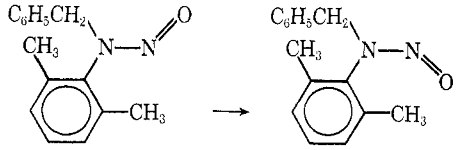
shielding environment of the benzene ring. Furthermore, molecular models show that steric interactions between the *o*-methyl and β-methyl groups of **9** are sufficient to force the β-methyl groups to stagger the NO group.

C. Determination of the Rotational Barrier in 4.— The partial double bond character of the N-N bond has already been shown[3] to give rise to syn and anti isomeric forms in **4**. In the room temperature nmr spectrum of this compound, the magnetic nonequivalence of the isopropyl groups gives rise to two doublets for the β-methyl protons. At higher temperature, these doublets are found to broaden and, at 113°, coalesce into one very broad signal. From a line-shape study of these coalescing doublets, it was possible to determine the enthalpy of activation ($\Delta H^{\ddagger}$) for the rotation. For the process *syn*-**4** → *anti*-**4**, $\Delta H^{\ddagger} = 25.8 \pm 0.8$ kcal/mol, while, for the process *anti*-**4** → *syn*-**4**, $\Delta H^{\ddagger} = 24.1 \pm 1.1$ kcal/mol.

These enthalpies of activation are not unlike other values which have been determined for nitrosamines. Blears[8] found the $\Delta H^{\ddagger}$ for dimethylnitrosamine (mol fraction = 0.21 in 1-chloronaphthalene) to be 24 kcal/mol, while Mannschreck, *et al.*,[9] obtained a $\Delta H^{\ddagger}$ of 24.2 kcal/mol (in CCl_4) for the following process.



The close agreement between the enthalpy of activation for **4** and other such determinations suggests that there is little contribution from the phenyl group to the partial double bond character of the N-N bond. This conclusion is not surprising, however, since we know from both nmr and uv spectra[1a] of **4** that electronic interactions between the ring and NNO group have been considerably reduced because of twisting.

Registry No.—**1**, 7633-57-0; **2**, 614-00-6; **3**, 612-64-6; **4**, 24642-83-9; **5**, 24642-84-0; **6**, 10596-01-7; **7**, 24690-69-5; **8**, 24699-12-5; **9**, 24699-13-6.

Acknowledgment.—The authors would like to thank Professor F. Kaplan for many helpful discussions.

---

[8] D. J. Blears, *J. Chem. Soc.*, 6256 (1964).

[9] A. Manschreck, H. Muensch, and A. Mattheus, *Angew. Chem.*, **5**, 728 (1966).

Notes

Mass Spectra of Dimethyl Fumarate and Maleate

SEYMOUR MEYERSON,* P. J. IHRIG, AND T. L. HUNTER

Research and Development Department, American Oil Company, Whiting, Indiana 46394

Received August 25, 1970

A recent review of stereoisomeric effects on mass spectra,[1] coauthored by one of us, carried an introductory statement, since repeated elsewhere,[2] that "the most striking instance... of stereoisomers with markedly different mass spectra is that of dimethyl fumarate and maleate." We have since found the literature report that led us to make this statement to be in error.

The statement was based on a report that the most abundant ion in the spectrum of dimethyl fumarate occurs at mass 112, corresponding to the loss of CH_3OH, in contrast to 113 in the spectrum of the maleate.[3] We have located two published spectra of dimethyl fumarate but none of the maleate. The first of the fumarate spectra,[4] which presumably furnished the basis for the qualitative statement above,[3] shows the strongest peak at mass 112 and an intensity at 113 of 21.02% that at 112. The other, presented in bar-chart form, shows the strongest peak at 113, an intensity at 114 about 21% that at 113, and nothing at 112.[5] The paper in which the latter spectrum appeared stated that the authors had measured the spectra of dimethyl maleate as well as fumarate and called attention to some spectral differences between the isomers. However, they said nothing about comparative intensities at 113 or 112, and they did not report the maleate spectrum.

We have now measured the two spectra, which are shown in Table I. Intensities are expressed as $\%\Sigma_{24}$, with all values $\geq 0.5\%$ reported here. Intensity at 112 on this scale is less than 0.1% in both spectra. Evidently, the original qualitative statement contrasting the spectra was based on an error in reading the mass scale.

Nonetheless, our spectra do show significant differences. In each spectrum, the most abundant ion is $[M - CH_3O]^+$, and this species breaks down further by losing CO, as shown by a metastable peak. The

$$68.3 \quad 113^+ \longrightarrow 85^+ + 28$$

intensities of the resultant fragment ions at masses 113 and 85 in the two spectra differ substantially and these differences, coupled with the difference in geom-

---

[*] Research Department, Standard Oil Co., Naperville, Ill. 60540.

[1] S. Meyerson and A. W. Weitkamp, *Org. Mass Spectrom.*, **1**, 659 (1968).

[2] F. Benoit, J. L. Holmes, and N. S. Isaacs, *ibid.*, **2**, 591 (1969).

[3] F. W. McLafferty, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 7.

[4] Uncertified Mass Spectral Data, The Dow Chemical Co., Midland, Mich., 1963, Spectrum No. 1309.

[5] J. H. Bowie, D. H. Williams, P. Madsen, G. Schroll, and S.-O. Lawesson, *Tetrahedron*, **23**, 305 (1967).

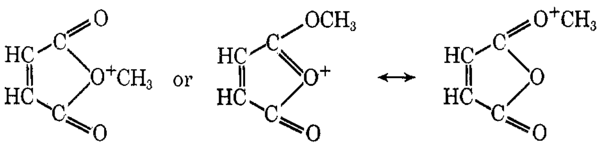
TABLE I

MASS SPECTRA OF DIMETHYL MALEATE AND FUMARATE[a]

Mass	Maleate	Fumarate
26	10.2	8.9
27	2.5	2.2
28	1.2	1.6
29	5.6	4.9
30	1.2	1.1
31	1.1	1.0
39	1.2	1.7
41	0.7	1.2
42	0.7	0.6
45	0.6	0.5
53	3.1	5.7
54	4.2	4.2
55	1.7	1.1
59	11.7	9.2
81		1.0
82	1.1	1.5
85	4.8	11.9
86		0.6
99		0.6
100		1.0
113	39.5	29.5
114	3.2	5.0
144	0.2	0.6

[a] Intensities are expressed as $\%\Sigma_{24}$.

etry, suggest that the $[M - CH_3O]^+$ ion from dimethyl maleate is stabilized by participation of an oxygen atom from the second carbomethoxy group to yield



The added stabilization apparently promotes the primary decomposition step and opposes the second one.

Such participation has a direct analogy in the mass spectra of the isomeric dimethyl phthalates, shown in Table II. Here, again, the masses of prominent peaks and supporting metastable peaks

$$137.1 \quad 194^+ \longrightarrow 163^+ + 31$$

and

$$111.8 \quad 163^+ \longrightarrow 135^+ + 28$$

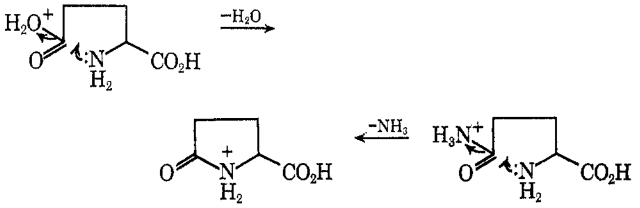
establish sequential loss of $CH_3O\cdot$ and CO in all three isomers. Dimethyl *o*-phthalate gives a sharply higher intensity for $[M - CH_3O]^+$ and lower intensities for the molecular ion and $[M - CO_2CH_3]^+$ than the iso- and terephthalates. Thus, this set of spectra also suggests that the $[M - CH_3O]^+$ ion from the *o*-phthalate is stabilized by participation of an oxygen atom from the second carbomethoxy group. Furthermore, this participation closely parallels that apparently involved in the respective loss of H_2O and NH_3 from the protonated molecules in the chemical ionization mass spectra of glutamic acid and glutamine.[6] Other examples of participation in electron-impact mass spectra have been described recently.[7]

TABLE II

PARTIAL SPECTRA OF THE ISOMERIC DIMETHYL PHTHALATES[a,b]

Mass	Ion	Ortho	Iso	Tere
135	$[M - CO_2CH_3]^+$	2.9	7.6	6.2
163	$[M - CH_3O]^+$	40.2	32.6	33.5
194	$[M]^{+\cdot}$	3.0	7.7	8.1

[a] Unpublished spectra, this laboratory, measured with 70-V electrons on a CEC Model 21-103 instrument. The spectra are qualitatively similar to those reported by F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, **31**, 2076 (1959). [b] Intensities are expressed as $\%\Sigma_{24}$.



Experimental Section

The methyl esters were prepared by refluxing the acids with anhydrous hydrogen chloride in methanol. The fumarate was purified by recrystallization from methanol; the maleate, by water extraction. Identities and purities were checked by ir and nmr spectra as well as by melting point of the fumarate and gas chromatography on the maleate. Titration of both esters with alcoholic potassium hydroxide established the absence of free acid.

Mass spectra were measured with 70-V electrons on a CEC Model 21-103 instrument with the inlet system and source at 350 and 250°, respectively. Another 21-103 with the inlet system at 150° gave virtually identical spectra.

Registry No.—Dimethyl fumarate, 624-49-7; dimethyl maleate, 624-48-6.

---

(6) G. W. A. Milne, T. Axenrod, and H. M. Fales, *J. Amer. Chem. Soc.*, **92**, 5170 (1970).

(7) R. H. Shapiro and K. B. Tomer, *Org. Mass Spectrom.*, **3**, 333 (1970), and references cited therein.

Pyrolysis of 1-Nitroadamantane

ALLEN I. FEINSTEIN AND ELLIS K. FIELDS*

Amoco Chemicals Corporation, Research and Development Department, Naperville, Illinois 60540

PHILIP J. IHRIG AND SEYMOUR MEYERSON

Standard Oil Company, Research Department, Naperville, Illinois 60540

Received November 5, 1969

A recent study showed that adamantane decomposed at 550–570° when aluminum silicate and aluminum chromate were present as catalysts.[1a] In the absence of catalysts, it decomposed at 660–675°.[1b] Both reactions gave complex mixtures of products consisting primarily of benzene, mono- and dialkylbenzenes, substituted naphthalenes, and C_2–C_4 hydrocarbons. The present investigation was undertaken to learn more about the thermal decomposition of the adamantane nucleus, with particular emphasis on the thermal reactions of the adamantyl radical derived from 1-nitroadamantane.

This compound is a member of a group of 1-substituted adamantane derivatives that characteristically lose the substituent readily upon electron impact in the mass spectrometer.[2] The subsequent fragmentation of

---

(1) (a) B. A. Kazanskiy, E. A. Shokova, and T. V. Korosteleva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **11**, 2642 (1968); (b) *ibid.*, **11**, 2640 (1968).

(2) Z. Dolejsek, S. Hala, V. Hanus, and S. Landa, *Collect. Czech. Chem. Commun.*, **31**, 435 (1966).