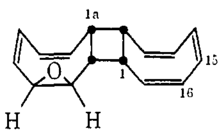
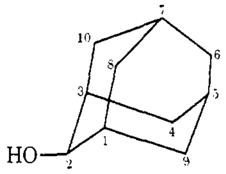


11

and between H_5 and H_7 may be inverted since they presumably were based on distance only considerations. To test this we obtained the best least-squares[34] fit using the three different assignments, and find that the fit with the cis, trans-$H_4(H_9)$ assignments reversed is much better (R 2.67) than either the original assignments (R 4.24) or the one with H_5 and H_7 reversed (R 8.68). The latter two models may be rejected at about the 98 and 99.5% confidence levels.



2-adamantanol

Summary and Conclusions

The analysis of LIS data using the McConnell–Robertson equation (eq 1) appears to be justifiable on the grounds of its apparent success. This success can be rationalized for one to one (seven coordinate) shift reagent–substrate complexes in terms of the approximate axial symmetry about the substrate–lanthanide bond and the averaging which results from rotation about this bond. Neglecting to average the shifts calculated by eq 1 over appropriate molecular orientations can result in incorrectly assigned spectra, as shown for 3,3-dimethylthietane 1-oxide. In this case it was necessary to average the calculated shifts of the three conformations resulting from rotation about the $EuO–SR_2$ bond, in order to properly fit the spectrum. Such averaging gives additional conformational information. Thus, it is our feeling that a variety of computational models should be applied to any structural problems. Models which closely mimic the internal motion(s) of a molecule are in our opinion the most reliable.[35]

The use of the C_2 shift equation (eq 8) and the explicit averaging of methyl protons, as opposed to treating them as a centrally located point nuclei, appears to be unnecessary in the molecules studied.

Acknowledgments. We thank Mr. Thomas A. Early for his help in preparing data sets. The purchase of the diffractometer was made possible by a National Science Foundation departmental instrument grant and a National Institutes of Health biomedical grant. Partial support for this research came from National Science Foundation Grant No. GP-19254 (R. M. W).

Supplementary Material Available. Documentation, listings, and sample computer runs will appear following these pages in the microfilm edition of this volume of the journal. A compilation of the observed and calculated structure factor amplitudes will also be included. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $5.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-6046.

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(34) The static model R factors were used since they were lowest.

(35) A similar conclusion has been recently expressed by Armitage, *et al.*, ref 23g.

Organic Ions in the Gas Phase. XXVII. Long-Range Intramolecular Interactions in 4-*n*-Alkyl Trimellitic Esters

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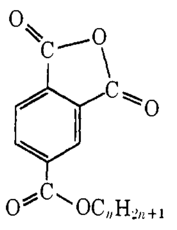
Received December 27, 1972

Abstract: Several decomposition products in the mass spectra of 4-*n*-alkyl esters of trimellitic anhydride stem from processes involving abstraction of an alkyl hydrogen by an oxygen atom in the anhydride group. Such hydrogen migration to the formally distant functional group occurs also in 4-*n*-alkyl trimellitimidates and 1,2-dimethyl 4-*n*-alkyl trimellitates, though not in methyl *n*-alkyl iso- or terephthalates. The mass spectra of triglycerides of long-chain aliphatic acids give evidence for a similar process, and a parallel in a different context has been reported in the photoinduced hydrogen migration from the alkyl chain to the ketonic oxygen in *n*-alkyl *p*-benzoylbenzoates. Deuterium labeling, ionizing voltage dependence, and metastable scanning data indicate that loss of small olefin molecules from 4-*n*-alkyl trimellitate anhydrides is a clean two-step process, consisting simply of hydrogen abstraction followed by β carbon–carbon bond cleavage. Thus, the carbon-number distribution of the olefins lost translates directly into a probability distribution of abstraction from the various alkyl carbons. This probability varies smoothly and symmetrically about a maximum which shifts slowly with increasing chain length to positions on the chain more remote from the ester linkage. The evidently low activation energies of reactions initiated by hydrogen abstraction support molecular coiling—internal solvation—rather than flailing as the mechanism by which the formally distant radical site and alkyl hydrogen in the gaseous molecule are brought into proximity.

In a preliminary study of the mass spectra of 4-*n*-alkyl esters of trimellitic anhydride (TMA), **1**, we found that esters in which the alkyl group contains six or more carbons lose C_nH_{2n-2}, that is, the alkyl group less three hydrogen atoms, in competition with

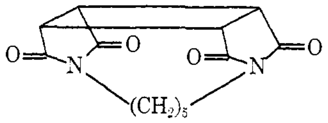
(1) (a) Standard Oil Company; (b) Amoco Chemicals Corporation.



1

loss of the alkyl group less two hydrogens, characteristic of alkyl esters of carboxylic acids.[2] One of the migrating atoms is apparently abstracted by a radical center at an anhydride oxygen atom,[2] in a process closely paralleling the photoinduced hydrogen migration from the alkyl chain to the ketonic oxygen in *n*-alkyl *p*-benzoylbenzoates.[3] These observations and others involving intramolecular reactions between formally distant parts of a sufficiently long flexible molecule were interpreted in terms of molecular coiling induced by attempts of isolated molecules to solvate themselves.[4] The concept of such coiling and internal solvation and the physicochemical consequences of this behavior are a matter of continuing interest both in systems restricted to neutral molecules[5] and in the mass spectrometer.[6–10]

A few further examples have been discovered of electron-impact induced reactions involving the migration of three[6,9] and even four[7a] hydrogen atoms. One such example, **2**, a derivative of a maleimide photodimer in which a pentamethylene chain connects the two nitrogen atoms, loses a C_5H_7 radical, that is, the pentamethylene chain less three hydrogen atoms.[9] In this system, in contrast with trimellitate anhydrides, migration of the third hydrogen is presumably facilitated because the far end of the "alkyl" group is bound directly to the second functional group destined to serve as the hydrogen acceptor. Loss of the N-substituent less two hydrogens is known to occur in the mass spectra of *N*-alkyl and, more prominently, *N*-cycloalkyl amides.[11]



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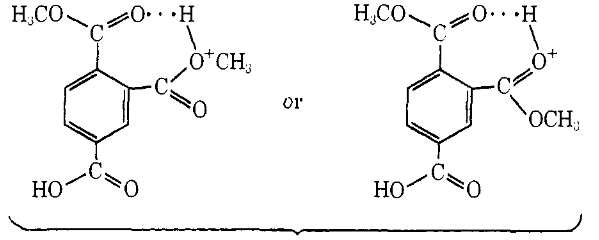
Our preliminary communication on trimellitate anhydrides[2] prompted a study by Cable and Djerassi[7b] that added substantially to knowledge of the system. To clarify and extend the system, these workers examined the spectra of the cyclic imides prepared from TMA esters. Loss of the alkyl group less three hydrogens persisted despite the structure change, and competition between the processes involving migration of three and two hydrogens showed chain-length dependence similar to that in the anhydrides. They also replaced the anhydride group with one carbomethoxy group in each of the originally occupied positions in turn and with two carbomethoxy groups. The spectra of these esters showed intense peaks for loss of the alkyl group less two hydrogens, but nothing attributable to loss of the alkyl group less three hydrogens. Evidence was found, however, for migration of an alkyl hydrogen to a carbomethoxy group in the 1,2-dimethyl 4-alkyl trimellitates, though not in the methyl alkyl iso- and terephthalates. In the trimellitates, primary loss of the alkyl group less two hydrogens is followed by loss of CH_3OH, and the alkyl group was confirmed by deuterium labeling as the source of the hydrogen atom lost with the CH_3O group.

We would picture the intermediate as **3** rather than **4**, shown by Cable and Djerassi,[7b] in recognition of the requirement of two carbomethoxy groups. Moreover, our measurements on Dreiding models suggest that a hydrogen atom on C-3 or any further removed alkyl carbon in the ester molecules can approach a carbomethoxy oxygen closely enough to allow migration,[12] but that a hydroxyl hydrogen in the CO_2H_2 group of **4** cannot. The dependence of this secondary loss of CH_3OH on the presence of carbomethoxy groups in both positions 1 and 2 was taken[7b] as evidence for participation of the second group, leading to the structure **5** or, we would add, **6**. Evidence has



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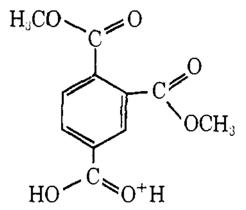

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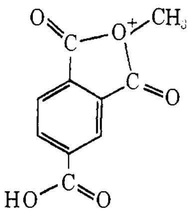

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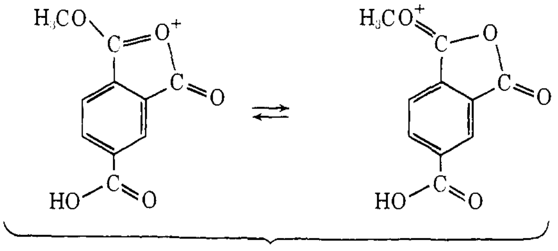

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been reported supporting a similar cyclic structure of the $[M - OCH_3]^+$ ions derived from dimethyl *o*-phthalate and maleate.[13]

To identify the original position(s) of the alkyl hydrogen migrating to the anhydride group in TMA esters, Cable and Djerassi[7b] studied a series of 4-*n*-nonyl TMA esters deuterated on alkyl carbons 3, 4, 5, 6, and 7, 8 and 9, and 9. No clear conclusions could be drawn from label retentions in the $[M - C_9H_{16}]^+$ ions because of uncertainty about the distribution of migrating atoms between the anhydride group and the ester carboxyl group. An alternative strategy was based on the discovery that $[M - C_9H_{18}O]^+$ derives directly from the molecular ion, and on evidence that the single alkyl hydrogen retained in this ion has migrated to the anhydride group. The data so obtained showed that the origin of the migrating atom is nonspecific—mainly positions 5, 6, and 7, a reduced amount from 8, and none from 9, the terminal position.

Lastly, loss of the alkyl group less three hydrogens in 4-*n*-alkyl TMA esters was enhanced, relative to loss of alkyl less two hydrogens, by reducing the ionizing voltage;[7b] and it was similarly enhanced in Cable and Djerassi's 70-eV spectra, measured on an Atlas Model CH4 instrument with the source at 190–200°,[7b] over our spectra, measured on a CEC Model 21-103 instrument with the source at 250°.[2] The most significant difference in operating conditions was most likely the source temperature.[14] The similar effects of reducing source temperature and ionizing voltage here parallel the effect of temperature on the coiling of long flexible polymers in dilute solution in poor solvents;[15] they support the view that hydrogen migration to the anhydride group is characterized by a low activation energy.[14,16]

In the meantime, the continuing study of the TMA ester system in our laboratories utilized essentially the same two approaches employed by Cable and Djerassi. First, we replaced the anhydride group in turn with a cyclic imide group, a single carbomethoxy group in original positions 1 and 2, and two carbomethoxy groups, and searched the resulting mass spectra for evidence of hydrogen migration from the alkyl group to the new functional group. Second, we prepared a series of labeled *n*-octadecyl, *6,7-d_2*, *9,10,d_2*, and *9,10,12,-13-d_4*, esters of TMA and sought *via* their mass spectra to estimate the extent of deuterium migration to the anhydride group. We selected these labeled species in view of the availability of a method suitable for specific deuterogenation of the double bonds, using tris(triphenylphosphine)rhodium(I) chloride as a homogeneous catalyst,[17] in readily available natural products or their derivatives. In part, our findings duplicate and hence confirm those of Cable and Djerassi; in other respects, they supplement them and define further aspects of the chemistry reflected in the spectra.

Experimental Section

The 4-alkyl esters of trimellitic anhydride discussed here and in the preliminary communication[2] were prepared by methods reported elsewhere.[18] Trimellitic anhydride acid chloride was the starting material in the preparation of the deuterium-labeled esters.

4-*n*-Octadecyl Trimellitimidate. Trimellitimide (9.55 g) and *n*-octadecanol (13.5 g) with about 0.2 g of *p*-toluenesulfonic acid were stirred at 250° in an apparatus equipped with a reflux condenser and a Dean–Stark trap. The reaction stopped after about one-third of the theoretical amount of water had collected in the trap, possibly because the catalyst was used up in side reactions. The desired ester was isolated from the crude mixture by extraction with hot benzene. The ester crystallized upon cooling; it was further purified by recrystallization from chloroform, mp 132–133°. Its infrared spectrum showed N-H (3215 cm^{-1}), imide (1785, 1768, 1720, 1702 cm^{-1}), and ester (1744, 1735 cm^{-1}) bands (in Nujol mull).

Methyl *n*-Octadecyl Isophthalate. To a stirred benzene–toluene solution of isophthaloyl dichloride (2.03 g) under nitrogen at 0° was added dropwise a solution of 1-octadecanol (2.7 g) and pyridine (0.82 ml) in benzene, followed by a solution of methanol (about 2 ml) and pyridine (about 2 ml) in benzene. The solvents and the pyridine hydrochloride were distilled off (final pot temperature 210° (0.2 Torr)). The residue, recrystallized from hexane, gave a small amount of dimethyl isophthalate, mp 67–68° (lit.[19] mp 68°), in the first crop. The mother liquors gave the crude mixed ester, which was recrystallized from methanol, mp 47–48°. *Anal.* Calcd for $C_{27}H_{44}O_4$: C, 75.0; H, 10.3. Found: C, 75.6; H, 10.0.

Methyl *n*-Octadecyl Terephthalate. The preparation was analogous to that of the isophthalate isomer, but with terephthaloyl dichloride. After the solvents and the pyridine hydrochloride were removed at 210° (0.2 Torr), the residue was treated with a large amount of hot methanol and filtered. The product crystallized from the filtrate in shining plates, mp 66–68°. *Anal.* Calcd

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Table I. Characterization of 1,2-Dimethyl 4-*n*-Alkyl Trimellitates

n-Alkyl group	Mp, °C	Formula	Elemental anal.	C	H
Butyl	Liquid	$C_{15}H_{18}O_6$	Calcd	61.2	6.2
			Found	61.3	6.3
Hexyl	Liquid	$C_{17}H_{22}O_6$	Calcd	63.3	6.9
			Found	63.0	6.9
Hexadecyl	43	$C_{27}H_{42}O_6$	Calcd	70.1	9.1
			Found	70.0	8.9
Octadecyl	45	$C_{29}H_{46}O_6$	Calcd	71.0	9.5
			Found	70.5	9.3

Table II. Physical Constants of *n*-Alkyl Benzoates

n-Alkyl group	Bp, °C (Torr) or mp, °C This study	Lit.[a]
Hexyl	96 (0.15)	138 (8.5)
Octyl	113–114 (0.25)	164 (7); 163 (9); 171–172 (12)
Undecyl	144–146 (0.2)	
Dodecyl	155 (0.2)	175 (1)
Hexadecyl[b]	34.5–36.0	28–30
Octadecyl[c]	42.5–44.0	

[a] Reference 19, pp 398–400. [b] Recrystallized from ethyl acetate–methanol. [c] Recrystallized from chloroform–methanol.

for $C_{27}H_{44}O_4$: C, 75.0; H, 10.3. Found: C, 75.5; H, 10.1. The methanol-insoluble material was dioctadecyl terephthalate, purified by recrystallization from hexane. *Anal.* Calcd for $C_{44}H_{78}O_4$: C, 78.8; H, 11.7. Found: C, 78.7; H, 11.5.

1,2-Dimethyl 4-*n*-Alkyl Trimellitates. Powdered 4-*n*-alkyl trimellitates[18] were added slowly with stirring to excess ethereal diazomethane solution, evolving nitrogen. Removal of solvent left the required esters as residues, which were recrystallized from methanol or hexane. Their characterization is given in Table I.

The labeled alcohols were prepared from olefinic precursors by homogeneous deuterogenation with tris(triphenylphosphine)-rhodium chloride.[17] Olefin isomerization and a measure of deuterium scrambling have been reported in this procedure,[20] but such side reactions are inhibited by the use of benzene, free of alcohol, as solvent.[21] In particular, methyl oleate and methyl linoleate are reported, when treated with this catalyst, to add deuterium specifically to the double bonds to produce the expected methyl stearates-d_2 and -d_4 of molecular weights 300 and 302, "with negligible higher peaks" in their mass spectra.[22]

1-Octadecanol-*9,10*-d_2. Oleyl alcohol (25 ml, Aldrich technical grade) in benzene (50 ml) was shaken in a rocking autoclave with tris(triphenylphosphine)rhodium chloride (50 mg, Alfa Inorganics) under deuterium (100 psi initial pressure) overnight. The crystallized product was filtered and washed with hexane, mp 57–58° (lit.[23] (unlabeled) mp 58°).

1-Octadecanol-*6,7*-d_2. Petroselinic acid (*cis*-6-octadecenoic acid) (2.0 g, Pfalz & Bauer) in benzene (30 ml) was shaken in a rocking autoclave with tris(triphenylphosphine)rhodium chloride (40 mg) under deuterium (80 psi initial pressure) for 8 hr. The solvent was removed and the residue crystallized from methanol to give crude stearic acid-*6,7*-d_2, mp 59–63° (lit.[24] (unlabeled) mp 69.39–70.5°), which was used without further purification. Powdered lithium aluminum hydride (0.6 g, excess) was slurried with dry tetrahydrofuran by stirring and powdered stearic-*6,7*-d_2 acid (0.95 g) was added in small portions under nitrogen. The mixture was refluxed for 0.5 hr; excess reagent was decomposed by adding ethyl acetate, then methanol and water. Solvents were then removed *in vacuo*. The residue was extracted with water and filtered. From the aqueous filtrates (surprisingly!) crude octadecanol-*6,7*-d_2 (0.35 g) crystallized in shining plates, mp 49–54°. From the water-insoluble filter cake, after drying, the organic materials were extracted with hot methanol, filtered, and crystallized to give another crop of octadecanol-*6,7*-d_2, 0.15 g, mp 55.5–56.5°.

1-Octadecanol-*9,10,12,13*-d_4. Methyl linoleate (25 ml, Aldrich) in benzene (100 ml) was shaken in a rocking autoclave with tris(triphenylphosphine)rhodium chloride (500 mg, Alfa Inorganics) under deuterium (100 psi initial pressure) for 24 hr. The solvent was removed *in vacuo* and the residue extracted with lukewarm (40–45°) methanol and filtered. From the filtrate, 14.5 g of methyl stearate-*9,10,12,13*-d_4 was isolated, mp 35–36° (lit.[25] (unlabeled) mp 37.78°). The methanol-insoluble material was a dimeric product, pictured tentatively, on the basis of inference from the mass spectrum, as having an ether linkage. Methyl stearate-*9,10,12,13*-d_4 was reduced with excess lithium aluminum hydride in refluxing ether for 20 hr. Excess reagent was decomposed with methanol and water. The precipitate was filtered with the aid of Celite, dried *in vacuo*, and extracted with chloroform. Removal of the solvent left a solid, which was extracted with hot methanol and filtered from the insolubles. The methanol filtrates gave octadecanol-*9,10,12,13*-d_4, mp 55–56°.

***n*-Octadecyl benzoates** were made by adding a solution of benzoyl chloride in benzene to the corresponding alcohol in benzene-pyridine solution under anhydrous conditions. After the solvents were removed, the residues were heated to 210° (0.5 Torr) to remove volatiles. The residues were crystallized from chloroform–methanol to give these *n*-octadecyl benzoates: d_0, mp 42.5–44°; *6,7*-d_2, mp 41–42°; *9,10*-d_2, mp 41–42°; and *9,10,12,13*-d_4, mp 40–41°.

***n*-Alkyl benzoates** on which mass spectral data were reported in the preliminary communication[2] were prepared by Fischer esterification of benzoic acid with the appropriate alcohols in the presence of 0.5% *p*-toluenesulfonic acid at 160–190° until the theoretical amount of water collected in a Dean–Stark trap (1–3 hr). The crude products were purified by either distillation or crystallization. Physical constants and literature data are listed in Table II.

Labeled *n*-Octadecyl Trimethylsilyl Ethers. To aid in the isotopic analysis, we converted the labeled octadecanols to trimethylsilyl ethers.[26] In a typical preparation, a solution of 1.15 g of chlorotrimethylsilane (Eastman, practical) in benzene was added with stirring at about 10° to a toluene–pyridine solution of octadecanol-*9,10*-d_2, which was then boiled briefly. Solvents were removed *in vacuo*, and the residue was heated to 210° (0.1 Torr) to remove volatiles. The residue was recrystallized from hexane. The first crop, white shiny plates, mp 56–57°, was evidently the starting alcohol, confirmed by ir. A second crop, mp 45–53°, was the required ester contaminated with octadecanol, as shown by ir and gas chromatography. It was used without purification for mass spectral isotopic analysis.

Mass spectra were measured on a CEC Model 21-103 instrument, with the inlet system at 350° and the source at 250°. The spectra of the *n*-octadecyl TMA esters and of some of the other materials gave evidence of incipient thermal decomposition; these were rerun on a Du Pont Model 21-104 instrument with the inlet system at 250–280°. The mass regions of interest were unaffected by the difference in inlet temperature except for small contributions from trimellitic anhydride at masses 192 and 175 in the TMA ester spectra and from analogous thermal reaction products in other spectra. Data reported here from spectral regions subject to such interference were taken from the spectra run at the lower temperature; all other data are from the original spectra. Conventional 70-eV spectra were in some cases supplemented by low-voltage measurements, chiefly to facilitate isotopic analysis. Low-voltage spectra were measured at 9.5 nominal ionizing volts except as otherwise noted, with the average repeller potential set at 3.0 V.

The estimation of isotopic composition suffered from low intensities of the relevant peaks in the spectra of all labeled materials. Moreover, in the octadecanols, isotopic analysis was subject to interference from an unidentified chemical impurity. Both our spectrum and a literature spectrum[27] of 1-octadecanol show strong $C_{18}H_{34}^+$ peaks accompanying $C_{18}H_{36}^+$, the expected [M −

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(22) A. J. Birch and K. A. M. Walker, *Tetrahedron Lett.*, 4939 (1966); *J. Chem. Soc. C*, 1894 (1966).

(23) Reference 19, Vol. 1, III, 1958, p 1834.

(24) Reference 19, Vol. 2, III, 1960, p 991.

(25) Reference 24, p 1012.

(26) S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

(27) "Catalog of Selected Mass Spectral Data," Serial No. 884, American Petroleum Institute Research Project 44, Thermodynamics Research Center, Texas A&M University, College Station, Texas (Loose-leaf sheets, extant, 1972).

Table III. Isotopic Compositions of *6,7-d_2* Materials

No. of D atoms	Stearic acid			Octadecyl benzoate		Octadecyl TMA ester			
	Ion used for analysis								
	M^+			$C_{18}H_{36}^+$		M^+		$C_{18}H_{36}^+$	
	Mass	%[a]	%[b]	Mass	%[a]	Mass	%[a]	Mass	%[a]
0	284	4	5	252	7	444	12	252	10
1	285	17	17	253	18	445	16	253	16
2	286	68	67	254	63	446	60	254	59
3	287	7	7	255	6	447	6	255	7
4	288	4	3	256	4	448	6	256	5
5	289		1	257	1			257	2
6				258	1			258	1

[a] 70-eV data. [b] Low-voltage data.

Table IV. Isotopic Compositions of *9,10-d_2* Materials

No. of D atoms	Octadecanol			Octadecyl benzoate		Octadecyl trimethylsilyl ether		Octadecyl TMA ester			
	Ion used for analysis										
	$C_{18}H_{36}^+$			$C_{18}H_{36}^+$		$[M - CH_3]^+$		M^+		$C_{18}H_{36}^+$	
	Mass	%[a]	%[b]	Mass	%[a]	Mass	%[a]	Mass	%[a]	Mass	%[a]
	250	2									
	251	5									
0	252	30		252	4			444	8	252	8
1	253	6	10	253	5	328	5	445	9	253	4
2	254	49	78	254	82	329	90	446	73	254	77
3	255	4	6	255	3	330	5	447	5	255	3
4	256	4	6	256	5			448	5	256	6
5				257	1					257	2
6										258	0.5

[a] 70-eV data. [b] Same data as in previous column, but normalized on a basis free of the species of masses 250, 251, and 252, which are attributed to a chemical impurity.

Table V. Isotopic Compositions of *9,10,12,13-d_4* Materials

No. of D atoms	Octadecanol			Octadecyl benzoate		Methyl stearate			Octadecyl trimethylsilyl ether		Octadecyl TMA ester			
	Ion used for analysis													
	$C_{18}H_{36}^+$			$C_{18}H_{36}^+$		M^+			$[M - CH_3]^+$		M^+		$C_{18}H_{36}^+$	
	Mass	%[a]	%[b]	Mass	%[a]	Mass	%[a]	%[c]	Mass	%[a]	Mass	%[a]	Mass	%[a]
	250	1												
	251	5												
0	252	3	4	252	3	298	5	4	327		444	3	252	3
1	253	4	4	253	2	299	1	3	328		445	4	253	3
2	254	15	16	254	13	300	13	13	329	15	446	13	254	13
3	255	15	17	255	13	301	14	14	330	13	447	15	255	12
4	256	42	44	256	51	302	51	50	331	59	448	49	256	51
5	257	11	11	257	12	303	11	11	332	10	449	12	257	13
6	258	4	4	258	4	404	4	3	333	3	450	4	258	5
7				259	2	305	1	2						

[a] 70-eV data. [b] See footnote *b*, Table IV. Only the species of masses 250 and 251 are omitted here. [c] Low-voltage data.

$H_2O]^+$ ion, although the proportions differ in the two spectra. The impurity responsible is apparently also present in our octadecanol-*9,10-d_2* and, at a much lower level, in octadecanol-*9,10,12,13-d_4*. Its concentration in octadecanol-*6,7-d_2* is so high that its contributions in the $C_{18}H_{36}^+$ mass region swamp those attributable to the octadecanol itself; data from this spectrum are therefore not reported here. The component responsible evidently caused no problem in the precursor acid and derived esters, however. Similar impurities were apparently responsible for the $[M - 2]^+$ and $[M - 20]^+$ peaks in literature spectra of *n*-hentriacontanol and eicosan-2-ol.[28] The compounds in question may be aldehydes, which would be removed in purifying the esterification products.

Isotopic compositions of the *6,7-d_2*, *9,10-d_2*, and *9,10,12,13-d_4* materials, respectively, are listed in Tables III–V. In every case, the most abundant isotopic species is that expected on the assumption of specific deuterogenation of the original olefinic bonds with no side reactions. However, more, as well as less, highly deuterated species are ubiquitous. In any case, for each of the three labeling patterns, the isotopic analyses of the various compounds analyzed are in fairly good agreement. On this basis, we judged that the isotopic compositions are well-enough defined to allow meaningful interpretation of label-retention data extracted from the spectra.

Our inference, from differences between Cable and Djerassi's and our data, that the competition between triple- and double-hydrogen migration accompanying *O*-alkyl bond cleavage in the TMA esters is temperature dependent was confirmed by measurements on the *n*-octadecyl ester made on a Du Pont Model 21-110 spectrometer over a range of source temperatures. Sample was introduced through the conventional heated inlet system at 250°; electron energy was 70 eV. Resolving power was about 5300, high enough to separate cleanly the O_5-containing and the hydrocarbon ions, confirming that hydrocarbon contributions at masses 192, 193, and 194 are negligible. The intensity distributions over these masses, corresponding to retention of 1, 2, and 3 alkyl hy-

Table VI. Temperature and Voltage Dependence of Product Distribution from *O*-Alkyl Cleavage with Hydrogen Migration in *n*-Octadecyl Trimellitate Anhydride

Mass	No. of alkyl hydrogens retained	Source Temp, °C[a]					
		150	200	250	250		
		Ionizing volts[a]					
		70			9.5	11.5	70
192	1	0.8	1.6	0.4	1.0	1.0	0.9
193	2	67.0	69.1	73.2	52.2	55.4	64.0
194	3	32.2	29.3	26.4	46.8	43.6	35.1

[a] Both source temperature and ionizing voltages are nominal. Temperature-dependence data were measured on a Du Pont Model 21-110 instrument; voltage-dependence data, on a Du Pont Model 21-104 instrument.

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(28) R. Ryhage and E. Stenhagen, *J. Lipid Res.*, 1, 361 (1960).

Table VII. Metastable Peaks for Paths Leading to Selected Fragment Ions

	4-*n*-Octadecyl TMA ester						1,2-Dimethyl 4-*n*-octadecyl trimellitate		
	Fragment-ion series								
	$[M - C_jH_{2j}]^+$			$[M - H_2O - C_jH_{2j}]^+$			$[M - CH_3OH - C_jH_{2j}]^+$		
j	Fragment-ion mass	Precursor mass	Intensity[a]	Fragment-ion mass	Precursor mass	Intensity[a]	Fragment-ion mass	Precursor mass	Intensity[a]
2	416	444[b]	0.2	398	416	1.0	430	462	1.1
					426[c]	0.6		490[b]	0.7
					444[b]	0.4			
3	402	444	3.2	384	402	4.7	416	448	0.6
					426	0.6		458[d]	0.8
					444	1.3		490	2.3
4	388	444	6.0	370	388	7.5	402	434	0.5
					426	0.6		458	0.8
					444	1.3		490	2.1
5	374	444	7.6	356	374	9.8	388	420	0.1
					384	0.2		458	1.2
					402	0.1		490	2.4
					426	0.6			
					444	1.2			
6	360	388	0.5	342	360	9.8	374	406	1.0
		416	0.2		370	0.2		458	1.0
		444	8.6		388	0.1		490	2.2
					426	0.2			
					444	1.4			
7	346	444	8.0	328	346	8.0	360	392	1.0
					356	0.1		458	1.3
					426	0.1		490	2.0
					444	1.0			
8	332	444	7.0	314	332	3.6	346	378	0.8
					342	0.1		458	1.4
					356	0.1		490	2.3
					426	0.1			
					444	0.4			
9	318	444	5.0	300	318	1.2	332	364	0.3
					328	0.2		458	1.5
					342	0.1		490	1.9
					426	0.1			
					444	0.2			
10	304	444	2.0	286	304	0.6	318	350	0.9
					314	0.2		458	0.9
					332	0.1		490	1.0
					444	0.1			
11							304	336	0.7
								458	0.1
								490	0.1
12							290	322	0.2
								490	0.1
13							276	308	0.1
								458	0.1
14							262	294	0.6
								458	0.1

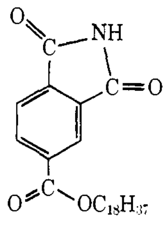
[a] Intensities are expressed on an arbitrary scale. [b] M^+. [c] $[M - H_2O]^+$. [d] $[M - CH_3OH]^+$.

drogens, respectively, are shown in Table VI. The analogous data measured at a fixed source temperature, 250°, but at different ionizing voltages, on the 21-104 instrument, also shown in Table VI, confirm the reported[7b] voltage dependence.

Selected fragment ions in the spectra of 4-*n*-octadecyl TMA ester and 1,2-dimethyl 4-*n*-octadecyl trimellitate were subjected to precise mass measurement and metastable scanning[29] on the 21-110 instrument to establish their compositions and origins. The precise masses confirm the compositions inferred from nominal masses in all cases. The parent-daughter relationships found by metastable scanning are listed in Table VII, along with metastable peak intensities, expressed on an arbitrary scale.

Results and Discussion

n-Octadecyl Trimellitimidate. The mass spectrum of the *n*-octadecyl ester of trimellitimide, **7**, shows the peaks at masses 192 and 193 reported by Cable and Djerassi[7b] for lower homologs, corresponding to loss of the alkyl radical less two and three hydrogens, respectively. The mass 193 : mass 192 intensity ratio, that is, the ratio of probabilities of triple- to double-hydrogen migration, is 30:70. This ratio is slightly lower than the analogous mass 194 : mass 193 intensity ratio in the spectrum of the *n*-octadecyl TMA ester, paralleling the observed[7b] behavior of the imide *vs.* anhydride esters with shorter alkyl groups.



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(29) J. H. Futrell, K. R. Ryan, and L. W. Sieck, *J. Chem. Phys.*, **43**, 1832 (1965); K. R. Jennings, *ibid.*, **43**, 4176 (1965).

Methyl *n*-Octadecyl Iso- and Terephthalates. The strongest peaks in the spectra of the isomeric methyl *n*-octadecyl phthalates, at mass 181, correspond to loss of the octadecyl group less two hydrogens, paralleling the behavior of lower homologs.[7b] Moreover, the intensity distribution between the peaks corresponding to loss of the octadecyl group with retention of one and two octadecyl hydrogens is essentially the same in the spectra of the mixed iso- and terephthalate esters and *n*-octadecyl benzoate: 5:95, 8:92, and 7:93, respectively. The close parallel suggests similar reactions, although such an inference is not so proved. Also paralleling the behavior of lower homologs,[7b] the mixed esters give peaks for primary loss of CH_3O but not of CH_3OH. Thus, the spectra of these esters furnish no evidence for hydrogen migration from the octadecyl group to the carbomethoxy group.

1,2-Dimethyl 4-*n*-Alkyl Trimellitates. Our spectra of the 1,2-dimethyl 4-*n*-butyl, 4-*n*-hexyl, 4-*n*-hexadecyl, and 4-*n*-octadecyl trimellitates closely resemble those reported[7b] for the 4-*n*-propyl, 4-*n*-butyl, 4-*n*-nonyl, and 4-*n*-dodecyl homologs. Each spectrum shows an intense peak at mass 239, corresponding to loss of the alkyl group less two hydrogens; nothing at 240, for a similar process with retention of three hydrogens; the most intense peak in the spectrum at 207, accompanied by a strong metastable peak identifying the ion of mass 239 as precursor to that of mass 207, the mass difference implying loss of CH_3OH;[30] a peak corresponding to the loss of CH_3O; and the characteristic[31,32] olefin peaks derived from the alkyl group. The intensity distributions between the peaks corresponding to loss of the alkyl group with retention of one and two alkyl hydrogens in these esters, all 1:99, agree less closely with those of the analogous benzoates: hexyl, 16:84; hexadecyl, 7:93; and octadecyl, 7:93. The difference is pronounced enough to suggest the intervention of some other reaction path in the trimellitates. In addition, the spectra of the hexadecyl and octadecyl esters, shown in part in Table VIII, contain several features not reported in the spectra of the lower homologs.

First, the $[M - CH_3O]^+$ ion is accompanied by $[M - CH_3OH]^+$, independently confirming the migration of an alkyl hydrogen to a carbomethoxy group. Second, the $[M - CH_3OH]^+$ ion breaks down further to some extent by losing a second CH_3OH molecule, demonstrating that, in at least some of the molecular ions, two alkyl hydrogen atoms migrate to carbomethoxy groups. Third, the homologous series of even-mass peaks corresponding to loss of olefin molecules from $[M - CH_3OH]^+$ appears unusual. Although the intensities of these peaks are not high, they stand out prominently in the mass region in which they occur and, in fact, comprise the strongest peaks in single carbon-number groups over a range of several carbon numbers. They are closely paralleled by series of peaks related similarly to the molecular ions and $[M - H_2O]^+$ of 4-*n*-alkyl TMA esters, described below, and would appear to arise by similar reactions.

Table VIII. Partial Spectra of 1,2-Dimethyl 4-*n*-Alkyl Trimellitates

	n-Hexadecyl		*n*-Octadecyl	
	Mass	Rel intensity[a,b]	Mass	Rel intensity[a,b]
M^+	462	0.64	490	0.53
$[M - CH_3O]^+$	431	2.69	459	1.69
$[M - CH_3OH]^+ \equiv Y^+$	430	2.48	458	1.74
$[Y - C_2H_4]^+$	402	0.13	430	0.09
$[Y - C_2H_5]^+$	401	0.20	429	0.21
$[Y - CH_3OH]^+$	398	0.37	426	0.42
$[Y - C_3H_6]^+$	388	0.41	416	0.34
$[Y - C_3H_7]^+$	387	0.18	415	0.06
$[Y - 44]^{+\,c}$	386	0.41	414	0.32
$[Y - C_4H_8]^+$	374	0.63	402	0.32
$[Y - C_4H_9]^+$	373	0.23	401	0.15
$[Y - C_5H_{10}]^+$	360	0.72	388	0.49
$[Y - C_5H_{11}]^+$	359	0.28	387	0.15
$[Y - C_6H_{12}]^+$	346	0.79	374	0.59
$[Y - C_6H_{13}]^+$	345	0.37	373	0.21
$[Y - C_7H_{14}]^+$	332	0.68	360	0.68
$[Y - C_7H_{15}]^+$	331	0.46	359	0.28
$[Y - C_8H_{16}]^+$	318	0.40	346	0.69
$[Y - C_8H_{17}]^+$	317	0.55	345	0.21
$[Y - C_9H_{18}]^+$	304	0.22	332	0.45
$[Y - C_9H_{19}]^+$	303	0.55	331	0.36
$[Y - C_{10}H_{20}]^+$	290	0.18	318	0.34
$[Y - C_{10}H_{21}]^+$	289	0.55	317	0.42
$[Y - C_{11}H_{22}]^+$	276	0.10	304	0.20
$[Y - C_{11}H_{23}]^+$	275	0.46	303	0.42
$[Y - C_{12}H_{24}]^+$	262	0.19	290	0.14
$[Y - C_{12}H_{25}]^+$	261	0.28	289	0.42
$[Y - C_{13}H_{26}]^+$			276	0.15
$[Y - C_{13}H_{27}]^+$			275	0.36
$[Y - C_{14}H_{28}]^+$			262	0.15
$[Y - C_{14}H_{29}]^+$			261	0.28
$[M - C_nH_{2n-1}]^{+\,d}$	239	12.9	239	11.0
$[M - C_nH_{2n+1}O]^+$	221	47.2	221	47.9
$[M - C_nH_{2n-1} - CH_3OH]^+$	207	100.0	207	100.0
$[C_nH_{2n}]^+$	224	1.93	252	3.12

[a] Corrected for naturally occurring heavy isotopic contributions. [b] Intensity scale defined by setting the value at 207 equal to 100.0. [c] Composition and origin uncertain. The mass suggests that the neutral particle lost may be CO_2. [d] n = the number of carbon atoms in the alkyl group, that is, 16 and 18 in the respective esters.

4-*n*-Octadecyl and Other Trimellitate Anhydrides. The $[M - C_nH_{2n}O]^+$ peak at mass 176 (in the unlabeled species), where n is the number of carbons in the alkyl group, proved useful in pinpointing the origins of alkyl hydrogens migrating to the anhydride group in 4-*n*-nonyl TMA ester because the $[M - C_nH_{2n+1}O]^+$ peak at 175 disappeared at reduced ionizing voltage, leaving the peak of interest free of interference.[7b] The pronounced difference between the appearance potentials of the two ions was ascribed to their nonparallel reaction paths. $[M - C_nH_{2n+1}O]^+$ appeared to arise in the main by a two-step sequence, in which C_nH_{2n-1} and H_2O are lost in succession, while $[M - C_nH_{2n}O]^+$ arose solely by loss of $C_nH_{2n}O$ from the molecular ion. In view of these disparate origins, the nearly identical mass 176:mass 175 and mass 194:mass 193 intensity distributions found in the spectra of the *n*-octyl, *n*-nonyl, *n*-decyl, and *n*-dodecyl esters[7b] would have to be a fortuitous result of the particular instrument conditions employed and the narrow range of alkyl chain lengths surveyed. This surmise is indeed confirmed by our data. The mass 176:mass 175

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(30) Similar combinations of normal and metastable peaks establish the loss of C_4H_9OH following primary loss of $C_{12}H_{23}$ and $C_{10}H_{19}$ from 1,2-di-*n*-butyl 4-*n*-dodecyl and 1,2-di-*n*-butyl 4-*n*-decyl trimellitates, respectively, and the loss of C_3H_5OH following primary loss of $C_{10}H_{19}$ from 1,2-diallyl 4-*n*-decyl trimellitate (unpublished spectra, this laboratory).

(31) R. Ryhage and E. Stenhagen in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 9.

(32) R. Ryhage and E. Stenhagen, *Ark. Kemi*, 14, 483 (1959).

Table IX. $[M - C_{18}H_{35}]^+$ Regions in Spectra of Labeled *n*-Octadecyl Benzoates and Trimellitate Anhydrides

	Benzoates					TMA esters			
	d_0	*6,7-*d_2	*9,10-*d_2	*9,10,12,13-*d_4		d_0	*6,7-*d_2	*9,10-*d_2	*9,10,12,13-*d_4
Mass	Rel intensity[a,b]				Mass	Rel intensity[a,c]			
122	5.45	5.42	5.45	5.47	192	0.91	1.41	1.98	0.94
123	90.2	83.7	87.0	84.7	193	61.7	57.4	52.9	45.9
124	0.54	6.70	3.42	5.54	194	33.8	33.6	36.2	38.2
125	2.24[d]	0.81	0.57	0.37	195	1.52[d]	5.12	6.29	10.9
126	1.31[d]	1.56	1.56	0.94	196	2.02[d]	2.10	1.98	2.46
127	0.22[d]	1.18	1.44	1.19	197	0.13[d]	0.38	0.66	1.02
128	0.03	0.46	0.50	1.02	198		0.15	0.15	0.42
129		0.11	0.12	0.61	199				0.15
130		0.03	0.02	0.20					
131				0.05					
132				0.01					

[a] Corrected for naturally occurring heavy isotopic contributions. [b] Total intensity from mass 122 to 130 (132 in the d_4 spectrum) is set equal to 100.0. [c] Total intensity from mass 192 to 199 is set equal to 100.0. [d] Hydrocarbon ions derived from the octadecyl group.

and mass 194:mass 193 intensity distributions, corrected for naturally occurring heavy isotopic contributions, vary from 7:93 and 3:97, respectively, in the *n*-hexyl ester to 26:74 and 35:65 in the *n*-docosyl ester; the respective values in the *n*-octadecyl ester are 27:73 and 33:67.

Increase of alkyl chain length brings in its wake other changes in the spectra: a progressive decrease in intensity at 175/176 relative to that at 193/194; and interfering hydrocarbon ions, with low appearance potentials, derived from the alkyl chain. These two effects together make the $[M - C_nH_{2n}O]^+$ ion useless for locating the positions from which alkyl hydrogens migrate to the anhydride group in the *n*-octadecyl ester. We have instead used two alternative and independent approaches: the first, comparison of the $[M - C_{18}H_{35}]^+$ regions of the spectra of labeled *n*-octadecyl benzoates and TMA esters; the second, mechanistic interpretation of the loss of small olefin molecules from 4-*n*-alkyl TMA esters and 1,2-dimethyl 4-*n*-alkyl trimellitates, supported by label retentions in ions so derived from the labeled *n*-octadecyl TMA esters.

Comparative Label Retention in $[M - C_{18}H_{35}]^+$ from Labeled Octadecyl Benzoates and TMA Esters. Several observations scattered through this report point to hydrogen migration to the anhydride, or other second functional, group in paths effecting loss of C_nH_{2n-1} as well as of C_nH_{2n-2}, that is, loss of the alkyl group less two, as well as three, hydrogens. With this shift in terminus of the migrating atoms in mind, we focused attention on the $[M - C_{18}H_{35}]^+$ ions in the spectra of the labeled benzoates and TMA esters. Partial spectra covering the pertinent mass regions are shown in Table IX. The regions of interest in the spectra of both esters contain peaks attributable to hydrocarbon ions derived from the octadecyl group. Our decision to work with the $[M - C_{18}H_{35}]^+$ ions was dictated by the need to minimize interferences from these extraneous species in the spectra of the labeled esters.

Intensity attributable to unlabeled $[M - C_{18}H_{36}]^+$ at 122 is the same in all the benzoate spectra, implying that the production of this ion involves no measurable hydrogen migration from positions 6, 7, 9, 10, 12, or 13. The intensity variation of the analogous peak at 192 in the TMA ester spectra reflects slight interference from labeled counterparts of hydrocarbon ions occurring at 191, 190, etc., in the spectrum of the unlabeled compound. In any case, the peaks at 123 and 193 are apparently free of contributions from labeled $[M - C_{18}H_{36}]^+$, and can be attributed solely to unlabeled $[M - C_{18}H_{35}]^+$. The per cent of labeled $[M - C_{18}H_{35}]^+$ ions, with either one or two deuterium atoms, can now be estimated for each labeled species as $(I_0 - I)/I_0$, where I and I_0 are the intensities of the labeled and unlabeled esters, respectively, at mass 123 or 193. The values so arrived at are listed in Table X. The differences between the values for the similarly labeled esters measure the preference for migration from the labeled positions in the TMA ester over that in the benzoate, and we view them as first approximations to the extent of migration to the anhydride group. Positions 6/7 appear to contribute but little. Positions 9/10 and 12/13 contribute roughly equally. Positions 9/10 and 12/13 also contribute about equally to migration to the carboxyl group in the benzoate, where migration from positions 6/7 is about twice as probable as from the farther removed carbons.

Table X. Per Cent Label Retention in $[M - C_{18}H_{35}]^+$ from Labeled *n*-Octadecyl Benzoates and Trimellitate Anhydrides

	Benzoates	TMA esters	Difference[a]
6,7-d_2	7.2	7.0	−0.2
9,10-d_2	3.5	14.3	10.8
9,10,12,13-d_4	6.1	25.6	19.5

[a] The TMA ester value minus the benzoate value.

Loss of Olefin Molecules. Over a wide region—the entire interval between $C_{18}H_{36}^+$, mass 252, and $[M - H_2O]^+$, mass 426, in the *n*-octadecyl ester, for example—the mass spectra of the longer 4-*n*-alkyl TMA esters are dominated by a homologous series of peaks corresponding to loss of olefin molecules C_jH_{2j} from the molecular ion. Such peaks are common in the spectra of olefins,[33] but otherwise rare. They intrigued us particularly in view of the similar series apparently stemming from the $[M - CH_3OH]^+$ ions in the spectra

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(33) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 56; J. H. Beynon, R. A. Saunders, and A. E. Williams, "Mass Spectra of Organic Molecules," Elsevier, New York, N. Y., 1968, p 106.

Table XI. Partial Spectra of 4-*n*-Alkyl Trimellitate Anhydrides

Ion	6	7	8	11	12	16	18	20	22
	n[a]								
	Rel intensity[b]								
M^+	0.43	0.76	0.12	0.57	0.67	0.45	0.43	0.51	0.19
$[M - C_2H_4]^+$		0.02	0.02	0.02	0.02	0.03	0.05	0.06	0.33[c]
$[M - C_2H_5]^+$		0.02				0.02	0.03		0.03
$[M - C_3H_6]^+$	0.05	0.14[d]	0.03	0.03	0.12	0.28	0.19	0.14	0.04
$[M - C_3H_7]^+$	0.38	0.10	0.05			0.02	0.02	0.02	0.02
$[M - C_4H_8]^+$		0.03	0.16[d]		0.05	0.40	0.30	0.26	0.09
$[M - C_4H_9]^+$	0.09	0.10				0.02	0.02	0.03	0.03
$[M - C_5H_{10}]^+$	0.05	0.05	0.03		0.02	0.44	0.42	0.37	0.19
$[M - C_5H_{11}]^+$	0.03	0.09	0.09			0.02	0.03	0.06	0.03
$[M - C_6H_{12}]^+$	*e*	0.04	0.05	0.02		0.33	0.44	0.43	0.27
$[M - C_6H_{13}]^+$		0.02	0.06			0.02	0.03	0.05	0.03
$[M - C_7H_{14}]^+$		*e*	0.03	0.05[d]	0.02	0.19	0.39	0.47	0.36
$[M - C_7H_{15}]^+$						0.02	0.03	0.03	0.04
$[M - C_8H_{16}]^+$			*e*	0.05	0.05[d]	0.07	0.27	0.44	0.42
$[M - C_8H_{17}]^+$					0.02	0.01	0.02	0.05	0.04
$[M - C_9H_{18}]^+$				0.02	0.02		0.16	0.38	0.45
$[M - C_9H_{19}]^+$				0.03	0.05		0.02	0.03	0.05
$[M - C_{10}H_{20}]^+$				0.03	0.02		0.05	0.26	0.43
$[M - C_{10}H_{21}]^+$					0.03		0.02	0.03	0.04
$[M - C_{11}H_{22}]^+$				*e*	0.03	0.02	0.02	0.15	0.35
$[M - C_{11}H_{23}]^+$					0.02	0.02	0.02	0.03	0.04
$[M - C_{12}H_{24}]^+$					*e*	0.02[d]	0.02	0.06	0.24
$[M - C_{12}H_{25}]^+$						0.03	0.02	0.03	0.03
$[M - C_{13}H_{26}]^+$						0.02	0.02		0.14
$[M - C_{13}H_{27}]^+$						0.05	0.02	0.03	0.03
$[M - C_{14}H_{28}]^+$						0.09	0.05[d]	0.03	0.07
$[M - C_{14}H_{29}]^+$						0.05	0.05	0.03	0.03
$[M - C_{15}H_{30}]^+$						0.04	0.03		0.02
$[M - C_{15}H_{31}]^+$						0.04	0.05	0.03	0.02
$[M - C_{16}H_{32}]^+$						*e*	0.05	0.06[d]	0.03
$[M - C_{16}H_{33}]^+$							0.03	0.05	0.04
$[M - C_{17}H_{34}]^+$							0.03	0.03	0.02
$[M - C_{17}H_{35}]^+$							0.05	0.07	0.04
$[M - C_{18}H_{36}]^+$							*e*	0.07	0.03[d]
$[M - C_{18}H_{37}]^+$								0.05	0.05
$[M - C_{19}H_{38}]^+$								0.05	0.03
$[M - C_{19}H_{39}]^+$									0.07
$[M - C_{20}H_{40}]^+$								*e*	0.08
$[M - C_{20}H_{41}]^+$									0.05
$[M - C_{21}H_{42}]^+$									0.04
$[M - C_{21}H_{43}]^+$									0.05
$[M - C_{22}H_{44}]^+$									*e*

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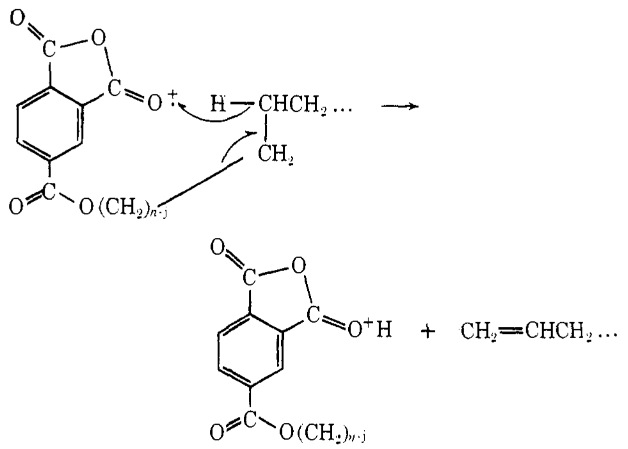
[a] Number of carbon atoms in the alkyl group. [b] Intensities are expressed as per cent of total ion yield from mass 26 to the end of the spectrum. No corrections have been made for naturally occurring heavy isotopic contributions. [c] Intensity seems unduly high, probably due to a trace of the eicosyl ester present as an impurity. [d] Loss of C_jH_{2j} where $j = n - 4$. [e] $j = n$.

of 1,2-dimethyl 4-*n*-alkyl trimellitates. Moreover, the 4-*n*-alkyl TMA esters show a second such series, lower in intensity than the first series by factors of 5–10, corresponding to loss of olefin molecules from $[M - H_2O]^+$. Table XI shows the $[M - C_jH_{2j}]^+$ and the neighboring $[M - C_jH_{2j+1}]^+$ peaks in the spectra of nine 4-*n*-alkyl TMA esters, in which *n*, the number of carbons in the alkyl group, varies from 6 to 22.

The peak for which $j = n - 4$ apparently stems from a process common to long-chain alkyl esters generally, which will be dealt with elsewhere. In the spectra of the longer 4-*n*-alkyl TMA esters, unlike those of benzoates and aliphatic acid esters, the product of this specific process is accompanied by a series of higher homologs corresponding to the loss of olefin molecules C_jH_{2j}, where $2 \leq j \leq n - 8$. This series of products can be plausibly accounted for by hydrogen abstraction by an anhydride oxygen from C-($n - j + 2$) in the alkyl chain, followed by β cleavage with respect to the resulting free radical.



β cleavage on the far side of the radical site would effect loss of an alkyl radical, and may well be the source of the observed $[M - C_jH_{2j+1}]^+$ ions. The generally lower abundance of these ions than of $[M - C_jH_{2j}]^+$ may reflect stabilization of the latter by some further interaction between the primary radical site and the protonated anhydride group.

Such a model for formation of the $[M - C_jH_{2j}]^+$ ion series is particularly attractive because, if it is valid, the intensity distribution of the corresponding peaks is a direct measure of the probability distribution of abstraction from the various alkyl carbons. Thus, the appropriate data, taken from Table XI and normalized to a total of 100% for all values of i from 2 to $n - 8$, are listed in Table XII. Also listed there for each ester is j', the value of j corresponding to maximum intensity, and n', the position of hydrogen abstraction corresponding to loss of $C_{j'}H_{2j'}$.

Table XII. Intensity Distributions of $[M - C_jH_{2j}]^+$ Peaks in Spectra of 4-*n*-Alkyl Trimellitate Anhydrides

	n^a					
j^b	11	12	16	18	20	22
	Rel intensity					
2	40	11	2	2	2	
3	60	63	16	9	5	1
4		26	23	15	9	3
5			25	19	12	6
6			19	21	14	9
7			11	15	16	12
8			4	10	14	14
9				5	12	15
10				4	9	14
11					5	11
12					2	8
13						5
14						2
j'^c	3	3	5	6	7	9
n'^d	10	11	13	14	15	15

[a] Number of carbon atoms in the alkyl group. [b] Number of carbon atoms in the olefin molecule lost. [c] The value of j corresponding to maximum intensity. [d] $n' = n - j' + 2$, the position of hydrogen abstraction corresponding to loss of $C_{j'}H_{2j'}$.

The distributions that emerge seem reasonable. Intensity varies smoothly and symmetrically about a maximum which shifts slowly with increasing chain length to positions farther out on the chain. The slowness of this shift is reminiscent of and can help to account for the decreasing rate of increase of triple-hydrogen relative to double-hydrogen migration accompanying rupture of the *O*-alkyl bond in 4-*n*-alkyl TMA esters as the alkyl group is lengthened.[2] The data suggest that, for a sufficiently long alkyl group, coiling about the anhydride group brings the hydrogens on carbons 14, 15, and 16 into most intimate contact with the oxygens, and that the density of hydrogen atoms within reactive distance of the oxygens approaches a maximum value, unaffected by further lengthening of the alkyl chain.

Tables XIII and XIV, respectively, show the analogous intensity distributions and derived values of j' and n' for the $[M - H_2O - C_jH_{2j}]^+$ peaks in the spectra of 4-*n*-alkyl TMA esters, and for the $[M - CH_3OH - C_jH_{2j}]^+$ peaks in those of 1,2-dimethyl 4-*n*-alkyl trimellitates. Loss of H_2O requires two alkyl hydrogens, of course, and the origin of the second hydrogen is obscure except that it must be closer in on the chain than the cleaved carbon–carbon bond. Nonetheless, the data closely parallel those for the $[M - C_jH_{2j}]^+$ peaks, with no change in the position of most probable hydrogen abstraction. The dimethyl *n*-alkyl trimellitate $[M - CH_3OH - C_jH_{2j}]^+$ series exhibits similar intensity distributions, with the position of most probable abstraction one to two carbons closer than in the TMA ester series, in accord with expectation based on examination of Dreiding models.

Table XIII. Intensity Distributions of $[M - H_2O - C_jH_{2j}]^+$ Peaks in Spectra of 4-*n*-Alkyl Trimellitate Anhydrides

	n^a			
j^b	16	18	20	22
	Rel intensity			
2	5	5	5	
3	17	10	7	5
4	26	15	10	6
5	23	18	13	8
6	17	19	15	9
7	7	16	15	11
8	5	9	15	14
9		4	12	14
10		4	5	13
11			3	11
12				6
13				3
j'^c	4	6	6, 7, 8	8, 9
n'^d	14	14	14, 15, 16	15, 16

[a,b,c,d] See footnotes to Table XII.

Table XIV. Intensity Distributions of $[M - CH_3OH - C_jH_{2j}]^+$ Peaks in Spectra of 1,2-Dimethyl 4-*n*-Alkyl Trimellitates

	n^a	
j^b	16	18
	Rel intensity	
2	3	2
3	9	7
4	14	7
5	16	11
6	18	13
7	15	15
8	9	15
9	5	10
10	4	7
11	2	4
12	4	3
13		3
14		3
j'^c	6	7, 8
n'^d	12	12, 13

[a,b,c,d] See footnotes to Table XII.

Despite the attractiveness of the proposed model, some possible complications remained. First, some of the ions in the series under consideration might arise by sequences in which loss of the first olefin molecule, triggered by hydrogen abstraction, is followed by loss of ethylene by β cleavage. Second, hydrogen migration within the alkyl chain might intervene between abstraction and β cleavage, or follow these events and induce loss of a second olefin molecule. In either case, the length of the retained alkyl chain segment would no longer define the position of abstraction. Any such intervening reaction step would presumably entail some additional energy requirement, however, so that the resulting intensity distribution might be energy dependent.[34] We therefore measured the intensity distributions of the $[M - C_jH_{2j}]^+$ peaks in the spectra of *n*-octadecyl and *n*-eicosyl TMA esters at

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(34) A referee has pointed out that such intramolecular hydrogen shifts may have very low activation energies. However, *cf.* G. Spiteller, M. Spiteller-Friedmann, and R. Houriet, *Monatsh. Chem.*, 97, 121 (1966).

7.5 eV. They are virtually identical with the analogous 70-eV data in Table XII, thus ruling out energy dependence and, to that extent, supporting the proposed model.

A more rigorous test is furnished by the metastable-scanning data shown in Table VII. Upon normalization to totals of 100%, the intensity distributions of metastable peaks leading to both the $[M - C_jH_{2j}]^+$ and the $[M - H_2O - C_jH_{2j}]^+$ series from *n*-octadecyl TMA ester and the $[M - CH_3OH - C_jH_{2j}]^+$ series from 1,2-dimethyl 4-*n*-octadecyl trimellitate match closely those derived from the normal peaks of the three series measured at 70 eV and those of $[M - C_jH_{2j}]^+$ at low voltage. Moreover, 99% of the total metastable-peak intensity leading to $[M - C_jH_{2j}]^+$ corresponds to the molecular ion as the precursor. Small contributions to the yield of $[M - C_6H_{12}]^+$, the most abundant ion in the series, arise *via* $[M - C_2H_4]^+$ and $[M - C_4H_8]^+$ intermediates. Intensities of the metastable peaks leading to the $[M - H_2O - C_jH_{2j}]^+$ series are distributed as follows in terms of the indicated precursors: $[M - C_jH_{2j}]^+$, 80%; $[M - H_2O]^+$, 5%; higher homologs of $[M - C_jH_{2j}]^+$, 0.5%; higher homologs of $[M - H_2O - C_jH_{2j}]^+$, 2%; M^+, 12%. Thus, the H_2O and olefin molecules may be lost in either order, and loss of the first olefin molecule may be followed by loss of a second. For the ions stemming from metastable transitions in which M^+ is identified as the precursor, the process consists doubtless of more than one step,[35] and the reaction sequence is undefined. The great bulk of the $[M - H_2O - C_jH_{2j}]^+$ ions, however, arise by a common path, loss of H_2O from $[M - C_jH_{2j}]^+$. Twenty-three per cent of the metastable-peak intensity for processes leading to the $[M - CH_3OH - C_jH_{2j}]^+$ series from 1,2-dimethyl 4-*n*-octadecyl trimellitate corresponds to loss of CH_3OH from $[M - C_jH_{2j}]^+$, even though no normal peaks attributable to such intermediates were detected. Twenty-seven per cent corresponds to loss of C_jH_{2j} from $[M - CH_3OH]^+$. Fifty per cent stems from the molecular ion as the precursor; here again, the reaction sequence remains undefined. No evidence was found for intervening loss of a second olefin molecule.

The labeling results permit yet a further independent check on the validity of the model, which requires that each $[M - C_jH_{2j}]^+$ ion retain all the hydrogen atoms originating on C-1 to C-$(n - j)$ plus one atom from C-$(n - j + 2)$. The isotopic compositions so predicted for the isotopically pure *6,7-d_2*, *9,10-d_2*, and *9,10,12,13-d_4* esters, ignoring possible isotope effects, are listed in Table XV. Because of the presence of isotopic impurities and of interference from ions of neighboring mass numbers, which may overlap in the labeled esters, precise calculation of the isotopic distributions of the $[M - C_jH_{2j}]^+$ ions derived from the labeled compounds is not feasible. However, in every case where the model calls for a single isotopic species, the peak corresponding to this species is the most intense in the appropriate mass region. Similarly, where the model calls for 50% each of two isotopic species, one of the corresponding peaks is the most intense in the region, and the other is nearly as intense. To illustrate, the pertinent data for j = 5, 6, and 7 are shown in Table XVI. The intensities listed, which are expressed as per cent of total ion intensity over the mass range 197–450, are corrected for naturally occurring heavy isotopic contributions. Although the origins of the contributing ions cannot be defined as rigorously as one might wish, the labeling evidence leaves little doubt that the proposed model is essentially correct.

Table XV. Predicted Isotopic Compositions of $[M - C_jH_{2j}]^+$ Ions in Spectra of *n*-Octadecyl-*6,7-d_2*, *-9,10-d_2*, and *-9,10,12,13-d_4* Trimellitate Anhydrides

j	*6,7-d_2*	*9,10-d_2*	*9,10,12,13-d_4*
2	d_2	d_2	d_4
3	d_2	d_2	d_4
4	d_2	d_2	d_4
5	d_2	d_2	d_4
6	d_2	d_2	d_3
7	d_2	d_2	d_2, d_3[a]
8	d_2	d_2	d_2, d_3[a]
9	d_2	d_1	d_1
10	d_2	d_0, d_1[a]	d_0, d_1[a]

[a] 50% of each species.

Table XVI. $[M - C_jH_{2j}]^+$ Regions, for j = 5, 6, and 7, in Spectra of Unlabeled and Labeled *n*-Octadedyl Trimellitate Anhydrides

j	Mass	No. of deuterium atoms in $[M - C_jH_{2j}]^+$	d_0	*6,7-d_2*	*9,10-d_2*	*9,10,12,-13-d_4*
			Rel intensity[a,b]			
5	373		0.3	0.7	0.7	0.5
	374	0	8.4	0.6	0.5	0.9
	375	1	0.0	1.6	0.8	0.5
	376	2	0.0	5.1	6.5	1.5
	377	3		0.4	0.3	1.7
	378	4		0.5	0.4	4.2
	379			0.1		0.6
6	359		0.4	0.8	0.8	0.7
	360	0	9.5	0.7	1.4	1.5[c]
	361	1	0.0	1.6	1.4	0.5
	362	2	0.0	5.6	7.5	3.1
	363	3		0.7	0.4	4.6
	364	4		0.2	0.3	1.7
	365					0.0
7	345		0.7	0.8	0.8	0.7
	346	0	7.8	0.9	1.3	0.5
	347	1	0.0	1.4	1.5	1.1
	348	2	0.0	5.5	6.3	4.8
	349	3		0.5	0.3	3.6
	350	4		0.3	0.0	0.6

[a] Per cent of total ion intensity from mass 297 to 450, inclusive.
[b] Corrected for naturally occurring heavy isotopic contributions.
[c] Attributable largely to $[M - H_2O - C_5H_{10}]^+$-d_4.

We have encountered the same features—series of peaks corresponding to $[M - C_jH_{2j}]^+$ and $[M - H_2O - C_jH_{2j}]^+$ in which intensity varies with j in essentially the same way as in the TMA esters—in the mass spectrum of tristearin,[36] and presumably they occur also in triglycerides of other long-chain alkanoic acids. The $[M - H_2O - C_jH_{2j}]^+$ peaks appear in a bar-chart representation of the mass spectrum of tristearin, and both series in that of 1-myristo-2-stearo-3-palmitin, in a published report,[37] but the accompanying text makes no explicit mention of them. No reference to either series appears in other papers on the mass spectra

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(35) *Cf.* S. Meyerson, R. W. Vander Haar, and E. K. Fields, *J. Org. Chem.*, 37, 4114 (1972), and references cited there.

(36) Unpublished spectrum, this laboratory, measured on a Du Pont Model 21-110 instrument using direct-probe injection; source temperature, 280°; electron energy, 70 eV.

(37) M. Barber, T. O. Merren, and W. Kelly, *Tetrahedron Lett.*, 1063 (1964).

Table XVII. Intensity Distributions of $[M - C_jH_{2j}]^+$ and $[M - H_2O - C_jH_{2j}]^+$ Peaks in Spectrum of Tristearin

j^a	$[M - C_jH_{2j}]^+$	$[M - H_2O - C_jH_{2j}]^+$
	Rel intensity	
3		3
4	5	6
5	14	9
6	9	10
7	10	12
8	14	15
9	19	14
10	15	14
11	9	9
12	5	7
j'^b	9	8, 9, 10
n'^c	11	10, 11, 12

[a,b,c] See footnotes *b*, *c*, *d*, respectively, in Table XII. *n'* refers here to position in the stearate moiety; that is, the count includes the carboxyl carbon.

of triglycerides.[28,38] Table XVII shows the intensity distributions of the two series in our spectrum of tristearin, with the derived values of j' and n'. Almost certainly the underlying chemical events also resemble closely those in the TMA esters. The spectra of long-chain *n*-alkynes contain a series of peaks corresponding to $[M - C_jH_{2j}]^+$ ions,[39] and these may comprise a third family of compounds in this category.

Conclusion

The trimellitate anhydrides, trimellitimidates, 1,2-dimethyl trimellitates, and triglycerides have in common bulky groupings containing several oxygen atoms, and in the imides one nitrogen as well. Such groupings seem well equipped to accommodate the charge and radical site before abstraction and also to use the abstracted atom, presumably *via* hydrogen bonding, to attain a new resonance-stabilized configuration. The homologous series of ions produced by loss of olefin molecules from M^+, $[M - H_2O]^+$, and $[M - CH_3OH]^+$ and by loss of H_2O or CH_3OH from $[M - C_jH_{2j}]^+$ in the various compounds reflect a delicate balance in which the vibrational energy available following abstraction is sufficient to cleave the β carbon–carbon bond with but little interference from processes that so often intervene in other molecules.[40] These observations complement the earlier noted temperature and voltage effects on the competition of triple- *vs.* double-hydrogen migration in 4-*n*-alkyl TMA esters. Both lines of evidence would seem to support the view that alkyl hydrogen migration to the formally distant functional group occurs in a coiled—internally solvated—molecule rather than *via* flailing, an alternative suggested by a referee of an earlier paper.[4]

Several recent papers describe attempts to locate olefinic bonds in long chains by specific deuterogenation, nonselective carbon–carbon bond breaking either thermally[41] or by electron impact,[17b,38a,42] and isotopic analysis of the resulting fragments. The high specificity of the olefin-loss processes reported here suggests that they may be particularly useful for studies of this type.

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Organometallic Chemistry. IV.[1a] Stable Mercurinium Ions

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Abstract: The direct observation of stable mercurinium ions is reported, and evidence for their structure is discussed. Mercurinium ions can be prepared by both σ and π routes in superacid media of low nucleophilicity. The ethylenemercurinium, *cis*- and *trans*-dimethylethylenemercurinium, propylenemethylmercurinium, cyclohexenemercurinium, cyclohexenemethylmercurinium, norbornylenemercurinium, and norbornylenemethylmercurinium ions were obtained and studied by ^1H and ^{13}C nmr and by quenching experiments. Rapidly equilibrating β-mercurycarbenium ions as an alternate possibility to bridged mercurinium were ruled out on the basis of the observed ^{199}Hg–H couplings and cmr data.

Solvomercuration reactions were originally discovered at the turn of the century by Hoffmann and Sand.[2] Since then, solvomercuration reactions have been developed[3] into valuable synthetic reactions of great versatility and stereospecificity.

As might be expected, the mechanism of solvomercuration reactions has received a great deal of atten-

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