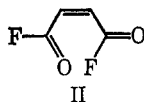


(II) which would account for the differences in $\delta(3)$, J_{13} and J_{14} , when compared with the same parameters of fumaryl fluoride.



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.

Acknowledgment.—We wish to thank Miss Verneda Wright for technical assistance and Mr. Walter Boyd for help in obtaining the fluorine nmr spectra. The spectra were recorded on an HA-100 nmr spectrometer purchased with the aid of a grant from the National Science Foundation.

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

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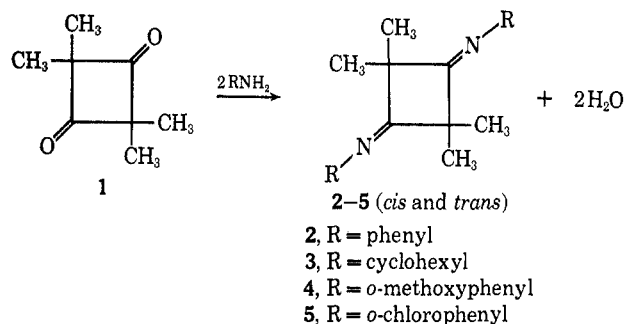
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Geometric isomerism of aliphatic and aromatic azomethines has been studied extensively by nmr.^{1–3} The configuration about the carbon–nitrogen double bond was established by the use of long-range coupling constants and by variable-temperature studies. 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).

At the probe temperature of 35° in CCl₄ the protons of the methyl groups of tetramethyl-1,3-cyclobutanedione (1) exhibit a single sharp resonance at δ 1.29. Under the same conditions the methyl groups of the bisimine derivatives show proton resonance at three distinct field positions (Table I).

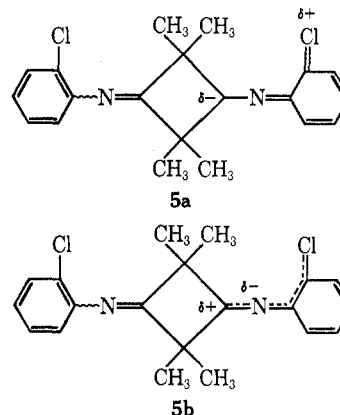
TABLE I
METHYL RESONANCES OF BISIMINES OF
TETRAMETHYL-1,3-CYCLOBUTANEDIONE

Compd	δ , ppm ^a	
	<i>trans</i>	<i>cis</i>
2	1.26	1.01, 1.52
3	1.32	1.20, 1.47
4	1.22	0.89, 1.55
5	δ 1.33 (broad singlet)	

^a δ values are reported in CCl₄ at a probe temperature of 35° using TMS as the internal standard.

The observed resonances are attributed to mixtures of *cis* and *trans* isomers. There are nonequivalent methyl groups for the *cis* isomers to which the combined high- and low-field singlets have been attributed. The proton resonance of the equivalent methyl groups of the *trans* isomers is assigned to the intermediate field singlet which is the most intense. The high- and low-field singlets of the *cis* isomer are of equal area and represent approximately 33% of the product mixture. To verify the isomerization the nmr spectra of 2, 3, and 5 were observed at different temperatures. When the temperature was raised, the three separate singlets of compound 2 coalesced to one broad singlet at a temperature of 100°. A similar phenomenon was observed for compound 3. In the latter case, however, the coalescence temperature was 165° which may be due to the more bulky cyclohexyl rings. On cooling the samples to room temperature the proton resonance of the methyl groups gradually returned to that of the original spectrum taken at 35° and possessed the same *cis* to *trans* ratio. That isomerization was being observed and that it was not simply restricted rotation about the R group attached to the nitrogen is demonstrated. Compound 5 at 35° shows a broad singlet for the proton resonance of the methyl groups, whereas three distinct singlets are observed at 10°. If simple rotation barriers were being observed, 3 would be expected to require a lower coalescence temperature than 5, and this is not observed. On the other hand, if *cis-trans* isomerization is being observed, 5 would be expected to have a lower coalescence temperature than

2 or 3 because of the contribution of resonance structures, of which 5a is a single contributing form, and inductive effects (5b) which impart partial single-bond character to the azomethine linkage. Similar resonance structures are less predominant in 2 and absent in 3.



It is impossible on the 60-MHz instrument to detect two separate *o*-methyl resonances for the *cis* and *trans* isomers of 4. The 100-MHz spectrum shows two distinct singlets with a separation of 2 Hz. The more intense low-field singlet represents the *o*-methyl resonance of the *trans* isomer.

Experimental Section

Nuclear magnetic resonance spectra were observed at 60 and 100 MHz. High-temperature studies were run in DMSO-*d*₆ and low temperature studies in CCl₄. The temperature was controlled to $\pm 2^\circ$ using the Varian V-6040 temperature controller.

The bisimines were prepared according to a procedure described by Hasek.⁶ All spectral properties were consistent with the structures. Compounds 2 and 3 were previously analyzed.⁶

Anal. Calcd for 4: C, 75.40; H, 7.48. Found: C, 74.44; H, 7.49. Calcd for 5: C, 66.86; H, 5.61. Found: C, 66.39; H, 5.89.

Registry No.—*cis*-2, 24627-15-4; *trans*-2, 24627-16-5; *cis*-3, 24627-17-6; *trans*-3, 24627-18-7; *cis*-4, 24627-19-8; *trans*-4, 24627-20-1; *cis*-5, 24627-21-2; *trans*-5, 24627-22-3.

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