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Asymmetrical [4+2]-Cycloaddition of (–)-Menthyl Acrylate and (–)-Menthyl Methacrylate to Cyclopentadiene in the Presence of BBr_3

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Abstract—An asymmetrical synthesis of bicyclo[2.2.1]hept-2-enes is described performed by [4+2]-cycloaddition of (–)-menthyl acrylate and (–)-menthyl methacrylate to cyclopentadiene in the presence of BBr_3. The effect of different factors on isomer composition, yield, and enantiomeric purity of the compounds obtained was investigated. Kovatch indices were determined and boiling points were estimated with the use of gas-liquid chromatography.

A norbornene moiety is inherent to a large number of natural and synthetic biologically active compounds. Introduction of a norbornene moiety into pharmaceuticals improves their therapeutic effect [1]. In the synthesis of bicyclo[2.2.1]heptene derivatives is used as diene the cyclopentadiene that is a known by-product of ethylene and coal-tar chemical industry [2].

Since often only a single optically active isomer possesses physiological activity the synthesis of bicyclic compounds with a bridged structure in the enantiomerically pure state is especially valuable. The asymmetrical diene synthesis is among the promising procedures leading to the above compounds in an optically active form.

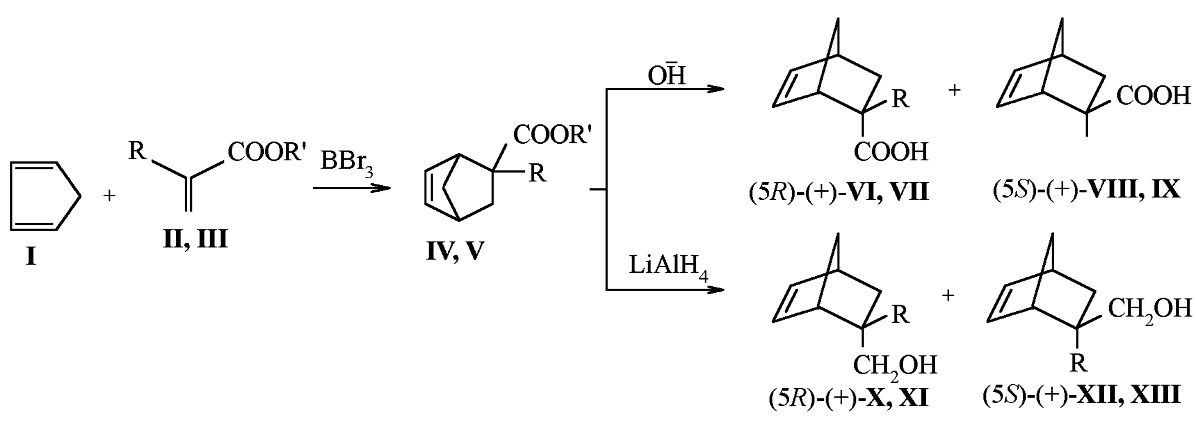
In these reactions Lewis acids ($AlCl_3$, $TiCl_4$, $SnCl_4$, BF_3–OEt_2) are known to be used as catalysts [3, 4]. The application of BH_2Br in combination with chiral polymers as catalyst in asymmetrical Diels–Alder reaction of cyclopentadiene with methacrolein afforded adducts in a good yield and with a fair enantiomeric purity [5, 6].

In extension of our studies on asymmetrical diene synthesis [7–11] we report here of the asymmetrical [4+2]-cycloaddition of (–)-menthyl acrylate (**II**) and (–)-menthyl methacrylate (**III**) to cyclopentadiene (**I**) in the presence of BBr_3 (Scheme 1).

The residual chiral alcohol, L-(–)-menthol (R') in compounds **IV, V** was removed by alkaline hydrolysis. The separation of isomeric *endo*-(**VI, VII**) and *exo*-(**VIII, IX**) acids was performed by conversion of the endo-isomers into lactones (Scheme 2).

On removing *exo*-acids **VIII, IX** from optically active iodolactones **XIV, XV** the reduction with the

Scheme 1.



R = H (**II, IV, VI, VIII, X, XII**), R = CH_3 (**III, V, VII, IX, XI, XIII**); R' = L-(–)-menthyl.

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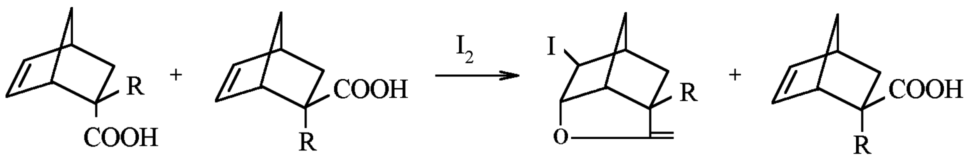
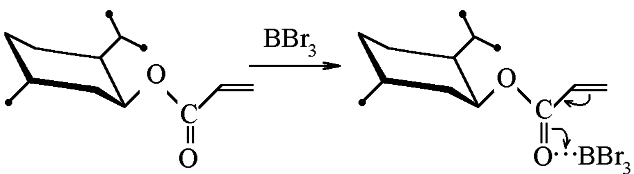
Scheme 2.



VI, VII **VIII, IX** **XIV, XV** **VIII, IX**

R = H (**VI, VIII, XIV**), R = CH_3 (**VII, IX, XV**).

system Zn + CH_3COOH afforded the corresponding optically *endo*-acids **VI, VII**. To avoid the concomitant racemization of adducts **IV, V** during alkaline hydrolysis their reduction was carried out with the use of $LiAlH_4$ (Scheme 1). The catalytic effect of BBr_3 may be attributed to formation of its complex with dienophiles **II, III**.



The electron deficiency arising therefrom on the multiple bond of the dienophiles **II, III** facilitates their interaction with diene **I**. This assumption is corroborated by the displacement of the ν(C=O) from 1730 to 1630 cm^{-1} on going from dienophiles **II, III** to their complexes with BBr_3. These results are consistent with the data reported in [12] on the shift of the C=O absorption band in methyl acrylate from 1720 to 1640 cm^{-1} effected by $AlCl_3$, $TiCl_4$, $SnCl_4$ due to complexing between the catalysts and dienophile.

The study was carried out in a wide temperature range (from –78 to 20°C) in different solvents at varying ratio between catalyst and dienophiles **II, III**. The effect of these parameters on the yield, isomer composition, and enantiomeric purity is presented in Table 1.

As seen from Table 1 in contrast to noncatalyzed reaction of asymmetrical diene synthesis where the changing temperature weakly affects the enantiomeric purity of compounds obtained [13], in the presence of BBr_3 this reactions at low temperature furnishes

Table 1. Effect of cycloaddition reaction parameters on the yield, isomer composition, and enantiomeric purity of compounds **IV**–**XIII**

Dienophile	Temperature, °C	Solvent	Molar ratio BBr_3/dienophil (**II, III**)	Yield of compounds (**IV, V**), %	Isomer ratio (**IV, V**), %		Prevailing enantiomer, %				$[\alpha]_D^{20}$, EtOH			
					endo	*exo*	**VI, VII**	**VIII, IX**	**X, XI**	**XII, XIII**	**V, VII**	**VIII, IX**	**X, XI**	**XII, XIII**
II	20	CH_2Cl_2	0.25	90	86.4	13.6	21	20	30	24	+30.28	+29.42	+22.98	+22.45
II	–10	CH_2Cl_2	0.25	81	91.7	8.3	32	30	49	–	+46.14	+45.13	+37.5	–
II	–40	CH_2Cl_2	0.25	73	98.7	5.3	40	31	53	–	+57.68	+55.3	+40.6	–
II	–70	CH_2Cl_2	0.25	62	96.5	3.5	69	–	80	–	+99.5	–	+88.31	–
II	–78	CH_2Cl_2	0.25	60	98.4	1.6	74	–	84	–	+104.47	–	+94.36	–
II	20	C_6H_6	0.25	91	87.3	12.7	19	19	28	27	+27.4	+24.25	+22.20	+20.45
II	20	C_6H_6	0.5	94	89.2	10.8	21	19	27	25	+27.10	+22.25	+22.19	+19.28
II	20	C_6H_6	0.75	96	80.3	9.7	27	–	29	–	+30.28	–	+22.93	–
II	20	$C_6H_5CH_5$	0.25	91	87.2	13.8	20	21	30	31	+29.95	+28.76	+21.97	+20.17
III	20	CH_2Cl_2	0.25	82	10	90	19	18	28	27	+20.12	+19.13	+19.33	+12.63
III	–10	CH_2Cl_2	0.25	63	11	89	28	27	47	45	+42.63	+41.09	+21.61	+20.59
III	–40	CH_2Cl_2	0.25	59	16	84	37	36	51	50	49.16	+43.45	+23.45	+22.99
III	–70	CH_2Cl_2	0.25	54	13	87	57	56	66	65	+60.33	+56.61	+30.35	+34.19
III	–78	CH_2Cl_2	0.25	52	15	85	65	64	70	67	+68.87	61.54	+32.19	+30.55

Table 2. Physical constants,IR spectra and elemental analyses of compounds **II**–**XIII**

Compd. no.	bp (*p*, mm Hg) or mp (heptane), °C	n_D^{20}	d_4^{20}	IR spectrum, ν, cm^{-1}	Found, %		Formula	Calculated, %	
					C	H		C	H
II	103–104 (11 mm Hg)	1.4610	0.9396	1730(C=O),3040(C=C), 1050 (C–O)	74.28	10.10	$C_{13}H_{22}O_2$	74.28	10.47
III	115–116 (7.5 mm Hg)	1.4600	0.9271	1730 (C=O), 1375 (C–H), 1050–1120 (C–O)	74.36	10.51	$C_{14}H_{24}O_2$	75.00	10.71
IV	138–140 (0.5 mm Hg)	1.4878	1.009	1730 (C=O), 1373 (C–H), 1060–1115 (C=O)	78.16	10.12	$C_{18}H_{28}O_2$	78.26	10.14
V	173–175 (4 mm Hg)	1.4758	0.9726	1725 (C=O), 1180 (C–O), 3060 (C=C)	78.34	10.25	$C_{19}H_{30}O_2$	78.62	10.34
VI	45–46	–	–	1730 (C=O), 3055 (C=C)	69.33	7.27	$C_8H_{10}O_2$	69.56	7.24
VII	98–99	–	–	1730 (C=O), 1060 (C–O)	70.93	7.67	$C_9H_{12}O_2$	71.06	7.89
VIII	38–39	–	–	1730 (C=O), 1065 (C–O), 3060 (C=C)	69.38	7.21	$C_8H_{10}O_2$	69.56	7.24
IX	84–85	–	–	1725 (C=O), 3050 (C=C)	70.96	7.23	$C_9H_{12}O_2$	71.06	7.89
X	80–82 (2 mm Hg)	1.4998	–	3300 (O–H), 3065 (C=C), 1775 (C–O)	77.39	9.65	$C_8H_{12}O$	77.41	9.67
XI	96	–	–	3300 (O–H), 3060 (C=C)	78.13	10.11	$C_9H_{14}O$	78.26	10.14
XII	81–82 (2 mm Hg)	1.4973	–	3300 (O–H), 3050 (C=C)	76.96	9.48	$C_8H_{12}O$	77.41	9.67
XIII	67–68	–	–	3300 (O–H), 3060 (C=C)	78.10	10.12	$C_9H_{14}O$	78.26	10.14

compounds **VI–XIII** of significantly higher purity: It attains 84% for adduct **IV** and 70% for adduct **V** at −78°C. With decreasing temperature the stereoselectivity of reactions grows, and the overall yield of products decreases.

The increase in catalyst BBr_3 amount virtually does not affect the enantiomeric purity of compounds **VI–XIII**, but their overall yield grows. The data of Table 1 also indicate that the character of solvent hardly affects the enantiomeric purity and the overall yield of the final products.

Under conditions of this study the reaction of dienophile **II** afforded predominantly *endo*-isomer, and that with dienophile **III** mostly *exo*-isomer.

Isomers of alcohols **X, XII** and **XI, XIII** were separated by preparative gas-liquid chromatography. The GLC data show that the isomer composition of alcohols **X, XI** and **XI, XIII** is the same as that of the adducts **IV** and **V** respectively.

The composition and structure of compounds synthesized were confirmed by elemental analysis, IR and ^{1}H NMR spectra (Tables 2, 3).

Mass spectra of compounds **X, XII** and **XI, XIII** support the structure of these compounds but are insensitive to the isomer composition.

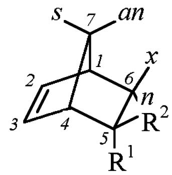
We also developed in this study the preparative GLC methods for separation of compounds obtained. We determined the retention volumes, relative retention volumes, Kovatch indices, and estimated the boiling points of the compounds under study. The Kovatch indices were calculated by Kovatch formula [14], and boiling points by Sakharov equation [15]. In both calculations was used the retention time of the normal paraffins om Dynochrom P with Apieson at the temperature and analysis modes the same as used with compounds under study (Table 4).

Optical purity and enantiomeric excess (%) of compounds **VI–XIII** were calculated from comparison of their specific rotation values with the corresponding figures for the enantiomerically pure samples of these compounds described in [16]. The relative configuration of products **VI–XIII** was estimated from the rule of correlation of the sign of optical rotation with that of structurally similar compounds of established configuration [14]: 5*R* for compounds (+)-(**VII**), (+)-(**X**), and (+)-(**XI**); 5*S* for compounds (+)-(**VIII**), (+)-(**IX**), (+)-(**XII**), (+)-(**XIII**).

EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 in the region of 4000–400 cm^{-1} from thin film

Table 3. ^{1}H NMR spectra of compounds **VI**–**XIII**, δ, ppm, coupling constants, Hz



R^1 = COOH, R^2 = H (**VI**), R^1 = COOH, R^2 = CH_3 (**VII**), R^1 = H, R^2 = COOH (**VIII**), R^1 = CH_3, R^2 = COOH (**IX**), R^1 = CH_2OH, R^2 = H (**X**), R^1 = CH_2OH, R^2 = CH_3 (**XI**), R^1 = H, R^2 = CH_2OH (**XII**), R^1 = CH_3, R^2 = CH_2OH (**XIII**)

No.	CH_3	CH_2O	OH	COOH	H^1	H^2	H^3	H^4	H^5_{endo}	H^5_{exo}	H^{6n}	H^{6x}	H^{7s}	H^{7an}	*J*, Hz
VI	–	–	–	11.8	2.85	6	5.85	2.71	–	2.85	1.30	1.71	1.30	1.30	$J_{2.3}$ 5.7, $J_{2.1}$ 3.0, $J_{3.4}$ 2.7, $J_{6_x,6_n}$ 12.0
VII	1.15	–	–	11.65	2.75	5.95	5.95	2.75	–	–	1.4	1.92	1.45	1.45	$J_{2.3}$ 5.8, $J_{2.1}$ 2.1, $J_{3.4}$ 2.8, $J_{6_x,6_n}$ 11.5
VIII	–	–	–	12.0	3.1	6.05	6.05	2.85	1.4	–	1.4	1.85	1.4	1.4	$J_{2.3}$ 5.7, $J_{2.1}$ 2.0, $J_{3.4}$ 2.7, $J_{6_x,6_n}$ 12.0
IX	1.12	–		11.60	2.75	5.95	5.95	2.77	–	–	1.4	1.92	1.47	1.47	$J_{2.3}$ 5.4, $J_{2.1}$ 3.2, $J_{3.4}$ 2.7, $J_{6_x,6_n}$ 11.9
X	–	3.20	3.81	–	2.81	6.15	5.9	2.71	–	2.18	1.31	1.71	1.30	1.30	$J_{2.3}$ 5.5, $J_{2.1}$ 2.5, $J_{3.4}$ 2.8, $J_{6_x,6_n}$ 12.0
XI	0.8	3.65	3.35	–	2.90	5.85	6.15	2.65	–	–	1.35	1.50	1.35	1.35	$J_{2.3}$ 5.4, $J_{2.1}$ 2.1, $J_{3.4}$ 2.8, $J_{6_x,6_n}$ 11.8
XII	–	3.35	3.81	–	3.15	6	5.85	2.85	1.52	–	1.3	1.82	1.3	1.30	$J_{2.3}$ 5.8, $J_{2.1}$ 2.5, $J_{3.4}$ 2.8, $J_{6_x,6_n}$ 11.8
XIII	0.88	3.41	3.95	–	2.75	5.94	5.94	2.5	–	–	1.15	1.82	1.42	1.42	$J_{2.3}$ 5.4, $J_{2.1}$ 2.5, $J_{3.4}$ 2.7, $J_{6_x,6_n}$ 12.0

Table 4. Retention volumes (V_r), relative retention volumes (menthol standard), Kovatch indices (Ik), and boiling points of compounds under study

Compound	Relative retention volume		Retention volume		log V_r (on Apiezon)	Ik	bp, °C
	PEGS	Apiezon	PEGS	Apiezon			
Menthol	1	1	288	446	–	–	–
II	1.13	0.75					
III	1.18	0.78	300	348	2.62	1174	210
V	7.95	2.45	2820	1152	3.06	1430	242
IV	6.02	2.45	2136	1152	3.06	1430	242
V	5.92	2.65	2100	1244	3.30	1544	260
V	5.27	2.65	1872	1244	3.30	1544	260
X	1.58	0.55	480	216	2.38	1050	185
XI	1.42	0.57	432	224	2.46	1089	191
XII	1.81	0.55	540	216	2.38	1050	185
XIII	1.72	0.57	513	224	2.46	1089	191
Octane	–	–	–	60	1.78	800	125
Nonane	–	–	–	99	1.99	900	151
Decane	–	–	–	168	2.23	1000	174
Undecane	–	–	–	266	2.43	1100	196
Dodecane	–	–	–	528	2.72	1200	216
Tridecane	–	–	–	888	2.95	1300	235
Tetradecane	–	–	–	1668	3.22	1400	253

or KBr pellets. ^1H NMR spectra were registered on spectrometer Tesla BS-487 (operating frequency 80 MHz) from solutions in CCl_4, internal references HMDS or TMS. Mass spectra were run on mass spectrometer MKh-1303 with the input from a gas bulb (ionizing voltage 30 and 12 eV). The optical rotation was measured on polarimeters Perkin–Elmer-141, Polamat A (546 nm), and spectropolarimeter Spectrol-1. Preparative separation was carried out on a column 900×0.8 cm packed with porovin with 5% PEGA [poly(ethylene glycole) adipate], evaporizer temperature 250°C, oven temperature 170°C, carrier gas nitrogen, gas flow rate 200 cm^3 min^{-1}, sample introduced 100μl, flame-ionization detector, chromatograph Varian–Aerograph. The chromatographic analysis and purity check of the compounds synthesized was performed with the use of columns 300×0.3 cm packed with Dynochrom P with 5% of Apiezon and PEGS [poly(ethylene glycol) succinate], carrier gas helium, gas flow rate 40 cm^3 min^{-1}, oven temperature 140–150°C, chromatograph LKhM-8MD, thermal conductivity detector.

(–)-Menthyl acrylate (II) was prepared by procedure [12], $[\alpha]_{546}^{20}$ –127° (*c* 4.4, MeOH). Cf.: $[\alpha]_D^{20}$ –77° [12].

(–)-Menthyl methacrylate (III) was prepared by the same procedure, $[\alpha]_{546}^{20}$ –113° (*c* 5.72°, MeOH). Cf.: $[\alpha]_D^{20}$ –91.75° [12].

(–)-Menthyl bicyclo[2.2.1]hept-2-ene-5-carboxylate (IV). To a solution of 10.52 g (0.05 mol) of compound **II** in 30 ml of anhydrous dichloromethane at –10°C was added dropwise 3.12 g (0.01 mol) of BBr_3 in 20 ml of dichloromethane. The mixture was cooled to –78°C, and then was added 3.96 g (0.06 mol) of cyclopentadiene (**I**) in 10 ml of dichloromethane. Then the mixture was stirred for 30 min at –78°C. The mixture was treated first with diluted HCl, then with 5% solution of $NaHCO_3$, washed with water, and dried on $MgSO_4$. On removing the solvent the residue was distilled in vacuo. We obtained 8.31 g (60%) of adduct **IV**, MD_D 79.50, calc. 80.39, $[\alpha]_D^{20}$ –48.18 (*c* 4.5, EtOH).

The other runs for preparation of compound **IV** were carried out similarly (the reaction conditions and results are listed in Table 1).

(–)Menthyl 5-methylbicyclo[2.2.1]hept-2-ene-5-carboxylate (V). From 11.2 g (0.05 mol) of compound **III** and 3.92 g (0.06 mol) of cyclopentadiene (**I**) along the above procedure at –78°C we obtained 7.4 g of adduct V (52%). MR_D found 83.04, calc. 84.07, $[\alpha]_{589}^{20}$ –54.48 (*c* 7.93 EtOH).

The other runs for preparation of compound **V** were performed similarly (the reaction conditions and results are listed in Table 1).

Isomeric bicyclo[2.2.1]hept-2-ene-5-carboxylic acids (VI, VIII). Compound **IV** (13.8 g, 0.05 mol) was boiled for 2 h in 30 ml of 5% KOH solution in methanol. On removing methanol the residue was dissolved in 30 ml of water, the products were extracted into ether. The water layer was treated with diluted HCl and repeatedly extracted with ether. The extract was washed with water, and dried on $MgSO_4$. On removing ether we obtained 5.6 g (89%) of isomers **VI** and **VIII** mixture. The separation of *endo* **VI** and *exo* **VIII** isomers was carried out as in [17]. 6.3 g of isomer mixture of **VI** and **VIII** was neutralized with 10% solution of KOH, treated with 76 ml of iodine solution (15 g of I_2, 30 g of KI were dissolved in 90 ml of water). The precipitated iodolactone **XIV** was extracted into ether, the water layer was acidified with diluted HCl, the extraction was repeated, the extract was washed with 5% sodium thiosulfate solution, then with water, and dried with $MgSO_4$. On removing the solvent by distillation we obtained *exo*-acid **VIII**. Its constants are given in Table 2.

Iodolactone **XIV**, isolated from the first extract, is a colorless crystalline substance, mp 59–60°C (from aqueous ethanol); cf.: mp 55–58°C [18]. *endo*-Acid **VI** was obtained from iodolactone **XIV** by procedure [17]. The constants of acid **VI** are given in Table 2.

Isomeric 5-methylbicyclo[2.2.1]hept-2-ene-5-carboxylic acids (VII, IX). Compound **V** (14.5 g) was boiled for 2 h in 30 ml of 5% KOH solution. Further hydrolysis was similar to that with adduct **IV**. We obtained 6.2 g (89.8%) of a mixture of *endo* **VII** and *exo* **IX** isomers. The separation thereof was carried out as above.

Iodolactone XV is a colorless crystalline compound, mp 86–87°C (from aqueous ethanol) (83–85°C [17]). IR spectrum, ν, cm^{-1} 1730 (C=O); 1100 (C–O). Found, %: C 38.21; H 3.9; I 45.51. $C_9H_{10}IO_2$. Calculated, %: C 38.84; H 3.98; I 45.68. By reduction of 6.95 g of iodolactone **XV** along procedure [17] we obtained 3.2 g of endo-acid VII.

Physical constants of acids VII and **IX** are given in Table 2.

Isomeric 5-hydroxymethylbicyclo[2.2.1]hept-2-enes (X, XII). To a dispersion of 4 g of $LiAlH_4$ in 200 ml of anhydrous ethyl ether was added dropwise 6.6 g of adduct **IV** solution in 50 ml of anhydrous ether. The mixture was stirred for 2 h at 20°C. The excess $LiAlH_4$ was hydrolyzed with water, then to the mixture was slowly added cooled diluted HCl. The ether layer was separated, washed with 5% solution of $NaHCO_3$ and with water till neutral, and then dried with $MgSO_4$. On removing ether we obtained 6.1 g of a mixture containing menthol and compounds **X, XII**. The mixture was separated by preparative chromatography. Physical constants of compounds **X** and **XII** are presented in Table 2. Mass spectra of both isomers are identical and have the following characteristics (relative intensity at 30 and 12 eV, %): M^+ 124 (17;67), 106 (10;40), 93 (5;09), 66 (100; 100).

5-Methyl- 5-hydroxymethylbicyclo[2.2.1]hept-2-enes (XI, XIII). From 7.3 g of adduct **V** by reduction with $LiAlH_4$ along the above procedure was obtained 6.9 g of mixture containing menthol and alcohols **XI, XIII** that was separated by preparative chromatography. Physical constants of compounds **XI** and **XIII** are presented in Table 2.

Mass spectra of both isomers are identical and have the following characteristics (relative intensity at 30 and 12 eV, %): M^+ 138 (95 : 32), 107 (12 : 14), 95 (24 : 26), 81 (26 : 50), 66 (100 : 100), 55 (21 : 5).

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