were characterized by their ir spectra, refractive indices, and elemental analyses.

The solid sulfoxides were isolated by dissolving the mixture in 200 ml of methylene chloride and washing thoroughly with water. After the solution was dried and the solvent was evaporated, the solids were recrystallized.

Registry No.—NCS, 128-09-6; NBS, 128-08-5.

Acknowledgment.—This work was performed under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract DA-01-021-ORD-11878(Z).

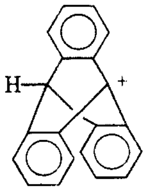
Electron-Impact Fragmentation of Triptycene. The Question of Bridgehead Carbonium Ions[1]

LEONARD H. SCHWARTZ

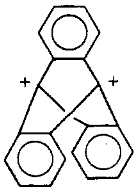
Department of Chemistry,
The City College of The City University of New York,
New York, New York 10031

Received June 6, 1968

The mass spectrum of triptycene was recently reported by Bruce.[2] The presence of relatively abundant ions at $(M - 1)^+$ and $(M - 2)^{2+}$ was explained by postulating structures **1** and **2**, respectively, for these ions. By analogy with the stabilized triphenylmethyl cation, which is obtained by loss of hydrogen from triphenylmethane upon electron impact, it was suggested that **1** and **2** should also be stabilized.



1



2

We desired to obtain further evidence concerning the structures of these ions. Stability considerations argue against formulations **1** and **2**. Because of the rigid carbon framework involved, ions **1** and **2** should not be stabilized by orbital overlap as is the triphenylmethyl cation. As a possible test of structures **1** and **2**, we decided to investigate the electron-impact fragmentation of triptycene and 9,10-dideuteriotriptycene under the same conditions. If **1** and **2** are correct, the $(M - 1)^+$ and $(M - 2)^{2+}$ ions of triptycene should be shifted in the mass spectrum of 9,10-dideuteriotriptycene to $(M - 2)^+$ and $(M - 4)^{2+}$, respectively. Table I lists the relative intensities of the singly charged ions of triptycene and 9,10-dideuteriotriptycene in the neighborhood of the molecular ions as obtained on Hitachi Perkin-Elmer RMU-6D and Jeolco JMS-01SG mass spectrometers. Because the 9,10-dideuteriotriptycene contains 85% d_2, 14% d_1, and 1% d_0 (see Experimental Section), exact quantitative comparisons cannot be made. Also included in Table I are the calculated spectra of this mixture. (The reasonable assumptions are made here that the ionization efficiencies[3] and volatilities of the three species are the same, *no bridgehead C–H or C–D bonds are broken*, and secondary isotope effects are negligible.)

TABLE I

MASS SPECTRA OF TRIPTYCENE AND 9,10-DIDEUTERIOTRIPTYCENE. SINGLY CHARGED IONS

	Triptycene		9,10-Dideuteriotriptycene[a]			
	m/e	Rel intensity	*m/e*	Rel intensity	Calcd rel intensity[b]	Difference[c]
Hitachi Perkin-Elmer RMU-6D Mass Spectrometer[d]						
$(M + 2)^+$	256	2.4	258	2.1	2.2	0
$(M + 1)^+$	255	20	257	19	19	0
$(M)^+$	254	91	256	89	85	+4
$(M - 1)^+$	253	100[e]	255	100[e]	104	−4
$(M - 2)^+$	252	54	254	58	64	−6
$(M - 3)^+$	251	9.0	253	25	17	+8
$(M - 4)^+$	250	16	252	12	16	−4
$(M - 5)^+$	249	2.6	251	10	4.8	+5
Jeolco JMS-01SG Mass Spectrometer[f]						
$(M + 2)^+$	256	2.7	258	2.3	2.5	0
$(M + 1)^+$	255	22	257	21	21	0
$(M)^+$	254	100[e]	256	100[e]	97	+3
$(M - 1)^+$	253	94	255	100[e]	103	−3
$(M - 2)^+$	252	50	254	58	62	−4
$(M - 3)^+$	251	6.6	253	22	15	+7
$(M - 4)^+$	250	17	252	11	18	−7
$(M - 5)^+$	249	1.5	251	8.5	4.1	+4

[a] Contains 85% d_2, 14% d_1, and 1% d_0 (see Experimental Section). [b] Calculated by assuming that each of the three species present exhibits a mass spectrum in the neighborhood of the molecular ion identical with that of triptycene, but displaced by one mass unit. These results are then adjusted for the small difference in total ionization (in the neighborhood of the molecular ion) compared to 9,10-dideuteriotriptycene, in order to make the calculated spectrum directly comparable with that of 9,10-dideuteriotriptycene. [c] Relative intensity minus calculated relative intensity, to the nearest whole number. [d] Morgan-Schaffer Corp., Montreal, Canada, 70 eV. [e] Base peak. [f] Jeolco, Inc., Medford, Mass., 75 eV.

A close parallel is observed between the calculated and experimental mass spectra of 9,10-dideuteriotriptycene from both instruments. We conclude that **1** is not the correct structure for the $(M - 1)^+$ ion of triptycene. Because the loss of a hydrogen atom is approximately equally probable from both compounds under study, the $(M - 1)^+$ ion must arise by loss of hydrogen originally bonded to one of the aromatic rings. Compared to the calculated spectra, the experimental spectra of 9,10-dideuteriotriptycene each show the same slight decrease in intensity of the $(M - 2)^+$ and $(M - 4)^+$ ions and a corresponding increase in intensity of the $(M - 3)^+$ and $(M - 5)^+$ ions. This suggests that, possibly in small part, the $(M - 2)^+$ and $(M - 4)^+$ ions of triptycene involve loss of a bridgehead hydrogen atom. Such cleavage with 9,10-dideuteriotriptycene would result in a shift to $(M - 3)^+$ and $(M - 5)^+$, and therefore to an increase in the intensity of these ions.[4]

Table II lists the relative intensities of the doubly charged ions of species in the neighborhood of the

---

[1] This work was supported in part by grants from the National Science Foundation (GP-6404), The City University of New York, and the General Faculty Research Committee of The City College of New York. The purchase of the Perkin-Elmer Model 621 spectrophotometer used in this work was made possible by a grant from the National Science Foundation (GP-6992) to The City College of The City University of New York.

[2] M. I. Bruce, *Chem. Commun.*, 593 (1967).

[3] K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 212.

[4] In order to definitely establish this point a mass spectrometer with resolution (M/ΔM) of approximately 160,000 would be required. The author does not have access to such an instrument.

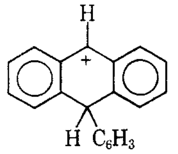
molecular ions. If **2** correctly represents the structure of the $(M - 2)^{2+}$ ion of triptycene, a similarly intense ion at the same m/e value (126) should be observed for 9,10-dideuteriotriptycene. If, however, as is the case with the singly charged ions, the hydrogens lost are those originally bonded to the aromatic ring, a shift to m/e 127 should be observed. Since the latter possibility is the case, it is concluded that structure **2** is not correct.

TABLE II
MASS SPECTRA OF TRIPTYCENE AND 9,10-DIDEUTERIOTRIPTYCENE. DOUBLY CHARGED IONS[a]

	Triptycene		9,10-Dideuteriotriptycene[b]	
	m/e	Rel intensity[c]	m/e	Rel intensity[c]
$(M)^{2+}$	127	9.3	128	7.6
$(M - 1)^{2+}$	126.5	14.7	127.5	11.1
$(M - 2)^{2+}$	126	32.4	127	27.0
$(M - 3)^{2+}$	125.5	5.8	126.5	13.5
$(M - 4)^{2+}$	125	15.1	126	9.2
$(M - 5)^{2+}$	124.5	2.8	125.5	7.0

[a] Hitachi Perkin-Elmer RMU-6D Mass Spectrometer. [b] Contains 85% d_2, 14% d_1, and 1% d_0 (see Experimental Section). [c] Relative to the $(M - 1)^+$ peak.

Since polycyclic aromatic hydrocarbons tend to exhibit molecular ions of unusually large abundance, for the $(M - 1)^+$ ion of triptycene to be of approximately equal intensity to the molecular ion suggests it to possess unusual stability. Structure **3**, which would arise by cleavage of a carbon–carbon bond to the bridgehead carbon atom and scission of the aromatic ring with loss of a hydrogen atom, is suggested for this ion.[5] This is consistent with open-chain formulations for aromatic ions which have been suggested by a number of recent mass spectral studies.[6]



3a, $C_6H_3 = HC{\equiv}C{-}CH{=}CH{-}C{\equiv}C{-}$
b, $C_6H_3 = HC{\equiv}C{-}\underset{|}{C}{=}CH{-}C{\equiv}CH$

Experimental Section

Melting points are corrected. Infrared spectra were determined on a Perkin-Elmer Model 621 spectrophotometer. Deuterium analyses were performed by J. Nemeth, Urbana, Ill.

9,10-Dideuteriotriptycene.—Solutions of anthranilic acid (3.80 g, 27.7 mmol) and n-butyl nitrite (3.09 g, 30.0 mmol), each in 45 ml of butanone, were simultaneously added over a 2-hr period to a stirred refluxing solution of 9,10-dideuterioanthracene[7] (0.997 g, 5.53 mmol). The reaction mixture was refluxed for an additional 1 hr and evaporated to dryness. The residue was mixed with 50 ml of xylene and 1.71 g (17.4 mmol) of maleic anhydride, and the resulting mixture was refluxed for 1 hr and evaporated to dryness. Sodium hydroxide solution (5%, 100 ml) was added, and the mixture was heated at 100° for 1.5 hr. Extraction with chloroform and evaporation of the dried chloroform solution yielded an orange solid. Chromatography on alumina (200 g, Woelm, acidic), using benzene as the eluent, gave a white solid which was recrystallized from hexane–benzene to give the product (0.44 g, 31%): mp 251–252°; ν^{KBr} 2209 cm^{-1}; deuterium analyses gave the atom fraction deuterium as 0.1296 and 0.1300 (calcd 0.1429) in duplicate runs; low voltage mass spectrometry at 11.5 eV indicated the composition 85% d_2, 14% d_1, and 1% d_0.

Registry No.—Triptycene, 477-75-8; 9,10-dideuteriotriptycene, 17375-18-7.

Acknowledgment.—The author thanks Dr. Y. Itagaki of Jeolco, Inc., for mass spectral measurements and Mr. L. Loew for infrared measurements.

The Use of (−)-Menthyl Chloroformate in the Optical Analysis of Asymmetric Amino and Hydroxyl Compounds by Gas Chromatography

JOHN W. WESTLEY AND B. HALPERN

Department of Genetics, Stanford University School of Medicine, Palo Alto, California 94304

Received June 7, 1968

The determination of optical purity of asymmetric alcohols by gas–liquid partition chromatography (glpc) of diastereoisomeric esters has been described by several investigators.[1-4] Application of these methods requires that the alcohol be quantitatively convertible into a pair of diastereoisomeric esters, so that only asymmetric alcohols which are stable during acid-catalyzed esterification conditions can be examined. We now describe the use of the reagent (−)-menthyl chloroformate (I)[5] for the optical glpc analysis of some acid-labile alcohols and α-hydroxy acids. Here diastereoisomeric carbonates, separable by glpc, can be formed in weakly basic medium at room temperature, and heat- and acid-labile compounds can be quantitatively derivatized. The reagent I is readily prepared from the commercially available (−)-menthol and phosgene; and a toluene solution of I can be kept without any noticeable deterioration over several months. The diastereoisomeric carbonates derived from α-phenylalkylcarbinols (Table I) and the common α-hydroxy fatty acid esters (Table II) have been completely resolved on packed columns, thus making this procedure suitable for quantitative optical analysis. The reagent I also reacts with amino compounds such as α-amino acid esters to form diastereoisomeric urethans separable by glpc (Table II). Since α-hydroxy and α-amino acids can be derivatized under the same reactions conditions and the diastereoisomers can be resolved on the same glpc column (Table II), we suggest the use of (−)-menthyl chloroformate for the optical analysis of depsipeptide hydrolysates. Finally some asymmetric amines such as α-phenylethylamine and α-(1-naphthyl)ethylamine have also been resolved,

---

[5] The two structures shown for the C_6H_3 chain are those which would arise directly from the molecular ion. Rearrangement processes would increase the number of possibilities.

[6] For a discussion and leading references, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, Chapter 1.

[7] D. E. Van Sickle and J. O. Rodin, *J. Amer. Chem. Soc.*, **86**, 3091 (1964).

(1) R. Charles, G. Fischer, and E. Gil-Av, *Israel J. Chem.*, **1**, 234 (1963); *J. Chromatog.* **17**, 408 (1965).

(2) G. E. Pollock, V. I. Oyama, and R. D. Johnson, *J. Gas Chromatog.*, **3**, 174 (1965).

(3) S. V. Vitt, M. B. Saporovskaya, I. P. Gudkova, and V. M. Belikov, *Tetrahedron Lett.*, 2575 (1965).

(4) B. Halpern and J. W. Westley, *Aust. J. Chem.*, **19**, 1533 (1966).

(5) L. A. Carpino, *Chem. Commun.*, 858 (1966).