18 as well as its ^{13}C NMR chemical shifts. We also thank Dr. David L. Harris, Mrs. Susan Morris-Natschke, and Mr. John C. Dyer for recording numerous ^{1}H and ^{13}C spectra related to this work. Purchase of the NMR instrument was made possible by NSF Instrument Grant No. GU-2059,2059-Amendment I and GP-37602 and by NIH Grant No. 5S05RR07072.

Registry No. 1, 624-92-0; 2, 110-81-6; 3, 4253-89-8; 4, 110-06-5; 5, 1518-72-5; 6, 505-20-4; 7, 20268-02-4; 8, 13882-12-7; 9, 18542-39-7; 10, 38739-06-9; 11, 31562-40-0; 12, 72360-72-6; 13, 7153-76-6; 14, 72360-73-7; 15, 2949-92-0; 16, 682-91-7; 17, 10027-69-7; 18, 31562-41-1; 19, 59917-29-2; 20, 18321-15-8; 21, 72360-74-8; 22, 4253-90-1; 23, 52754-01-5; *trans*-1,2-bis(mercaptomethyl)cyclohexane, 72401-49-1; *trans*-1,2-bis(mercaptomethyl)cyclohexane diacetate, 72360-75-9; *trans*-2,3-dithiadecalin, 20268-02-4.

Asymmetric Induction in Liquid Crystals: Optically Active *trans*-Cyclooctene from Hofmann Elimination in New Cholesteric Mesophases

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Optically active *trans*-cyclooctene was obtained by Hofmann elimination of trimethylcyclooctyl ammonium hydroxide in new cholesteric liquid crystals. The extent of asymmetric induction rose 7%. Enantiomeric equilibration of racemic *trans*-cyclooctene in cholesteric medium, at 180 °C, leads to a 2% enantiomeric excess. These asymmetric induction results are interpreted in terms of solute–solvent interactions enhanced by the local ordering of the mesophase.

Recently several papers pointed out a large controversy on the possibility of controlling the stereochemistry of reactions by a chiral organized medium such as cholesteric liquid crystals.

On one hand, several research groups reported moderate extents of asymmetric induction during high-temperature reactions conducted in cholesteric mesophases such as the Claisen rearrangement of *O*-allyl aryl ethers,[1] enantiotopic decarboxylation,[2] or enantiomeric equilibration of sulfoxides.[3]

On the other hand, Kagan and co-workers[4] did not succeed in reproducing these literature results and reported no detectable asymmetric induction during several photochemical processes. On the basis of these results these authors concluded by stating that they doubted that a cholesteric mesophase could afford appreciable asymmetric induction and that the effect of mesomorphic anisotropy ordering on asymmetric induction remains to be clearly established.

In this paper, we report our own results, dealing with Hofmann pyrolysis of quaternary ammonium salts in cholesteric medium and enantiomeric equilibration of *trans*-cyclooctene. We also offer evidence that the stereochemical outcome of the reactions conducted in liquid crystals is dependent on the nature of the mesophase. All these results suggest that the asymmetric induction is governed by the "local" asymmetry of the mesophase.

Results

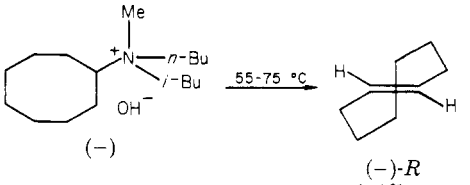
Our first work using cholesteric liquid crystals as solvent was actually a pyrolysis study of *N*-amine oxides. By heating *N*,*N*-dimethyl-4-methyl and *N*,*N*-dimethyl-4-*tert*-butylcyclohexylamine *N*-oxide in cholesteryl benzoate and propionate, we did not detect any significant optical activity in the produced substituted cyclohexene. Table I reports some of our results.

This absence of asymmetric induction is consistent with the results obtained by Dewar,[7] during a study of Claisen rearrangements in nematic liquid crystals, who claimed that the orientation effect of the mesophase should have a very small effect on intramolecular rearrangements.

For this reason we turned our attention to the Hofmann degradation of quaternary ammonium salts which proceeds by polar transition states and so could be more sensitive to a liquid crystal environment.

Since the pionneering work of Cope,[8] *trans*-cyclooctene can be produced by Hofmann elimination of a cyclooctyl quaternary ammonium salt.

(−)-*trans*-Cyclooctene (1.4% ee) was also obtained by Cope[9] by pyrolysis of a chiral cyclooctylammonium hydroxide as the result of a chirality transfer from the asymmetric nitrogen atom to the dissymetric cyclooctene.



(−) (−)-*R*
1.4% ee
34/66 cis/trans

(1) F. D. Saeva, P. E. Sharpe, and G. R. Olin, *J. Am. Chem. Soc.*, **97**, 204 (1975).
(2) L. Verbit, T. R. Halbert, and R. B. Patterson, *J. Org. Chem.*, **40**, 1649 (1975).
(3) W. H. Pirkle and P. L. Rinaldi, *J. Am. Chem. Soc.*, **99**, 3510 (1977).
(4) C. Eskenazi, J. F. Nicoud, and H. B. Kagan, *J. Org. Chem.*, **44**, 995 (1979).
(5) G. Belluci, G. Ingroso, A. Marsili, E. Mastrorilli, and J. Morelli, *J. Org. Chem.*, **42**, 1079 (1977).
(6) G. Berti and G. Belluci, *Tetrahedron Lett.*, 3853 (1964).
(7) M. J. S. Dewar and B. D. Nahlovsky, *J. Am. Chem. Soc.*, **96**, 460 (1974).
(8) A. C. Cope, K. Banholzer, F. N. Jones, and H. Keller, *J. Am. Chem. Soc.*, **88**, 4700 (1966).
(9) A. C. Cope, W. R. Funke, and F. B. Jones, *J. Am. Chem. Soc.*, **88**, 4693 (1966).
(10) A. C. Cope and B. A. Pawson, *J. Am. Chem. Soc.*, **87**, 3649 (1965).

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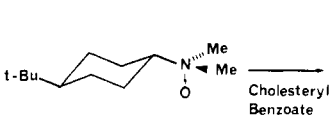
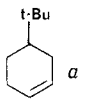
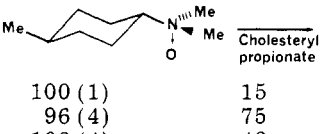
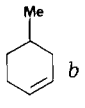
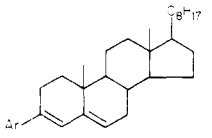
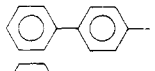
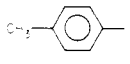
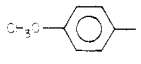
Table I. *N*-Amine Oxide Pyrolysis in Cholesteric Liquid Crystals

% *N*-oxide	cholesteric range, °C	temp (time)[c]	yield,[d] %	α_{365} ($CHCl_3$)	$[\alpha]_{365}$	ee, %
		 Cholesteryl Benzoate	 *a*			
5.5	150-171	160 (6)	65	+0.019	+0.43	0.18
9.9	150-170	165 (7)	49	+0.009	+0.47	0.19
4.2	150-172	160 (6.5)	52	+0.007	+0.20	0.08
3.6	150-172	160 (2.5)	68	0	0	0
7.0	144-174	160 (6)	54	0	0	0
		 Cholesteryl propionate	 *b*			
9.3	93-105	100 (1)	15	0	0	0
4.7	93-105	96 (4)	75	0	0	0
5.91	93-105	100 (4)	43	0	0	0

[a] $[\alpha]^{25}_{365}$(max) + 247.1°, *R*[5]. [b] $[\alpha]^{15}_{365}$(max) + 331°, *R*[6]. [c] Pyrolysis temperature (°C) and time of reaction (h). [d] Of cyclohexene.

Table II. New Cholesteric Liquid Crystals



Ar	*T*[a]	$[\alpha]^{23}_D$, deg (*c*, $CHCl_3$)
	101-108	−109.6 (1.648)
	111-128	−111.8 (1.05)
	140-149	−102.6 (0.93)
	158-174	−122.4 (1.623)
	174-197	−126.1 (1.282)
	156-231	−128.4 (2.19)

[a] Transition temperatures (°C) for s → CH → liq; s = solcholesteric, liq = isotropic liquid.

Our purpose was to pyrolyze the achiral cyclooctyltrimethylammonium hydroxide in a cholesteric liquid crystal in order to see if a chirality transfer from the mesophase could be observed.

However, most of the known cholesteric liquid crystals are cholesterol esters which interact with the counterion HO^- and so do not allow the Hofmann elimination.

Therefore, it was necessary to prepare new cholesteric liquid crystals which do not interact with the ammonium salt and have a mesomorphic range suitable with the pyrolysis temperature. In this way, we chose to synthesize 3-aryl-substituted 3,5-cholestadienes which, by analogy with substituted stilbenes, could show mesomorphic properties.

Six substituted 3-aryl-3,5-cholestadienes were prepared (Table II), but only the 3-phenyl-, 3-(*p*-anisyl)-, and 3-(*p*-tolyl)-3,5-cholestadienes have cholesteric ranges large enough to be used as the solvent for a chemical reaction around 160–180 °C.

Table III. New Cholesteric Mixtures

mixture	*T*[a]
C: 52.5% 3-(*p*-anisyl)-3,5-cholestadiene 47.5% 3-phenyl-3,5-cholestadiene	146-183
D: 15.3% *p*-azoxyanisole 44.5% 3-(*p*-anisyl)-3,5-cholestadiene 40.2% 3-phenyl-3,5-cholestadiene	117-189

[a] Transition temperature (°C) for s → Ch → liq.

It was also possible to obtain lower temperature cholesteric mesophases by mixing two of these cholestadienes (mixture C, Table III) or diluting this mixture with a nematic phase such as *p*-azoxyanisole (mixture D).

The results of the pyrolysis of the ammonium salt in a set of different liquid crystals are reported in Table IV.

After pyrolysis, the cyclooctene was carefully purified by vacuum distillation from the reaction mixture and its purity checked by NMR (see Experimental Section). The optical rotations were determined by diluting the product in chloroform, and the cis/trans ratio was determined by VPC analysis.

From Table IV it can be seen clearly that asymmetric induction occurred during these pyrolyses, and four comments have to be pointed out. (1) A lower reaction temperature enhances, as expected, the stereoselectivity (runs 1, 4, and 5), 7% at 130 °C. (2) In an isotropic phase (run 3) racemic *trans*-cyclooctene is produced. (3) In a nematic phase twisted by a small amount of cholesterol–OTHP (run 6), no asymmetric induction was detected.[11] (4) An enantiomeric excess (ee) of 3% was obtained at 180 °C (run 1). At this temperature, *trans*-cyclooctene racemizes very quickly[10] (ΔE = 35.6 kcal/mol; half-life values are 15 h at 156.4 °C and 1 h at 183.9 °C). The detected optical activity should result from enantiomeric equilibration of the product.

This last observation prompted us to investigate enantiomeric equilibration of *trans*-cyclooctene in a set of cholesteric liquid crystals.

The three cholesteric 3-aryl-3,5-cholestadienes A, B and F (runs 1, 2, and 3) afforded enantiomeric excesses of 1–1.9% (Table V) whereas cholesterol esters such as cholesteryl *p*-nitrobenzoate (G, run 4) and cholesteryl benzoate

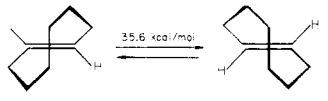
(11) Pitches were estimated from our results concerning twisting powers of optically active molecules.[12]

Table IV. Trimethylcyclooctylammonium Hydroxide Pyrolysis in Cholesteric Liquid Crystals

run	crystal (T, t)[f]	ammonium salt, %	cholesteric range, °C	cyclooctene yield, %	α^{23}_D ($CHCl_3$)	$[\alpha]^{23}_D$ [g]	ee, %
1	A (180, 8)	7.7	163-215	46[a]	−0.28	−17.5	3.8
		9.4	167-209	69[a]	−0.185	−14.9	3.3
		10.1	168-209	68[a]	−0.172	−12.7	2.8
2	B (163, 8)	6.4	159-174	53[b]	−0.112	−6	1.3
		4.9	158-174	41[b]	−0.034	−4.6	1
		7.1	160-173	50[b]	−0.221	−6	1.3
3	B (162, 8)	7.8	isotropic	57[b]	0	0	0
4	C (152, 6)	7.1	146-183	60[c]	−0.174	−17.4	3.8
		6.7	146-188	63[c]	−0.146	−18.1	3.9
5	D (129, 7)	8.4	121-184	47[d]	−0.710	−33.0	7.2
	(132, 7)	7.7	121-184	52[d]	−0.583	−32.3	7.1
6	E (130, 8)[h]	8.1	122-135	55[e]	0	0	0
	(118, 8)[i]	4.3	114-122	45[e]	0	0	0
	(121, 8)[j]	5	117-125	50[e]	0	0	0
	(122, 8)[k]	4.2	115-128	53[e]	0	0	0
	(122, 8)[l]	9.8	120-126	43[e]	0	0	0

[a] 60/40 cis/trans. [b] 68/32 cis/trans. [c] 60/40 cis/trans. [d] 50/50 cis/trans. [e] 25/75 cis/trans. [f] T = temperature (°C) and t = time (h). A = 3-(*p*-anisyl)-3,5-cholestadiene, B = 3-phenyl-3,5-cholestadiene, C = 52.5% A + 47.5% B, D = 44.5% A + 40.2% B + 15.3% *p*-azoxyanisole, and E = *p*-azoxyanisole. [g] For *trans*-cyclooctene. $[\alpha]^{25}_D$ −458° for pure *trans*-cyclooctene. [h] Cholesterol-OTHP, 4.9%. [i] Cholesterol-OTHP, 8.2%. [j] Cholesterol-OTHP, 4.3%. [k] Cholesterol-OTHP, 4.3%. [l] Cholesterol-OTHP, 2.6%.

Table V. Enantiomeric Equilibration of *trans*-Cyclooctene in Cholesteric Liquid Crystals



(−)-*R* (+)-*S*

run	crystal (T, t)[b]	cyclooctene yield, %	cholesteric range, °C	recovered cyclooctene, %	α^{23}_D [a] ($CHCl_3$)	$[\alpha]^{23}_D$ [d]	ee, %
1	A (182, 8)	2.8	161-225	53	−0.237	−8.83	1.9
	(192, 5.5)	3.7	162-222	61	−0.113	−8.57	1.8
2	B (153, 24)	5.8	151-164	67	−0.069	−4.87	1.06
	(153, 25)	6.6	151-162	62	−0.087	−5	1.09
	(153, 25)	6.0	151-163	57	−0.092	−4.87	1.06
3	F (185, 8)	5.7	177-201	58	−0.075	−5.38	1.17
	(183, 8)	6.2	177-200	61	−0.153	−6.41	1.40
4	G (185, 8)	4.8	182-253	64	0	0	0
	(190, 8)	4.3	182-253	62	−0.055	−0.68	0.15
5	H (170, 10)[c]	4.63	150-167	62	+0.027	+0.3	0.06
	(160, 30)	2.28	150-169	63	0	0	0
6	A + decaline (180, 7)	2.0	isotropic	62	+0.007	+0.06	0.014
7	N + 19% F (180, 7)[c]	6.9	150-175	74	0	0	0
	N + 26% F (170, 12)	7.3	166-178	70	0	0	0
	N + 13% F (180, 8)	4.4	176-194	57	0	0	0
	N + 17% A (175, 9)	8.2	164-194	65	0	0	0
	N + 15% A (175, 9)	5.4	164-195	69	0	0	0

[a] 55/45 cis/trans. [b] T = temperature (°C) and t = time (h). A = 3-(*p*-anisyl)-3,5-cholestadiene, B = 3-phenyl-3,5-cholestadiene, F = 3-(*p*-tolyl)-3,5-cholestadiene, G = cholesteryl *p*-nitrobenzoate, H = cholesteryl benzoate, N = bis(*p*-ethoxybenzylidine)hydrazone. [c] Isotropic. [d] For *trans*-cyclooctene.

(H, run 5) did not give any asymmetric induction. A similar negative result is obtained in a nematic liquid crystal doped with cholestadiene A (run 6). Finally we have checked that in an isotropic phase, resulting from cholestadiene A diluted with decaline (run 7), no optical activity of recovered *trans*-cyclooctene could be detected.

The discrepancy of the results in phase A between the ammonium pyrolysis (ee 3%) and cyclooctene equilibration (ee 1.9%) probably comes from the fact that at this temperature a small amount of cyclooctene distilled out of the medium during the heating period.

Discussion

From our results it is clear that some amount of asymmetric induction can be obtained by performing a reaction in a cholesteric liquid crystalline phase. However, the enantiomeric equilibration of *trans*-cyclooctene pointed out that the induction is dependent on the nature of the cholesteric molecules: 3-aryl-3,5-cholestadienes are suitable whereas cholesterol esters are not.

It is reasonable to think, as it was suggested before,[3,4] that the macrostructural handedness of the mesophase cannot control the stereochemistry of an asymmetric transformation. Most of the cholesteric helices have pitches around 0.3 μm which correspond to about 10^3 molecular layers. The solute molecules, sandwiched between cholesteric planes, will "see" a very weak helical chirality, the angle of the main axis of the mesophase molecules between two molecular layers being extremely small.

This is confirmed by our experiment in cholesteryl *p*-nitrobenzoate which has the smallest pitch (green reflection light) and did not lead to any optically active cyclooctene.

The origin of the observed asymmetric induction is best understood in terms of diastereoisomeric solute–solvent interactions.

We have recently studied[12,13] the twisting powers of optically active molecules dissolved in nematic liquid crystals, which is the reverse phenomenon: chirality transfer from the solute to the solvent. We have shown that these twisting powers, β_M, are controlled by molecular interactions between the optically active molecules and the solvent. The location of a polar function on the solute molecule and its dipole moment, the structural analogy of both solute and solvent and hydrogen bonding, are factors which can drastically affect the β_M value.

It is reasonable to think that the same factors which control packing of the molecules play a predominant role in asymmetric induction of a cholesteric liquid crystal.

It is well-known that in isotropic chiral solvents, asymmetric induction occurs when the solvent plays a special role by means of specific interactions with species along the reaction coordinates (Grignard additions or Meerwein reductions are typical examples).[14]

In our case, we should expect small solute–solvent interactions. The polar transition state obtained from the quaternary ammonium salt probably has some charge-transfer-complex interactions with 3-(*p*-anisyl)-3,5-cholestadiene. The nature of the interactions between arylcholestadienes and cyclooctene is less obvious. Our results conducted in chiral 3-aryl-3,5-cholestadienes show clearly that these small molecular interactions allow asymmetric induction only in the anisotropic phase.

In his recent paper, Kagan[4] concluded that the effect of mesomorphic anisotropic ordering on asymmetric induction remained to be clearly established. Our results showed that small solute–solvent interactions, which are inoperative in isotropic medium, are increased by the local ordering of the liquid crystal matrix (the lifetime of these diastereoisomeric solute–solvent associations being enhanced) and control to some extent the stereospecificity of the reaction. In this context, one cannot expect to reach very high optical yields although it should be possible to improve the extent of asymmetric induction by increasing the solute–solvent interactions and using a solute having a structural analogy with the cholesteric molecules.

Experimental Section

NMR spectra were measured on a Perkin-Elmer R24 (60 MHz) instrument, infrared spectra on a Perkin-Elmer 257 spectrometer, and UV spectra on a Beckmann DB-G instrument. Optical rotations were measured on a Perkin-Elmer 241 MC spectropolarimeter. Transition temperatures of the liquid crystals were determined with a polarizing microscope, Leitz-Orthoplan Pol. The abbreviations used in the transition temperature data are as follows: s = solid, Ch = cholesteric, liq = isotropic liquid.

3-Aryl-3,5-cholestadienes. A fivefold excess of aryl Grignard reagent or aryllithium was added dropwise to Δ^5-cholesten-3-one[15] in ether and the mixture refluxed 6 h. After cooling, the reaction mixture was decomposed by ammonium chloride and extracted with ether. After evaporation of the solvent, the crude 3-aryl-3-hydroxy-Δ^5-cholestene was dehydrated in the following way: 1 g of alcohol dissolved in 50 mL of acetone, 2 mL of concentrated HCl, and 3 mL of water were refluxed for 4.5 h. Ether extraction, followed by washing with sodium carbonate and water, led, after evaporation of the solvent, to the crude product which was purified by column chromatography on silica gel (solvent hexane 95–98%–ether 5–2%) and then by preparative low-pressure chromatography (p = 2 atm).

3-Phenyl-3,5-cholestadiene from phenyl Grignard: yield 60%; $[\alpha]^{23}_D$ −122.4° ($CHCl_3$, c 1.62, $CHCl_3$);[16] transition temperatures 142 °C (s → Ch), 170 °C (Ch → liq); UV (pentane) λ_{nm} (ϵ) 282 (28 400), 235 (11 500), 228 (12 300), 195 (45 300); IR ($CHCl_3$) 3080, 3060, 3020 (ν_{C-H}) 1640, 1600 ($\nu_{C=C}$) cm^{-1}; NMR (CCl_4) δ 0.6, 0.7, 0.85, 0.9, and 1.1 (br m, 41 H), 5.1–5.4 (1 H, m, H_6), 6.05 (1 H, s, H_4), 6.8–7.2 (5 H, m, H_{Ar}). Anal. Calcd for $C_{33}H_{48}$: C, 89.19; H, 10.19. Found: C, 89.06; H, 10.86.

3-(*o*-Tolyl)-3,5-cholestadiene from *o*-tolyl Grignard: yield 60%; $[\alpha]^{23}_D$ −111.8° (c 1.05, $CHCl_3$); transition temperatures 111 °C (s → Ch), 128 °C (Ch → liq); UV (pentane) λ_{nm} (ϵ) 251 (15 600), 242 (15 600), 218 (15 600), 145 (19 100); IR ($CHCl_3$) 3010 ($\nu_{C-H_{Ar}}$), 2940, 2860 (ν_{C-H}), 1650, 1570 cm^{-1} ($\nu_{C=C}$); NMR ($CDCl_3$) δ 0.7, 0.8, 0.9, 1, and 1.3 (br m, 41 H), 2.35 (3 H, s, CH_3 benzylic), 5.5 (1 H, m, H_6), 5.8 (1 H, s, H_4), 7 (4 H, s, H_{Ar}). Anal. Calcd for $C_{34}H_{50}$: C, 89.01; H, 10.99. Found: C, 89.10; H, 10.98.

3-(*m*-Tolyl)-3,5-cholestadiene from *m*-tolyl Grignard: yield 65%; $[\alpha]^{23}_D$ −109.6 (c 1.65, $CHCl_3$); transition temperatures 101 °C (s → Ch), 108 °C (Ch → liq); UV (pentane) λ_{nm} (ϵ) 281 (25 500), 238 (sh, 12 300), 231 (sh, 14 800), 217 (sh, 18 900), 196 (26 400); IR (CCl_4) 3070, 3020 ($\nu_{C-H_{Ar}}$), 2950, 2870 (ν_{C-H}), 1460, 1380, 1370 cm^{-1} ($\nu_{C=C}$); NMR ($CDCl_3$) δ 0.7, 0.8, 0.9, 1, and 1.2 (br m, 41 H), 2.4 (3 H, s, H_4), 7.35 (4 H, AB, J_{AB} = 9 Hz, $\Delta\nu$ = 15 Hz). Anal. Calcd for $C_{34}H_{50}$: C, 89.01; H, 10.99. Found: C, 89.16; H, 11.03.

3-(*p*-Tolyl)-3,5-cholestadiene from *p*-tolyl Grignard: yield 75%; $[\alpha]^{23}_D$ −126.1 (c 1.28, $CHCl_3$); transition temperatures 174 °C (s → Ch), 197 °C (Ch → liq); UV (pentane) λ_{nm} (ϵ) 283 (28 300), 237 (10 700), 230 (12 400), 221 (14 100), 198 (15 000); IR ($CHCl_3$) 3050 ($\nu_{C-H_{Ar}}$), 2950, 2880 (ν_{C-H}), 1520, 1460 cm^{-1} ($\nu_{C=C}$); NMR ($CDCl_3$) δ 0.7, 0.8, 0.9, 1.0 and 1.2 (br m, 41 H), 2.4 (3 H, s, benzylic CH_3), 5.4 (1 H, m, H_6), 6.2 (1 H, s, H_4), 7.35 (4 H, AB, J_{AB} = 9 Hz, $\Delta\nu$ = 15 Hz). Anal. Calcd for $C_{34}H_{50}$: C, 89.01; H, 10.99. Found: C, 89.10; H, 10.90.

3-(*o*-Anisyl)-3,5-cholestadiene from *o*-anisyl Grignard: yield 70%; $[\alpha]^{23}_D$ −108.4° (c 1.08, $CHCl_3$); transition temperatures 79 °C (s → Ch), 90 °C (Ch → liq); UV (pentane) λ_{nm} (ϵ) 268 (14 700), 225 (13 800), 205 (18 900), 195 (27 200); IR ($CHCl_3$) 3060–2900 (ν_{C-H}), 2860 (ν_{C-CH_3}), 1595, 1485, 1465 cm^{-1} ($\nu_{C=C}$); NMR ($CDCl_3$) δ 0.7, 0.8, 0.9, 1.1, and 1.2 (br m, 41 H), 3.65 (3 H, s, OCH_3), 5.45 (1 H, m, H_6), 6.05 (1 H, s, H_4), 6.6–7 (4 H, m, H_{Ar}). Anal. Calcd for $C_{34}H_{50}O$: C, 86.01; H, 10.61. Found: C, 86.14; H, 10.56.

3-(*p*-Anisyl)-3,5-cholestadiene from *p*-anisyl Grignard: yield 75%; $[\alpha]^{23}_D$ −128.4 (c 2.19, $CHCl_3$); transition temperatures 156 °C (s → Ch), 231 dec (Ch → liq); UV (pentane) λ_{nm} (ϵ) 315 (32 200), 235 (9300), 226 (13 300), 195 (48 200); IR (CCl_4) 3060, 3020 ($\nu_{C-H_{Ar}}$), 2940, 2850 (ν_{C-H}), 1600, 1505 cm^{-1} ($\nu_{C=C}$); NMR ($CDCl_4$) δ 0.7, 0.85, 0.9, and 1.1 (br m, 41 H), 3.6 (3 H, s, OCH_3), 5.2 (1 H, m, H_6), 6.6 (1 H, S, H_4), 7.05 (4 H, AB, J_{AB} = 9 Hz, $\Delta\nu$ = 32 Hz). Anal. Calcd for $C_{34}H_{50}O$: C, 86.01; H, 10.61. Found: C, 86.12; H, 10.50.

3-(*p*-Biphenyl)-3,5-cholestadiene from *p*-biphenyllithium: yield 60%; $[\alpha]^{23}_D$ −102.6 (c 0.93, $CHCl_3$); transition temperatures 140 °C (s → Ch), 149 (Ch → liq); UV (pentane) λ_{nm} (ϵ) 302 (25 700), 242 (11 100), 235 (12 400), 204 (35 100); IR ($CHCl_3$) 3040 ($\nu_{C-H_{Ar}}$), 2840 (ν_{C-H}), 1590 cm^{-1} ($\nu_{C=C}$); NMR ($CDCl_3$) δ 0.7, 0.8, 0.9, 0.95, 1.0, and 1.1 (br m, 41 H), 5.6 (1 H, m, H_6), 6.5 (1 H, s, H_4), 7–7.7 (9 H, m, Ar). Anal. Calcd for $C_{39}H_{52}$: C, 89.94; H, 10.06. Found: C, 87.51; H, 10.04.

Pyrolyses of *N*-Amine Oxides in Cholesteric Liquid Crystals. *N,N*-Dimethyl-4-methylcyclohexylamine *N*-oxide and *N,N*-dimethyl-4-*tert*-butylcyclohexylamine *N*-oxide were prepared by known procedures.[17,18]

Then 10 g of cholesteric material was intimately mixed with the *N*-amine oxide (5–10% by weight). The cholesteric range of this mixture was then determined with a microscope. After the mixture was heated at the required temperature for 6 h, sub-

(12) P. Seuron, Thèse de Docteur-Ingénieur, Université Louis Pasteur, Strasbourg, France, 1979.
(13) J. M. Ruxer, G. Solladie, and S. Candau, *Mol. Cryst. Liq. Cryst.*, 41, 109 (1978).
(14) J. D. Morisson and H. S. Mosher in "Asymmetric Organic Reaction", Prentice Hall, 1971, pp 411–8.
(15) W. S. Johnson, D. G. Martin, "Organic Syntheses", Collect Vol. IV, Wiley, New York, 1963, p 195.
(16) J. Urushibara, T. Ando, Y. Araki, A. Ozawa, *Bull. Chem. Soc. Jpn.*, 12, 353 (1937).
(17) R. Michelot, *Bull. Soc. Chim. Fr.*, 4277 (1969).
(18) A. C. Cope, E. R. Trumbull, *Org. React.*, 11, 317 (1960).

stituted cyclohexene was carefully distilled from the reaction mixture under vacuum and collected in a trap cooled at -78 °C. The optical rotation was determined in chloroform.

4-Methylcyclohexene (6): IR ($CHCl_3$) 3020 (ν_{C-H}), 2940, 2920, 2860, 2780 (ν_{C-H}), 1600, 1450 cm^{-1} ($\nu_{C=C}$); NMR ($CDCl_3$) δ 0.7-2.2 (m, 10 H), 5.6 (2 H, m, vinylic H).

4-*tert*-Butylcyclohexene (5): IR ($CHCl_3$) 3020 (ν_{C-H}), 2980-2840, 2870 (ν_{C-H}), 1660, 1480, 1470 cm^{-1} ($\nu_{C=C}$); NMR ($CDCl_3$) δ 0.7-2.2 (m, 7 H), 0.9 (s, 9 H, *t*-Bu), 5.65 (2 H, m, vinylic H).

***N,N,N*-Trimethylcyclooctylammonium Hydroxide.** By ion exchange on Amberlite IRA 400 (HO^-), *N,N,N*-trimethylcyclooctylammonium iodide, $F = 267°$,[19] gave quantitatively the corresponding oily quaternary ammonium salt: NMR ($CDCl_3$) δ 1.5-2 (15 H, m), 3.3 (9 H, S, $^+NMe_3$).

Pyrolysis of *N,N,N*-Trimethylcyclooctylammonium Hydroxide in Cholesteric Liquid Crystals. The cholesteric material (10 g) was intimately mixed with the quaternary ammonium salt (5-10% by weight). The cholesteric domain of this mixture was then determined with a microscope. After the mixture was heated at the required temperature for 6 h, cyclooctene was carefully distilled from the reaction mixture under vacuum and collected in a trap cooled at -78 °C. The purity of the product was checked by NMR. The optically active contaminant could only be the substituted cholestadiene used as solvent (these compounds are stable at the pyrolysis temperature). A detected optical activity of, for example, -12.7 or -32.3° (Table IV) would correspond to 10-25% of pollutant which would have been easily detected by NMR. Cyclooctene shows a high intensity signal at 1.5 ppm; meanwhile, the substituted cholestadienes are characterized by high-intensity signals below 1.1 ppm and aromatic protons: IR (CCl_4) 3010 (ν_{C-H}), 2920, 2850, 2760 (ν_{C-H}), 1470, 1450 cm^{-1} ($\nu_{C=C}$); NMR ($CDCl_3$) δ 1.5 (br s, 12 H), 5.1-6.6 (2 H, m, vinylic H).

(19) A. Cope, R. D. Bach, *Org. Synth.*, **49**, 39 (1969).

The cis and trans stereochemistry of cyclooctene was determined by irradiation of the methylenic protons at 2.3 ppm. The vinylic protons gave two singlets at 5.4 and 5.6 ppm, corresponding respectively to the cis and trans cyclooctene as shown by simulated ^1H NMR spectra.[12]

The cyclooctene cis/trans ratio was determined by VPC: column Triton X 305 (10%); temperature 60 °C; retention time cis, 10 min; trans, 11 min.

The optical rotations were determined in chloroform.

Enantiomeric Equilibration of *trans*-Cyclooctene. The cholesteric phase (10 g) was intimately mixed with a mixture of *cis*- and *trans*-cyclooctene obtained by the usual way[18] (cis/trans ratio = 55/45) and heated at the racemization temperature for several hours (Table IV). Cyclooctene is then recovered and analyzed as in the preceding section.

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Registry No. Δ^5-Cholesten-3-one, 601-54-7; 3-phenyl-3,5-cholestadiene, 2309-35-5; 3-(*o*-tolyl)-3,5-cholestadiene, 72390-28-4; 3-(*m*-tolyl)-3,5-cholestadiene, 72390-29-5; phenyl bromide, 108-86-1; *o*-tolyl bromide, 95-46-5; *m*-tolyl bromide, 591-17-3; 3-(*p*-tolyl)-3,5-cholestadiene, 72390-30-8; 3-(*o*-anisyl)-3,5-cholestadiene, 72390-31-9; *p*-tolyl bromide, 106-38-7; *o*-anisyl bromide, 578-57-4; 3-(*p*-anisyl)-3,5-cholestadiene, 72390-32-0; 3-(*p*-biphenyl)-3,5-cholestadiene, 72390-33-1; *p*-anisyl bromide, 104-92-7; *p*-biphenyllithium, 1201-71-4; *N,N*-dimethyl-4-methylcyclohexylamine *N*-oxide, 72390-34-2; *N,N*-dimethyl-4-*tert*-butylcyclohexylamine *N*-oxide, 72390-35-3; trimethylcyclooctylammonium iodide, 72390-36-4; trimethylcyclooctylammonium hydroxide, 13310-46-8; 4-methylcyclohexene, 591-47-9; (+)-4-*tert*-butylcyclohexene, 61062-50-8; (*R*)-(*E*)-cyclooctene, 22770-27-0; (*S*)-(*E*)-cyclooctene, 3958-30-3; (*Z*)-cyclooctene, 931-87-3.

Notes

Guanidinium Ion: SCF Calculations

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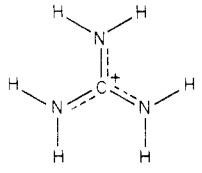
The guanidinium ion $C(NH_2)_3^+$



is of quantum chemical and biochemical interest. This is true both for itself and because of its role as an important fragment in a variety of larger biochemical compounds whose functions are much dependent upon the properties of the ion.[1-8]

The rotational barrier about a single CN bond of the ion has been obtained by an NMR experiment and has a value of 13 kcal mol^{-1}. Two recent quantum mechanical studies in the literature give calculated values for all three rotational barriers associated with this molecule.[6] In the first of these,[4] a MINDO/3 SCF calculation yielded values of 8.9, 15, and 31.0 kcal mol^{-1}, respectively, for single, double, and triple rotational barriers (see Figure 1). By the phrase single (double or triple) barrier we mean the energy difference for the molecule's planar geometry and that cor-

(1) S. Subramanian, T. S. Sarma, D. Balasubrananian, and J. C. Ahluwalia, *J. Chem. Phys.*, **75**, 815 (1971).
(2) C. A. Swanson, *Arch. Biochem. Biphys.*, **117**, 494 (1966).
(3) S. Katz, *Biochim. Biophys. Acta*, **154**, 468 (1968).
(4) T. Bally, P. Diehl, E. Haselback, and A. Tracey, *Helv. Chim. Acta*, **58**, 2398 (1975).
(5) J. F. Capitani and L. Pedersen, *Chem. Phys. Lett.*, **54**, 547 (1978).
(6) See also the paper of Kollman, McKelvey, and Gund, *J. Am. Chem. Soc.*, **97**, 1640 (1975). The geometry of the guanidinium ion obtained with a STO 431 G basis is essentially the same as that obtained in this work and that obtained by Capitani and Pedersen in ref 5. However, the total optimized energy reported is -204.22345 au, a value higher than ours at -204.44910 au, while the reported single barrier is 14.1 kcal mol^{-1}, to be compared to our value of 14.73 kcal mol^{-1} and to the Capitani and Pedersen value of 14.97 kcal mol^{-1} also obtained with the 4-31 G basis.
(7) H. R. Mahler and E. H. Cordes, "Biological Chemistry", 2nd ed., Harper and Row, New York, p 49.
(8) A. Santoro, *J. Org. Chem.*, submitted.

0022-3263/80/1945-0719$01.00/0