv max 262 m μ (ϵ 12,000); ir (CCl₄) 1764 cm⁻¹; nmr (CCl₄) δ 7.03–7.95 (broad multiplet, 10 H), 6.33 (s, 1 H), 2.14 (s, 3 H).

Anal. Calcd for C₁₆H₁₄O₂: C, 80.65; H, 5.92. Found: C, 80.68; H, 6.04.

Kinetic Runs.—An aliquot (10–50 μ l) of a stock solution of the substrate in ethanol was mixed with 3 ml of the appropriate acid solution in a stoppered cuvette. The kinetics were followed on a Gilford Model 2000 spectrophotometer with a thermostated cell compartment (25°). The rate constant obtained showed no dependence on the concentration of ethanol (0.3–1.6 vol %). For *cis*- α -acetoxystilbene reactions were followed at 280 m μ and showed good first-order behavior to greater than 85% reaction. For *trans*- α -acetoxystilbene the kinetics were followed at 288 m μ . All reactions of the *trans* compound showed excellent first-order behavior to greater than 95% reaction. Infinity spectra were recorded on a Cary Model 14 spectrophotometer, and were identical with those obtained for an authentic sample of desoxybenzoin in the same acid media. The rate constants were obtained from the slopes of the plots of $\log (A_\infty - A_t)$ vs. time.

Registry No.—*trans*- α -Acetoxystilbene, 13892-81-4; *cis*- α -acetoxystilbene, 24647-07-2.

(16) No attempt was made to maximize the yield.

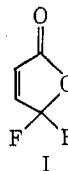
Preparation of Maleoyl Fluoride. Nuclear Magnetic Resonance Spectra of Maleoyl Fluoride, Fumaryl Fluoride, and Fumaryl Chloride Fluoride

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The preparation of maleoyl fluoride from maleic anhydride and sulfur tetrafluoride has been reported by Hasek, *et al.*¹ We have repeated their reaction conditions (13 hr at 150°) and observe that the products are fumaryl fluoride, unreacted anhydride, and a compound we believe to be 4,4-difluoroisocrotonolactone (I). Under the above conditions it is likely that maleoyl fluoride will be isomerized to fumaryl fluoride.



We have used lower reaction temperatures and find that if the mixture is heated to about 75° for 5 hr maleoyl fluoride is one of the products. The amount produced varies from run to run but usually is in the range

(1) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960).

(11) K. Yates and R. A. McClelland, *J. Amer. Chem. Soc.*, **89**, 2686 (1967).

(12) C. A. Lane, M. F. Cheung, and G. F. Dorsey, *ibid.*, **90**, 6492 (1968).

(13) R. A. Robinson and O. J. Baker, *Trans. Proc. Roy. Soc. N. Z.*, **76**, 250 (1946).

(14) In the previous study, ref 3, it was observed that the slope of the plot for $\log k$ vs. $-H_0$ was close to unity for the carbonium ion pathway.

(15) Analyses are by the Microanalytical Laboratory of the Department of Chemistry, University of California.

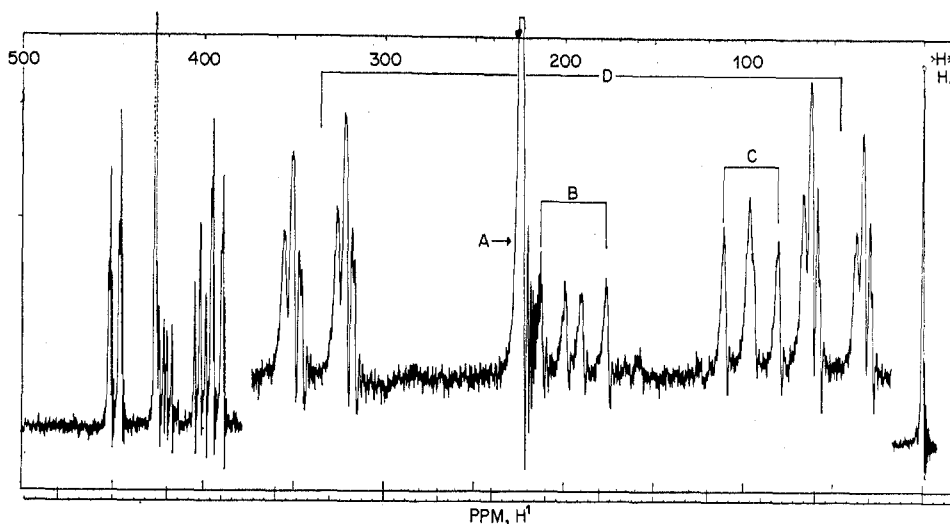


Figure 1.—Nmr spectrum of the products obtained from the action of SF_4 on maleic anhydride: A (maleic anhydride), B (fumaryl fluoride), C (maleoyl fluoride), and D (4,4-difluoroisocrotonolactone).

of 20 to 50% as determined from the nmr spectrum (see Figure 1) after removal of the SF_4 and HF. In several instances all of the reaction mixture was not removed from the cylinder after it had been heated. This remaining portion, after standing for several days at room temperature in the cylinder, invariably gave a greater amount of maleoyl fluoride relative to that of I. Higher reaction temperatures result in a larger percentage of I and fumaryl fluoride.

It should be pointed out that the commercial grade SF_4 (Matheson) used in our work contained HF. It is possible that the discrepancy between our work and that of ref 1 is due to this fact, since HF might catalyze the isomerization of maleoyl fluoride to fumaryl fluoride at 150° . However, it is known that maleic acid isomerizes to fumaric acid on heating. There is a reason to suspect a similar isomerization will occur in the case of maleoyl fluoride. Furthermore, maleoyl fluoride was identified by infrared spectroscopy in the earlier work. Both it and fumaryl fluoride will give similar infrared spectra.² Finally the boiling point reported for maleoyl fluoride ($100\text{--}105^\circ$)¹ is near that of fumaryl fluoride (106°).

A complete separation of maleoyl fluoride from I was not achieved in our work even though numerous vacuum trap-to-trap distillations were tried. Maleoyl fluoride is the less volatile component but there is evidence that concentrated samples of it slowly equilibrate to a mixture of maleoyl fluoride, fumaryl fluoride, anhydride and I. The normal boiling point of maleoyl fluoride was not determined but it is expected to be in excess of 106° . The mass spectrum of a sample containing about 90% maleoyl fluoride (by nmr) showed a m/e peak at 120. This was the highest m/e peak of any significance. Except for the relative intensities of the fragment peaks the spectrum was very similar to the one obtained from a pure sample of fumaryl fluoride.

A comparison of the nmr parameters of maleoyl fluoride with those of fumaryl fluoride gives additional evidence of its preparation. Both give rise to AA'-

XX'-type spectra and eight of the ten lines theoretically possible are observed in the A and X parts of the spectra. The outer four lines, symmetrically displaced about the center, are weak, particularly in the spectrum of the latter compound, and are not visible in Figure 1. A complete analysis of the spectra, including the ^{13}C satellites and using the computer program LAOCN3,³ gives the parameters listed in Table I. The ^{13}CF couplings and isotopic shifts are in good agreement with those of the related compounds.⁴

TABLE I
NMR PARAMETERS OF MALEOYL FLUORIDE
AND FUMARYL FLUORIDE

	OFC—CH=CH—CFO ^a	
	(3)	(1) (2) (4)
	Maleoyl fluoride	Fumaryl fluoride
$\delta(1) = \delta(2),^b$ ppm	6.73	6.94
$\delta(3) = \delta(4),^c$ ppm	41.18	30.40
J_{12}	± 12.13	± 15.77
$J_{13} = J_{24}$	± 4.17	± 7.51
$J_{14} = J_{23}$	± 1.83	∓ 0.21
J_{34}	4.78	± 0.22
$J_{13\text{CH}}$	178	
$J_{13\text{CF}}$	346	345
$J_{13\text{CCF}}$		72
$\delta_{13\text{CF}} - \delta_{13\text{CF}'}$ ppm	0.15	0.12

^a Approximately 15% in CFCl_3 . ^b From TMS. ^c From CFCl_3 (downfield).

The parameters listed in Table I are actually conformationally averaged ones. J_{13} in particular has been found to be temperature and solvent dependent and this information, along with a study of the vibrational spectra,⁵ has been used to determine the relative stabilities of the isomers in these compounds and in fumaryl chloride. There is probably a large concentration of the unsymmetrical isomer of maleoyl fluoride

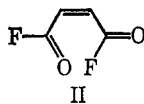
(3) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(4) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, London, 1965.

(5) T. P. Vasileff and D. F. Koster, unpublished work.

(2) This would not necessarily be true if fumaryl fluoride existed only as the more symmetric C_{2h} isomer. We find that several rotational isomers are present.

(II) which would account for the differences in $\delta(3)$, J_{13} and J_{14} , when compared with the same parameters of fumaryl fluoride.



The small negative coupling constant, J_{14} , in fumaryl fluoride appears to be real. In the calculations it was originally assigned a value of zero. Allowing it to vary to the value listed results in an improved calculated spectrum. To further substantiate this, fumaryl chloride fluoride was prepared and its nmr spectrum analyzed. It is possible to determine the relative signs of the coupling constants from the analysis of this ABX spectrum and indeed J_{AX} is opposite to J_{BX} . The parameters are as follows: δ_A 6.923 ppm, δ_B 7.143 ppm (from TMS), δ_X 31.414 ppm (downfield from CFCl_3) ($J_{AB} = \pm 15.60$, $J_{AX} = \pm 7.11$, and $J_{BX} = \mp 0.28$ cps). Since the magnitude of the coupling constants here are very nearly the same as those of fumaryl fluoride it is reasonable to assume that the sign J_{14} is opposite to J_{13} in fumaryl fluoride.

Compound I has been identified solely from its nmr spectrum. This product should not be unexpected since SF_4 is reported¹ to react with carbonyl groups to give *gem*-difluoro compounds. The proton and fluorine spectra are consistent with the ABX₂ type expected. The parameters are as follows: δ_A 6.501 ppm, δ_B 7.411 ppm (from TMS), δ_X -83.5 ppm (upfield from CFCl_3) ($J_{AB} = 5.7$, $J_{AX} = 0.8$ and $J_{BX} = 0.9$ cps). The *cis* HH coupling (J_{AB}) is identical with the *cis* HH coupling in maleic anhydride.⁶

An unambiguous assignment of the protons A and B is not possible. It is more likely that the low field proton is the one β with respect to the carbonyl group and this assignment is chosen here. The small three-bond HF coupling is not unreasonable⁷ since the dihedral angle is about 60 degrees.

Experimental Section

Fumaryl Fluoride.—A 2:1 molar ratio of antimony trifluoride and fumaryl chloride was stirred and heated at 100° for about 1 hr. The more volatile fumaryl fluoride (bp 106°) was then distilled from the mixture and subsequently identified by nmr and mass spectroscopy.

Fumaryl Chloride Fluoride.—A 2:1 molar ratio of fumaryl chloride and antimony trifluoride was heated for about 1 hr at 100°. Fumaryl chloride fluoride was not completely separated from fumaryl chloride but an enriched sample (approximately 80%) was prepared by vacuum trap-to-trap distillation. The compound was identified by its ABX nmr pattern.

Reaction of Maleic Anhydride with Sulfur Tetrafluoride.—A 11.3-g (0.12 mol) sample of maleic anhydride was weighed into a 125-ml monel cylinder fitted with a needle valve. The cylinder and its contents were vacuum degassed. Sulfur tetrafluoride (0.23 mol) was vacuum transferred and condensed into the cylinder. Following a heating period of about 5 hr at 75–80° the cylinder was allowed to cool to room temperature and the volatile components were vented. Small amounts of dissolved SF_4 and HF were removed by vacuum degassing. Partial separation of maleoyl fluoride was achieved by vacuum trap-to-trap transfer. The product was identified by its nmr and mass spectra. Compound I, a product of the reaction was identified by its proton and fluorine nmr spectrum.

(6) D. F. Koster, unpublished results.

(7) K. L. Williamson, Y. L. Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Amer. Chem. Soc.*, **90**, 6717 (1968).

Spectra.—The nmr spectra were recorded with A-56/60 and HA-100 nmr spectrometers. A CEC 21-104 mass spectrometer was used in recording the mass spectral data.

Registry No.—I, 24647-21-0; II, 692-71-7; fumaryl fluoride, 24647-23-2; fumaryl chloride fluoride, 24647-24-3.

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Geometrical Isomers of Bisimines of Tetramethyl-1,3-cyclobutanedione

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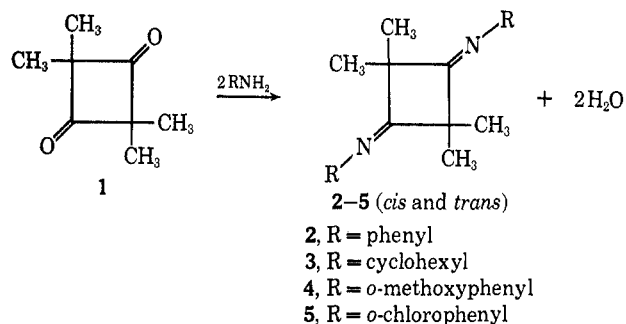
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Geometric isomerism of aliphatic and aromatic azomethines has been studied extensively by nmr.^{1–3} The configuration about the carbon–nitrogen double bond was established by the use of long-range coupling constants and by variable-temperature studies. More recently a report on the nmr conformational analysis of conjugated diimines has appeared.⁴ The factors influencing isomerization about the azomethine grouping are still only vaguely understood.⁵

We wish to report the first example of geometrical isomerization of bisimines of alicyclic β diketones. Steric crowding as well as transannular participation are two factors which may influence the position of equilibrium about the carbon–nitrogen double bond making these systems unique.

The bisimines 2–5 were prepared by the reaction of tetramethyl-1,3-cyclobutanedione (1) with 2 mol of the



appropriate amine according to previously described procedures.⁶ All spectral properties and elemental analyses were consistent with the structures.

(1) D. A. Nelson and R. L. Atkins, *Tetrahedron Lett.*, 5187 (1967).

(2) G. J. Karabatsos and S. S. Lande, *Tetrahedron*, **24**, 3907 (1968), and references therein.

(3) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Amer. Chem. Soc.*, **88**, 2775 (1966), and ref 4, 32, and 36 therein.

(4) J. M. Kliegman and R. K. Barnes, *Tetrahedron Lett.*, 1953 (1969).

(5) N. P. Marullo and E. H. Wagener, *ibid.*, 2555 (1969).

(6) R. H. Hasek, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **26**, 4340 (1961).