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High-Pressure Addition Reactions Involving Cycloheptatriene–Norcaradiene Equilibrium

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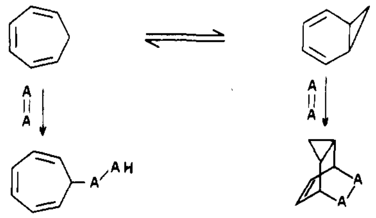
Several high-pressure reactions of cycloheptatriene (CHT) were investigated with various unsaturated compounds. With homonuclear bonds (C═C, C≡C, N═N), norcaradiene adducts were formed, whereas with the unsymmetrical C═O bond, only ene-type addition was observed. There is a general tendency to form norcaradiene adducts under high pressure (reactions of CHT with acrylonitrile and acetylenic bonds). Several unprecedented peculiar features are observed under pressure: inter- and intramolecular formation of the norcaradiene adduct (CHT–dimethyl acetylenedicarboxylate), homo-Diels–Alder reactions involving bicyclooctadiene systems (CHT–methyl propiolate), formation of the unknown norcaradiene adduct with the N–N fragment (CHT–diethyl azodicarboxylate) showing interesting NMR properties reflecting conformational changes.

The ring inversion and cyclotautomerization processes are interesting properties of the cycloheptatriene structure. While the ring inversion is generally so rapid that it could be observed only at very low temperatures,[1,2] the valence isomerization cycloheptatriene–norcaradiene[3] can be evidenced even at relatively high temperatures via the reaction products (Scheme I).[4]

Scheme I



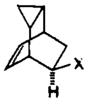
At the usual temperatures needed to achieve these reactions, norcaradiene can exist only as a transient molecule.[5] Considering that norcaradiene adducts are formed[6,7] at temperatures as high as 120–180 °C, it is evident that the diene is an extremely reactive molecule in comparison with cycloheptatriene (CHT).[8] However, products derived from [6 + 4] cycloaddition and ene reaction on the CHT ring are usually also observed,[6,7] especially at high temperatures. We thought that such reactions would be susceptible to be minimized when the temperature is lowered. However, this procedure introduces a beneficial effect on norcaradiene reactions, only if the system keeps sufficient reactivity. In this respect, we were prompted to use high pressures, since it is a common feature that addition reactions with volumes of activation in the order of −30 to −50 mL/mol are greatly facilitated by the application of pressure, if concertedness is proved.[9] The aim of this paper is to examine the pressure effect on the product distribution in some reactions between CHT and multiple homo- or heteronuclear activated bonds (C═C, C≡C, N═N, C═O).

1. Reaction with Tetracyanoethylene. The reaction of CHT with the reactive TCNE is known to produce only one 1:1 adduct whose formation has been rationalized in terms of the Diels–Alder reaction involving the norcaradiene form.[10]

Under high pressure (900 MPa) at ambient temperature, the norcaradiene adduct was formed as unique product with 100% yield after a couple of hours.

2. Reaction with Acrylic Esters. The reaction of CHT with acrylonitrile and methyl acrylate were studied at atmospheric pressure under high-temperature conditions (170–200 °C, 18–24 h).[7]

They give several products which were identified (in addition to CHT dimers) as norcaradiene adducts 1 and 2 and as the product 3 resulting from a formal 1,6-addition.[11] 1–3 were produced in a 9:9:2 ratio (when X = CN) and a 2:11:1 ratio (when X = CO_2CH_3).



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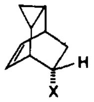

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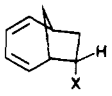

3

Repeating these experiments in CH_2Cl_2 at ambient pressure in the temperature range of 160–180 °C (24 h), we found following ratios: when X = CN, 1:2:3 = 4:4:1, total yield 65%; when X = CO_2CH_3, 1:2:3 = 3:12:1, total yield 38%.

Under 900 MPa at 80 °C, only 1 and 2 were produced in the ratio 1:1 when X = CN and 1:5 when X = CO_2CH_3. No trace of 3 nor dimers of CHT could be detected. Yields were respectively 80% and 62% (reaction time, 24 h). In order to verify whether 3 transforms into norcaradiene adducts, we submitted to 900 MPa (80 °C) the adduct mixture (free from reactants) resulting from the atmospheric runs. No change in the composition of the mixture occurred.

This study shows that, under high pressure and at moderate temperatures, the CHT–acrylic esters reactions lead selectively to norcaradiene adducts in agreement with our initial hypothesis. In addition, it should be remarked

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[1] Anet, F. A. *J. Am. Chem. Soc.* **1964**, *86*, 458.

[2] Takeuchi, K.; Kitagawa, T.; Senzaki, Y.; Okamoto, K. *Chem. Lett.* **1983**, 73.

[3] Hoffmann, R. *Tetrahedron Lett.* **1970**, 2907.

[4] The tricyclic adduct retaining the norcaradiene unit can theoretically also be formed via a [4 + 2] homocycloaddition to cycloheptatriene: Balci, M.; Atasoy, B. *Tetrahedron Lett.* **1984**, *25*, 4033.

[5] Norcaradiene has been isolated by a matrix technics at −196 °C: Rubin, M. *J. Am. Chem. Soc.* **1981**, *104*, 7791.

[6] Goldstein, M. J.; Gevirtz, A. H. *Tetrahedron Lett.* **1965**, 4413.

[7] Belluš, D.; Helferich, G.; Weis, C. D. *Helv. Chim. Acta* **1971**, *54*, 463.

[8] Friedman, P. K.; Balls, D. M.; Brown, D. J. *J. Org. Chem.* **1968**, *33*, 2211.

[9] Jenner, G. *Bull. Soc. Chim. Fr.* **1984**, 275.

[10] Wahl, G. H. *J. Org. Chem.* **1968**, *33*, 2158.

[11] Belluš claimed 3 to be the endo isomer. However, the NMR spectrum clearly shows that 3 is a mixture endo + exo (the relative proportions could not be determined), since no full decoupling could be made by irradiation. Besides the NMR data in ref 7 are incorrect. The complete δ values are reported in the Experimental Section of this paper.

0022-3263/86/1951-0585$01.50/0

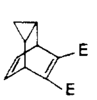
Table I. Pressure Effect on Product Distribution[a]

p, MPa	time, h	% 4	% 5
0.1	8–48	68	32
100	6–20	73	27
200	15	78	22
400	1	82	18
400	5	90	10
400	16	90	10
600	5.5	95	5
800	3	97	3
800	15	99	1
900	1	100	0

[a] At 80 °C, in CH_2Cl_2 solution.

that pressure does not affect the exo–endo ratio in accordance with a previous finding.[12]

3. Reaction with Dimethyl Acetylenedicarboxylate. The reaction was studied a long time ago[6] in refluxing toluene. Two adducts 4 and 5 in the ratio 2:1 (total yield, 38%) are formed. The major product 4 was shown to be the norcaradiene adduct, whereas 5 was the result of an ene-type addition (see Scheme II) (E = CO_2CH_3).



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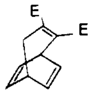


5

Application of 900 MPa of pressure at room temperature during one day yielded 4 as the only product in 16% yield. Total conversion occurred by heating a touene or a CH_2Cl_2 solution of reactants at 80 °C (900 MPa, 15 h), giving again exclusively 4 despite the higher temperature. It was obviously of interest to examine the temperature and the pressure effect on the formation of 4 and 5.

Examination of the temperature dependence (in the range 70–120 °C) of the second-order rate constants[13] gave linear Arrhenius plots yielding the following (the subscript refers to the corresponding adduct):

$$E_4 = 81.9 \text{ kJ/mol} \qquad E_5 = 79.0 \text{ kJ/mol}$$

$$A_4 = 1.20 \times 10^5 \qquad A_5 = 1.18 \times 10^5$$

$$\Delta S_4^{\ddagger} = -156.7 \text{ kJ/mol·K} \qquad \Delta S_5^{\ddagger} = -157.2 \text{ kJ/mol·K}$$

Visibly the formation of both adducts show similar temperature dependence. Additionally we have verified that there was no interconversion of products in the examined temperature range.

The kinetics[13] was further followed in the low-pressure region (0–120 MPa) at 96.5 °C. Application of the transition-state theory leads to the determination of the apparent volumes of activation:

$$\Delta V_4^{\ddagger} = -33.8 \text{ mL/mol} \qquad \Delta V_5^{\ddagger} = -28.8 \text{ mL/mol}$$

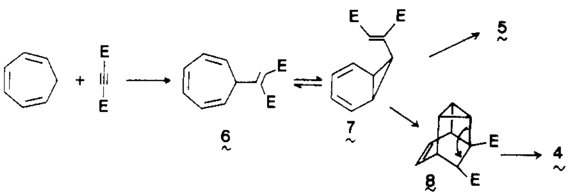
If the mechanism for each reaction is not altered by the pressure, the application of Elyanov's selectivity relationship,[14]

$$\frac{\partial}{\partial p} \ln (k_4/k_5) = -\frac{\Delta V_4^{\ddagger} - \Delta V_5^{\ddagger}}{RT}$$

$$\ln \frac{k_4^p/k_5^p}{k_4^0/k_5^0} = -\frac{\Delta V_4^{\ddagger} - \Delta V_5^{\ddagger}}{T}\Phi$$

(Φ is a function of pressure, independent on reaction; the exponents p and 0 refer to pressure p and 0.1 MPa)

Scheme II



should give (for example, for p = 800 MPa, Φ = 24.3) 74% of 4 and 26% of 5. However, the 800-MPa run showed selectivities for 5 as low as 3% after 3 h of reaction and 1% after 15 h; Table I reports the pressure effect on product distribution.

These results indicate a time dependence of the product ratio above 100 MPa. There is a detrimental pressure effect on the formation of 5 which ultimately vanishes at a sufficient high pressure.

Adduct 5 is believed to form sequentially[6] (Scheme II). The first step in this sequence is an ene reaction which should be considerably accelerated by pressure providing full concertedness.[15] The last step (7 → 5) considers a (3,3)-sigmatropic process for which the volume of activation has been reported as negative.[16] Pressure should therefore also accelerate the formation of 5, probably to the same extent as for 4, as is inferred by the fairly negative value of $\Delta V_5^{\ddagger}$.

At higher pressures, there could be a subsequent reaction involving 5 (homo-(1,5)-sigmatropic shift and skeletal rearrangement to form 4). However, it is also possible that the course of the reaction is altered during the formation process of 5. We therefore submitted a 65:35 mixture of 4 + 5 to 1100 MPa of pressure at 85 °C during 18 h. The ratio changed to 69:31 only. The result is not convincing regarding a possible transformation of 5 into 4. Therefore, to account for the exclusive formation of 4 at the higher pressures, we propose the sequential process 7 → 8 → 4 (Scheme II).

The norcaradiene intermediate 7 is thus presumed to be reactive enough under high pressure to undergo an intramolecular [4 + 2] reaction to give the highly strained caged molecule 8 which eventually rearranges into 4. According to this proposal, the volume of activation of the intramolecular Diels–Alder process should exhibit a much higher absolute value than the $\Delta V^{\ddagger}$ for the (3,3)-sigmatropic shift.[17]

Again, as in the reaction involving acrylic esters, high pressure makes the reaction between CHT and the acetylenic diester very selective toward the norcaradiene adduct.

4. Reaction with Methyl Propiolate. This acetylenic monoester was allowed to react with CHT in high-pressure conditions, since at ambient pressure and at 180 °C, the reaction gave numerous unidentified products in poor yield (about 5–8%). Compared to the diester, the acetylenic bond in methyl propiolate was less reactive: at 80 °C under 900 MPa, the product yield was 73% (after 68 h) (cf. with the 100% conversion after 15 h in the former case). As exposed previously,[18] four products were formed, all exhibiting the norcaradiene structure (E = CO_2CH_3).

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[12] Seguchi, K.; Sera, S.; Maruyama, K. *Tetrahedron Lett.* **1973**, 1585.

[13] Kinetic values are available upon request.

[14] Elyanov, B. S.; Gonikberg, M. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 1044.

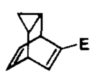
[15] Jenner, G.; Papadopoulos, M. *J. Org. Chem.* **1982**, *47*, 4201.

[16] Claisen and Cope rearrangements have negative $\Delta V^{\ddagger}$ (−5 to −15 mL/mol): (a) Brower, K. R. *J. Am. Chem. Soc.* **1961**, *83*, 4370. (b) Walling, C.; Naiman, M. *J. Am. Chem. Soc.* **1962**, *84*, 2628. However, other sigmatropic shifts were described as stepwise processes: le Noble, W. J.; Daka, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 5961.

[17] A value of −25 mL/mol was reported for an intramolecular Diels–Alder reaction: Isaacs, N. S.; van der Beeke, P. *Tetrahedron Lett.* **1982**, *23*, 2147.

[18] Papadopoulos, M.; Jenner, G. *Tetrahedron Lett.* **1985**, *26*, 3335.

11 and **12** are polyadducts resulting from a further 1,4-addition of the acetylenic bond to the norcaradiene adducts **9** and **10**, respectively. These additions occur only under



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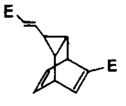

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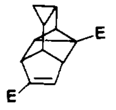
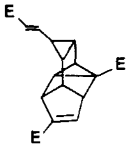
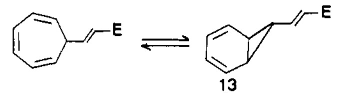


11



12

high pressure and provide examples for an extension of the synthetic possibilities of the homo-Diels–Alder reaction to bicyclooctadiene systems. Another point to be outlined is that, while **9** is the product of the typical [4 + 2] cycloaddition, **10** results from the [4 + 2] addition of methyl propiolate on the initial ene monoadduct in equilibrium with the corresponding norcaradiene **13**.

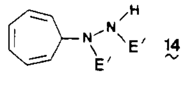


13

The relative proportion of **9** + **11** vs. **10** + **12** is 2:1, e.g., the same ratio as with the acetylenic diester. However, in the present case, the reactivity of the external double bond in **13** is different (compared to **7**); **13** prefers to undergo an intermolecular [4 + 2] cycloaddition rather than to react in an intramolecular way.

5. Reaction with Diethyl Azodicarboxylate. The reaction was investigated by Cinnamon and Weiss[19] who detected an adduct **14** resulting from an ene process. The reaction was further investigated with cycloheptatriene-7-*d* and the suggestion was made that the ene reaction could involve not only a six-membered but also a ten-membered transition state.[20] Since ene and (4 + 2) addition seem to be equally accelerated by pressure[9,15] (see also reaction 3), it was not evident whether pressure will promote the norcaradiene addition.

Under high pressure (900 MPa) at ambient temperature, three compounds in the ratio 2:1:1 were detected by gas chromatography. Conversion of the azo diester was 100% within 3–5 h. The main product was shown to be the expected ene compound **14** (E′ = $CO_2C_2H_5$). The two others were separated and characterized as the norcaradiene adduct **15** and 1,2-dicarbethoxyhydrazine **16**. The latter is known to form easily in reactions involving azodicarboxylates.[21]



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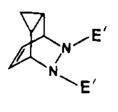


15

At ambient pressure, **15** is not produced, whereas **16** is formed with a low yield, although it was not reported in the former study.[19] Thus, again, pressure has a beneficial effect on the formation of the norcaradiene addition product. It is interesting to note that the ratio **15**:**14** here is 1:2 (the inverse of the value found in the CHT reactions involving acetylenic esters), due to the enophilic character of the diazene ester.

The new adduct **15** possesses peculiar NMR properties which are reported below. The ^1H NMR spectrum recorded at ambient temperature shows two distinct vinylic protons, each of them resolved as a triplet, suggesting a molecular dissymmetry. A variable-temperature NMR study revealed that both triplets transform into broad signals and eventually collapse into a unique triplet at 90 ± 2 °C.

Scheme III

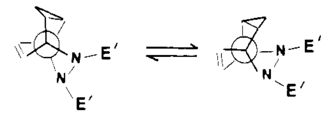
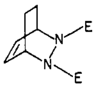
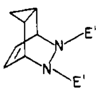
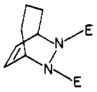


Table II. Interconversion Barriers and Flexibility Indexes

compd	$\Delta G^{\ddagger}$,[a] kJ/mol	$\Delta G_{80}^{\ddagger}$,[a] kJ/mol	flexibility[b]	ref
	68.6	70.2	0.75	22
	78.2	76.1	0.80	this work
	80.7	81.5	0.85	22

[a] Since T_c depends on compound and type of signals which collapse (E or vinylic protons), the $\Delta G_c^{\ddagger}$ values were standardized for T = 80 °C. [b] Defined as the ratio $\Delta G^{\ddagger}$(compound):$\Delta G^{\ddagger}$(reference) at 80 °C.

Taking into account earlier conformational studies[22] involving [2.2.*n*] bicyclic systems containing also the fragment NE–NE, we ascribe the phenomenon to conformational changes (preference for a twisted conformation, which was clearly detected in bicyclic systems, with $n = 2$)[22] (Scheme III).

The origin of the two distinct signals for the vinylic protons results from an out-of-plane structure for the N–N fragment.

Lehn presented a method permitting to calculate approximate values of the barriers hindering the above interconversion:[23]

$$\Delta G^{\ddagger} = 4.57T_c[9.7 + \log T_c/\Delta\nu]$$

where T_c is the coalescence temperature and $\Delta\nu$ is the separation of the signals. $\Delta\nu$ is correlated with the rate constant of the process.

In the related paper,[22] Lehn defined for the investigated bicyclic systems a "flexibility index" (reference: *N,N′*-dibenzyl-*N,N′*-dicarbomethoxyhydrazine) which is believed to be a measure of the height of the energy barrier relative to the considered interconversion: the lower the flexibility, the higher the rigidity of the system and therefore the lower the interconversion barrier (Table II).

As clearly shown in Table II, the compound **15** fits fairly well the general trend. The $\Delta G^{\ddagger}$ value and the flexibility number for **15** are intermediate between the corresponding values for the [2.2.2] and the [2.2.3] systems. Compared to the latter, $\Delta G_{80}^{\ddagger}$ for **15** is lowered by 5.4 kJ/mol, due to the presence of the rigid cyclopropane ring.

6. Reaction with Dimethyl Mesoxalate. Activated carbonyl bonds are much less reactive than activated C=C, C≡C, and N=N bonds. The unprecedented reaction between CHT and dimethyl or diethyl mesoxalate does not occur at normal pressure (at least up to 140 °C). Submitted to high pressure (950 MPa) at 80 °C, the reaction

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[19] Cinnamon, J. M.; Weiss, K. *J. Org. Chem.* **1961**, *26*, 2644.

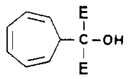
[20] E. Koerner von Gustorf cited by: Hoffmann, H. M. R. *Angew. Chem.* **1969**, *81*, 597; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 566.

[21] (a) Shah, A.; George, M. V. *Tetrahedron* **1971**, *27*, 1291. (b) Franzus, B. *J. Org. Chem.* **1963**, *28*, 2954.

[22] Lehn, J. M.; Wagner, J. *Tetrahedron* **1969**, *25*, 677.

[23] (a) Lindscheid, P.; Lehn, J. M. *Bull. Soc. Chim. Fr.* **1967**, 992. (b) Anderson, J. E.; Lehn, J. M. *Tetrahedron* **1968**, *24*, 123. (c) Anderson, J. E.; Lehn, J. M. *J. Am. Chem. Soc.* **1968**, *89*, 81.

affords two products in the ratio 95:5 (72% yield after 24 h). The dominant product 17 was shown to be the ene adduct ($E = CO_2CH_3$).



17

The other product could not be separated from 17. No norcaradiene structure, however, could be evidenced. This is not surprising in view of the electronic dissymmetry of the C=O bond in the mesoxalate molecule which behaves as a remarkably good enophile.[15,24]

Conclusion

Application of high pressure is an effective way to increase the reactivity of the cycloheptatriene system. The large negative volumes of activation are in agreement with concerted reactions enabling the use of lower temperatures and leading to [4 + 2] and [2 + 2 + 2] cycloadditions when feasible. The net effect is that adducts retaining the norcaradiene structure are selectively produced under pressure, especially when reactive symmetrical bonds (C=C, C≡C) are involved. With the N=N bond, the norcaradiene adduct, which is not formed under normal pressure conditions, is produced in fair amount at high pressure. With the less reactive unsymmetrical C=O bond, only hydrogen abstraction takes place.

The examples shown in this paper can be extended to other reactive bonds (some are under investigation) and demonstrate the synthetic utility of high pressure in generating new compounds.

Experimental Section

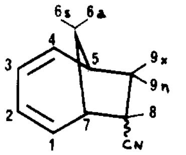
General. CH_2Cl_2 and toluene were dried and distilled prior to use. Cycloheptatriene and the titled dienophiles were distilled under vacuum. Dimethyl mesoxalate was prepared as previously described.[15]

Melting points (mp) were determined with a Reichert hot stage microscope (mp uncorrected). Routine GLC analyses were performed in the following conditions: IGC 120 instrument (catharometer; He as gas carrier; program 60–230 °C, 8 °C/min) with columns FFAP (reaction 2), OV210 (reactions 3 and 4), Apiezon (reaction 5), and SE 30 (reaction 6). High-resolution GLC analyses were carried out on a Hewlett-Packard 5880 A instrument (FID; N_2 as gas carrier; column, capillary fused silica cross-linked 5% phenylmethylsilicone, 0.2 mm × 12.5 m; program 50–210 °C, 5 °C/min). The retention time values (t_R) for products refer to this column. The kinetics of reaction 3 was followed in the usual way[15] by GLC (column OV210 and 1,2,3,4-tetramethylbenzene as standard). TLC was performed on silica gel 60GF254 (Merck) and preparative-layer chromatography on silica gel 60 (Merck 9285, 230–400 mesh) (2-mm thickness). R_f values refer to silica gel and corresponding eluent system.

^1H NMR spectra were taken with a Varian XL 100 spectrometer. Fine resolution was achieved with a Brucker WH-360 instrument (Me_4Si as standard, chemical shifts in ppm, coupling constants in Hz). Mass spectra were recorded with a CH-4 MAT instrument and IR spectra with Perkin-Elmer spectrometer.

1. **Reaction with Tetracyanoethylene.** TCNE (100 mg, 0.78 mmol) was dissolved in 2 mL of CH_3CN. After addition of 90 mg (0.98 mmol) of CHT, the reaction tube was closed and introduced into a high-pressure vessel kept at room temperature. After reaction, the solvent and CHT were removed and pure 7,7,8,8-tetracyanotricyclo[3.2.2.$0^{2,4}$]non-6-ene[10] as shown by NMR was isolated.

2. **Reaction with Acrylonitrile.** The reaction was conducted at atmospheric pressure on a CH_2Cl_2 solution of 450 mg (4.90 mmol) of CHT and 400 mg (7.54 mmol) of acrylonitrile with 10 mg of hydroquinone in a small autoclave at 160–180 °C. After reaction and GLC analysis (t_R: **1**, 13.42; **2**, 14.46; **3**, 14.94), the solvent was removed and the residue placed onto a silica gel column. Elution with hexane–ether (75:25) yielded **1** (R_f 0.27), **2** (R_f 0.16), and **3** (R_f 0.12 as a mixture of endo and exo isomers). The spectra were given previously.[7] The spectrum of **3** is as follows:



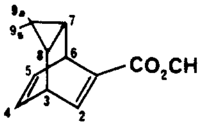
^1H NMR ($CDCl_3$) 6.87 (q, H-1, $J_{1,2} = 11$, $J_{1,7} = 8.5$, $J_{1,8} \simeq 1$), 6.00 (q, H-4, $J_{3,4} = 11$, $J_{4,5} = 6$, $J_{2,4} \simeq 1$), 5.97 (t, H-2 and H-3, $J_{3,4} = 11$, $J_{2,3} = 6.6$, $J_{2,4} \simeq 1$), 2.94 (m, H-7, $J_{1,7} = 8.5$), 2.78 (m, H-5, $J_{4,5} = 6$), 2.35 (m, H-9x, $J_{9,9} = 13.5$), 2.17 (m, H-9n), 2.08 (m, H-6s and H-6a).

3. **Reaction with Dimethyl Acetylenedicarboxylate.** A toluene solution (2.5 mL) of 540 mg (5.86 mmol) of CHT and 694 mg (4.88 mmol) of the acetylenic compound was introduced into a small autoclave and heated at 120 °C under atmospheric pressure during 110 h. After reaction, the solvent was evaporated and excess CHT removed by short-path distillation. GLC analysis showed the presence of two products: **4** (t_R 22.81) and **5** (t_R 23.35). Column chromatography using hexane–ethanol (90:10) as eluent led to the separation of **4** (R_f 0.27) and **5** (R_f 0.21), which were easily proved to be identical with those reported in the literature.[6]

4. **Reaction with Methyl Propiolate.** A solution of 215 mg (2.56 mmol) of methyl propiolate and 285 mg (3.10 mmol) of CHT in CH_2Cl_2 (2 mL) was heated at 170–180 °C during 1 day. GLC analysis showed the formation of at least 10 products (overall conversion: 5–8%), which were not separated.

The high-pressure reaction (900 MPa, 80 °C, 68 h) was performed with 688 mg (8.19 mmol) of methyl propiolate and 1100 mg (11.96 mmol) of CHT in CH_2Cl_2 (1 mL). GLC analysis revealed the presence of four products (overall yield: 73%). Column chromatography with hexane–ether (3:2) as eluent separated **9** (R_f 0.52), **10** + **11** (R_f 0.30), and **12** (R_f 0.15). To resolve **10** and **11**, a second chromatography was necessary with hexane–ethyl acetate (4:1) (R_f 0.26 for **10** and R_f 0.20 for **11**).

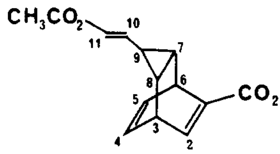
(a) Adduct 9:



9

liquid; t_R 13.8; IR ($CDCl_3$) 3090, 3050, 3025, 2980, 1730, 1640, 1605 cm^{-1}; NMR 7.54 (dd, H-2, $J_{2,3} = 6$, $J_{2,6} = 1.5$), 6.02 (dt, H-5, $J_{5,6} = 6$, $J_{4,5} = 7$, $J_{3,5} = 1.5$), 5.92 (dt, H-4, $J_{3,4} = 6$, $J_{4,5} = 7$, $J_{4,6} = 1.5$), 4.17 (m, H-6, $J_{6,5} = 6$, $J_{6,7} = 3$, $J_{6,2} = J_{6,4} = 1.5$), 3.73 (m, H-3, $J_{3,4} = J_{2,3} = 6$, $J_{3,8} = 3$, $J_{3,5} = 1.5$), 3.10 (s, OCH_3), 1.26 (m, H-7, $J_{7,8} = J_{7,9a} = 7$, $J_{7,9s} = 3.5$, $J_{7,6} = 3$), 1.15 (m, H-8, $J_{7,8} = J_{8,9a} = 7$, $J_{8,9s} = 3.5$, $J_{8,3} = 3$), 0.78 (dt, H-9, $J_{9a,9s} = 6$, $J_{8,9s} = J_{7,9s} = 3.5$), 0.54 (dt, H-9a, $J_{7,9a} = J_{8,9a} = 7$, $J_{9a,9s} = 6$). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.50; H, 6.70.

(b) Adduct 10:



10

solid; mp >300 °C; t_R 21.8; IR ($CDCl_3$) 3070, 3040, 1720, 1645 cm^{-1}; NMR (when not indicated, coupling constants are similar to those given for the corresponding protons in **9**) 7.53 (dd, H-2), 6.52 (dd, H-10, $J_{10,11} = 16$, $J_{9,10} = 10$), 6.13 (dt, H-5), 6.04 (dt, H-4), 5.71 (d, H-11, $J_{10,11} = 16$), 4.33 (m, H-6, $J_{6,7} = 4.5$), 3.94 (m, H-3, $J_{3,8} = 4.5$), 3.72 (d, OCH_3 on C-1), 3.67 (s, OCH_3 on C-11), 1.76 (dt, H-9, $J_{9,10} = 10$, $J_{7,9} = J_{8,9} = 2.8$), 1.59 (m, H-7, $J_{7,8} = 8.5$, $J_{6,7} = 4.5$, $J_{7,9} = 2.8$), 1.50 (m, H-8, $J_{7,8} = 8.5$, $J_{3,8} = 4.5$, $J_{8,9} = 2.8$) [the trans structure for H-10 and H-11 is substantiated by the coupling constant $J_{10,11} = 16$ Hz; the constant $J_{9,10} = 10$ Hz represents a

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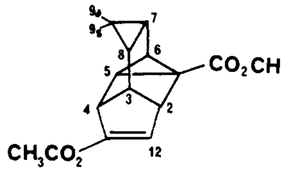
[24] (a) Achmatowicz, O.; Pietraskiewicz, M. *Tetrahedron Lett.* **1981**, *22*, 4323. (b) Jenner, G.; Papadopoulos, M.; Jurczak, J.; Kozłuk, T. *Tetrahedron Lett.* **1984**, *25*, 5747. (c) Papadopoulos, M.; Jenner, G. *Nouv. J. Chim.* **1984**, *8*, 729.

mean value for the rotation around the bond C_9–C_{10}]; MS, *m/e* 260, 245, 228, 196, 169, 141, 128. Anal. Calcd for $C_{14}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.08; H, 6.11.

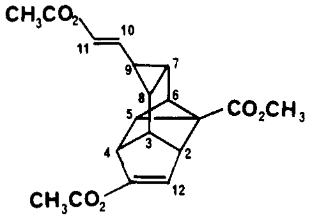
(c) Adduct 11:



11

solid, mp > 300 °C; t_R 20.1; IR ($CDCl_3$) 3035, 3020, 1720, 1590 cm^{-1}; NMR (7.42 (d, H-12, $J_{2,12} = 3$), 3.72 (s, OCH_3 on C-13), 3.65 (s, OCH_3 on C-1), 3.12 (dt, H-2, $J_{2,3} = 1.5$, $J_{2,4} = 1.8$), 2.92 (br, H-4, $J_{4,3} = J_{4,5} = 1.5$, $J_{4,6} = 1$), 2.75 (ddd, H-6, $J_{6,7} = 5$, $J_{5,6} = 8$, $J_{6,4} = 1$), 2.16 (dq, H-3, $J_{3,8} = 5.8$, $J_{3,2} = J_{3,4} = J_{3,5} = 1.5$), 1.82 (dt, H-5, $J_{5,6} = 8$, $J_{5,4} = J_{5,3} = 1.5$), 1.23 (m, H-7, $J_{7,8} = J_{7,9a} = 8$, $J_{7,9s} = 4$, $J_{7,6} = 5$), 0.90 (m, H-8, $J_{8,3} = J_{8,7} = 8$, $J_{8,9a} = J_{8,9s} = 4$), 0.52 (dt, H-9a, $J_{9a,8} = J_{9a,7} = 8$, $J_{9a,9s} = 5$), 0.28 (q, H-9s, $J_{9s,9a} = 5$, $J_{9s,7} = J_{9s,8} = 4$); MS, *m/e* 260, 245, 228, 200, 169, 141, 129, 115.

(d) Adduct 12:



12

solid, mp > 300 °C; t_R 25.0; IR ($CDCl_3$) 3030, 3000, 1720, 1590 cm^{-1}; NMR (concerning coupling constants, see note for product **10**) 7.41 (d, H-12), 6.42 (dd, H-10), 5.86 (d, H-11), 3.73 and 3.71 (s, OCH_3 on C-11 and C-13), 3.66 (s, OCH_3 on C-1), 3.15 (dt, H-2), 2.98 (br, H-4), 2.81 (ddd, H-6), 2.24 (dq, H-3), 1.91 (dt, H-5), 1.60 (m, H-7, $J_{7,9} = 3$), 1.49 (dt, H-9, $J_{9,10} = 10$, $J_{9,7} = J_{9,8} = 3$), 1.25 (m, H-8, $J_{8,7} = 8$, $J_{8,3} = 5.8$, $J_{8,9} = 3$); MS, *m/e* 344, 277, 252, 237, 225, 193, 165, 152, 128, 115.

5. Reaction with Diethyl Azodicarboxylate. The low- and high-pressure procedures were repeated as above at room temperature with 622 mg (6.77 mmol) of CHT and 555 mg (3.18 mmol) of enophile in CH_2Cl_2 solution (1.5 mL). After reaction, the content of the reaction tube was analyzed by GLC and submitted to the usual workup. The high-pressure runs were shown to contain three compounds which were separated by column chromatography followed by preparative-layer chromatography (with ether–hexane (2:1) as eluent). The first compound was proved to be **16**, diethyl hydrazine-1,2-dicarboxylate (mp 131–132 °C; t_R 12.9; R_f 0.11) by comparison with a commercial sample (Fluka). The other compounds were shown to be the ene adduct **14** already reported[19] (t_R 19.3; R_f 0.36) and the unprecedented norcaradiene adduct **15** (t_R 19.3; R_f 0.29): IR ($CDCl_3$) 3070, 3005, 1730, 1530 cm^{-1}; NMR (numeration as for **9**) 6.23 and 5.97 (t, H-4 and H-5, $J_{4,5} = 8$), 5.20 and 5.12 (br, H-3 and H-6), 4.22 (q, OCH_2), 1.77 and 1.61 (br, H-7 and H-8), 1.26 (t, CH_3), 0.42 (q, H-9a, $J_{9a,9s} = 6$, $J_{9a,7} = J_{9a,8} = 7$), 0.13 (dt, H-9, $J_{9s,9a} = 6$, $J_{9s,8} = J_{9s,7} = 3.5$); MS, *m/e* 266, 176, 93. Anal. Calcd for $C_{13}H_{18}O_4N_2$: C, 58.63; H, 6.81; N, 10.52. Found: C, 58.59; H, 6.74; N, 10.53.

6. Reaction with Dimethyl Mesoxalate. The high-pressure procedure (900 MPa) was repeated with a CH_2Cl_2 solution of 622 mg (6.77 mmol) of CHT and 920 mg (6.29 mmol) of dimethyl mesoxalate at 80 °C during 24 h. The yield of products was 72%. GLC analysis showed the formation of two compounds (95:5). Column chromatography with ether–hexane (2:1) as eluent gave a slightly yellow solid **17** (t_R 16.6; R_f 0.40; mp 76–78 °C): IR (KBr) 3500, 1750, 1620 cm^{-1}; NMR ($CDCl_3$) 6.71 (t, 2 H, C=C), 6.25 (dm, 2 H, C=C), 5.27 (dd, 2 H, C=C), 4.06 (br, 1 H, OH), 3.82 (s, 6 H, OCH_3); MS, *m/e* 238, 220, 147, 119, 91. Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.70; H, 6.17.

Acknowledgment. We thank Dr. A Rahm (University of Bordeaux I) for performing the 1100-MPa run (isomerization attempt of **5**), Dr. R. Breault for linguistic assistance, and E. Schleiffer for GC analyses.

Registry No. 1, 31456-54-9; **2**, 54382-95-5; *exo*-**3**, 100191-06-8; *endo*-**3**, 31576-25-7; **4**, 5932-77-4; **5**, 100191-07-9; **9**, 100191-08-0; **10**, 100191-09-1; **11**, 100191-10-4; **12**, 100191-11-5; **14**, 100191-12-6; **15**, 100191-13-7; **16**, 4114-28-7; **17**, 100191-14-8; TCNE, 670-54-2; CHT, 544-25-2; 8,8,9,9-tetracyanotricyclo[3.2.2.0^{2,4}]non-6-ene, 16118-23-3; acrylonitrile, 107-13-1; dimethyl acetylenedicarboxylate, 762-42-5; methyl propiolate, 922-67-8; diethyl azodicarboxylate, 1972-28-7; dimethyl mesoxalate, 3298-40-6.

Induction of the Cholesteric Mesophase in Nematic Liquid Crystals: Correlation between the Conformation of Open-Chain Chiral 1,1′-Binaphthyls and Their Twisting Powers

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The twisting powers β_M of 10 optically active open-chain 2,2′-disubstituted 1,1′-binaphthyls of known absolute configuration were measured in biphenyl nematic liquid crystals. The results show that it is possible to correlate the conformation (cisoid or transoid) of the optically active compounds to the sign of their twisting powers: for the absolute configuration *S*, a positive β_M value corresponds to a cisoid conformation while a negative β_M value corresponds to a transoid conformation. These conformational conclusions were in agreement with CD and X-ray data.

Induced cholesteric mesophases are generated by the addition of traces of chiral compounds to nematic liquid crystals.[1-4]

Different substances show a different ability to twist a nematic phase. The twisting power of chiral dopant can

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