$-47.8°$ (c=0.995). UV $\lambda_{max}^{alc.}$ mμ (ε): 221 (13,050), 268.5 (11,860), 304 (2430). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3496, 1694, 1660, 1573, 1490. NMR (τ): (18-H) 9.21; (19-H) 8.83; ($COCH_3$) 7.71; (thiophen-CH_3) 7.28; (OH) 6.98. *Anal.* Calcd. for $C_{23}H_{30}O_3S$: C, 71.46; H, 7.82; S, 8.30. Found: C, 71.49; H, 7.82; S, 8.35.

b) *via* the enol acetate (X). The oily 6α-acetylthio-4-en-3-one (Ⅷ, 1.680 g.) prepared from the thiolacetate (Ⅶ, 1.753 g.) was dissolved into a mixture of AcOH (20 ml.) and Ac_2O (10 ml.), and *p*-toluenesulfonic acid (180 mg.) was added. The mixture was left to stand overnight at room temp., poured into H_2O, and extracted with ether. The extract was washed with Na_2CO_3 solution and H_2O, dried over Na_2SO_4, and evaporated to give an oily enol acetate (X, 1.996 g.). UV: $\lambda_{max}^{alc.}$ 255 mμ (ε 17,290). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1758 (sh), 1739, 1718, 1700, 1664, 1617 (v. w), 1251, 1209, 1154, 1133. A part of this enol acetate (882 mg.) was dissolved into 80% MeOH (30 ml.) and K_2CO_3 (240 mg.) was added. The mixture was allowed to stand overnight at room temp. and treated as described above. Only the thieno compound (Ⅺa, 90 mg.), m.p. 240~242°, was obtained as crystals.

5′-Methyl-17α-acetoxythieno[4′,3′,2′-4,5,6]pregn-5-ene-3,20-dione (XIb)——The above thieno compound (Ⅺa, 1.18 g.) was dissolved into a mixture of AcOH (10 ml.) and Ac_2O (5 ml.) and *p*-toluenesulfonic acid (120 mg.) was added. The mixture was left to stand for 2 days at room temp. and poured into H_2O. The appeared crystals were collected by filtration, washed with H_2O, dried, and recrystallized from acetone-MeOH to give an acetate (Ⅺb, 1.057 g.), m.p. 267~269° (decomp.), $[\alpha]_D^{24.5}$ $-39.0°$ (c=0.981). UV $\lambda_{max}^{alc.}$ mμ (ε): 221 (12,390), 268.5 (11,320), 302 (2380). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1729, 1718 (sh), 1664, 1574, 1493. *Anal.* Calcd. for $C_{25}H_{32}O_4S$: C, 70.06; H, 7.53; S, 7.48. Found: C, 70.08; H, 7.55; S, 7.74.

Summary

By treatment of potassium thiolacetate 6β-bromo-4-en-3-one steroids were converted to 6α-acetylthio-4-en-3-ones, which were further converted to 5′-methylthieno[4′,3′,2′-4,5,6]-5-en-3-ones by heating with sodium hydride in toluene.

(Received August 29, 1964)

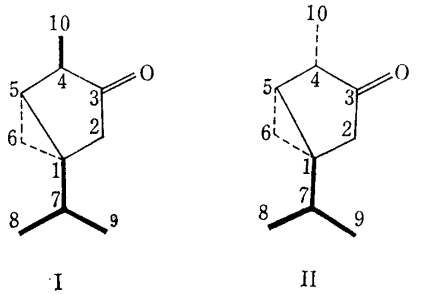
[Chem. Pharm. Bull. 12(12)1439~1446(1964)]

UDC 547.91.02 : 543.422.25

196. Kazuo Tori: Conformations of α- and β-Thujones.

(*Shionogi Research Loboratory, Shionogi & Co., Ltd.**1)

In connection with another problem in this laboratory, it became necessary to study in detail the proton magnetic resonance (NMR) spectra of α- and β-thujones (or (−)-thujone and (+)-isothujone (I and Ⅱ) respectively).*2 Thereafter, the author has published



I

II

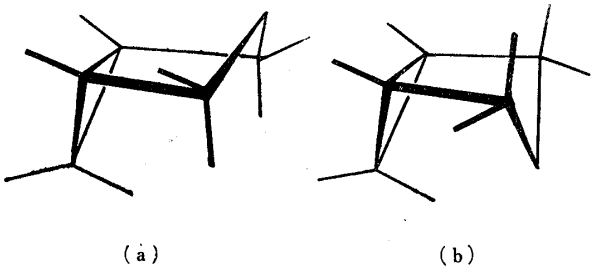


Fig. 1. Conformations of a Bicyclo-[3.1.0]hexane Ring

*1 Fukushima-ku, Osaka (通 和夫).

*2 Numbers in these compounds (I and Ⅱ) are affixed according to Bergqvist and Norin.[4]

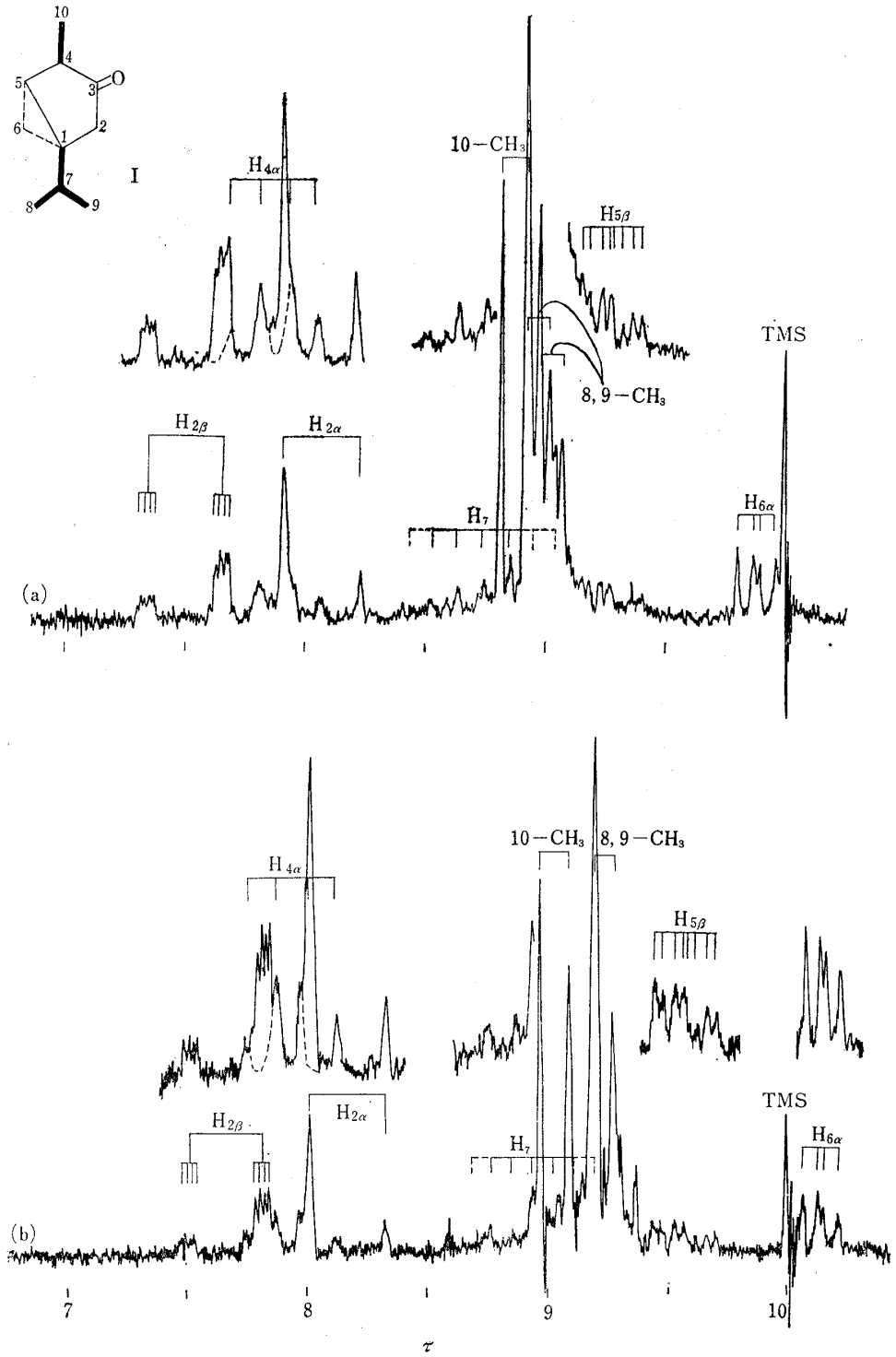


Fig. 2. The Proton Magnetic Resonance Spectra of α-Thujone (I) in Carbon Tetrachloride (a) and in Benzene (b) at 60 Mc.p.s.

a paper[1] studying the long-range shielding effects of the cyclopropane rings upon the methyl groups in I and II, which differ only in configuration at the C_4-atom,[2~4] to obtain

1) K. Tori : Ann. Repts. Shionogi Research Lab., **14**, 94 (1964).
2) T. Norin : Acta Chem. Scand., **16**, 640 (1962); H. E. Smith, G. A. Waters : J. Am. Chem. Soc., **84**, 2840 (1962).
3) T. Norin : Acta Chem. Scand., **17**, 738 (1963).
4) M. S. Bergqvist, T. Norin : Arkiv Kemi, **22**, 137 (1964).

a satisfactory result. However, it remains to report the full analyses of the spectra which were recognized to be useful for estimating their conformations.*3,*4

It was reported that a cyclopentane ring fused by another ring can take an envelope or a half-chair conformation depending on the number and position of various substituents on the cyclopentane ring.[5] Thus the bicyclo[3.1.0]hexane ring is of considerable interest from the conformational view-point. In a recent paper[4] dealing with the stereochemistry of the thujane group, Bergqvist and Norin have described that thujyl alcohols and thujones takes a boat-like envelope conformation as shown in Fig. 1 (b) from the chemical, optical rotatory dispersion (ORD), and particularly, NMR evidences. However, their spectral assignments and the procedure that led to the conclusion are somewhat different from those made in this laboratory. This point has indeed driven the author to publish promptly his results in the interpretation of the spectra of I and II.

Results and Discussion

Assignment of the Proton Magnetic Resonance Spectra

The NMR spectra of I and II in carbon tetrachloride are represented in Figs. 2 (a) and 3 (a), respectively. Since the spectra are somewhat complicated owing to overlapping

Table I. Proton Magnetic Resonance Data on α- and β-Thujones

Proton position	Chemical shift (τ) in CCl_4[a]		in $CDCl_3$	in pyridine	in benzene	Difference in chemical shifts $\delta_{CCl_4\text{-benzene}}$	Peak multiplicity[b]	Coupling constant J (c.p.s.) in CCl_4[a]
α-Thujone (I)								
2α-H	8.05	(8.04)	7.92	7.93	8.12	+0.07	d	$\|J_{2\alpha,2\beta}\|$=19.0 (18.5)
2β-H	7.57	(7.55)	7.46	7.43	7.72	+0.15	d-q (1)	$J_{2\beta,5\beta}$=2.1
4α-H	7.90	(7.90)	7.78	7.80	7.93	+0.03	q	$J_{2\beta,6\beta}$=1.0
5β-H	9.28	(9.0)	9.23	9.34	9.57	+0.29	q-d (1)	$J_{4\alpha,CH_3}$=7.0 (7.5)
6α-H	9.89	(9.91)	9.88	9.96	10.13	+0.24	q	$J_{4\alpha,5\beta}$~0 (~0)
6β-H	[c]	(9.35)	[c]	[c]	[c]			$J_{5\beta,6\beta}$=7.8
7-H	8.67	(8.7)	8.62	8.64	8.93	+0.26	m	$J_{5\beta,6\alpha}$=5.1
8- and 9-H	9.05	(9.03)	9.04	9.17	9.27	+0.23	d	$\|J_{6\alpha,6\beta}\|$=3.9
(CH_3)	9.00	(8.99)	9.00	9.12	9.23	+0.23	d	
10-H (CH_3)	8.88	(8.86)	8.86	8.92	9.03	+0.15	d	
β-Thujone (II)								
2α-H	7.95	(7.97)	7.86	7.91	8.07	+0.12	d	$\|J_{2\alpha,2\beta}\|$=18.5 (18.5)
2β-H	7.53	(7.56)	7.44	7.46	7.78	+0.25	d-q (1)	$J_{2\beta,5\beta}$=2.0
4β-H	7.43	(7.50)	7.35	7.38	7.77	+0.34	q-d-d (1)	$J_{2\beta,6\beta}$=1.5
5β-H	9.44	(9.2)	9.41	9.49	9.75	+0.31	q-d-d (1)	$J_{4\beta,CH_3}$=7.0 (7.0)
6α-H	10.05	(10.07)	10.05	10.12	10.28	+0.23	q	$J_{4\beta,5\beta}$=2.0 (~7)
6β-H	8.61	(9.45)	8.57	8.68	8.78	+0.17	q-t (1)	$J_{4\beta,6\beta}$~1
7-H	8.63	(8.6)	8.52	8.63	8.98	+0.35	m	$J_{5\beta,6\beta}$=8.0
8- and 9-H	9.05	(9.05)	9.07	9.17	9.28	+0.23	d	$J_{5\beta,6\alpha}$=5.2
(CH_3)	8.97	(9.00)	8.98	9.08	9.23	+0.26	d	$\|J_{6\alpha,6\beta}\|$=4.0
10-H (CH_3)	9.01	(8.97)	8.97	8.95	9.00	−0.01	d	

a) Data in parentheses are Bergqvist and Norin's assignments and values.[4]
b) Presented by d (doublet), t (triplet), q (quartet), m (multiplet), and l (long-range coupling). For example, d-q represents a quartet of doublets.
c) Obscured by the methyl signals.

*3 The author was not aware of Bergqvist and Norin's contribution[4] when submitted the previous paper.[1] Since Norin's assignment for the structures of the two thujones from the ORD evidence[3] was fully believed, the investigation was made, the result of which was also consistent with the structures.[1]

*4 The NMR spectra of the thujones cannot be thought to be very useful for their structure estimation. The configurations of the C_4-methyl groups cannot be fully established from the coupling constants between the C_4- and $C_{5\beta}$-protons without any assumptions on the conformations of the rings.

5) F. V. Brutcher, Jr., D. Roberts, S. J. Barr, N. Pearson: J. Am. Chem. Soc., 81, 4915 (1959); F. V. Brutcher, Jr., W. Bauer, Jr.: *Ibid.*, 84, 2233, 2236 (1962); and references cited therein.

of signals, the solvent effect was applied to make full interpretation of the spectra. Thus the spectra of I and II were also observed in deuteriochloroform, pyridine, and benzene. As anticipated, the spectral patterns are changed by the solvents, particularly by benzene. The spectra observed in benzene are shown in Figs. 2 (b) and 3 (b). We examine the spectra, dividing them into the four regions; 8.8~9.2 τ (signals due to three methyl groups), 7.3~8.2 τ (signals due to three protons), 9.1~10.2 τ (signals due to two protons), and 8.5~9.0 τ (signals due to two protons).

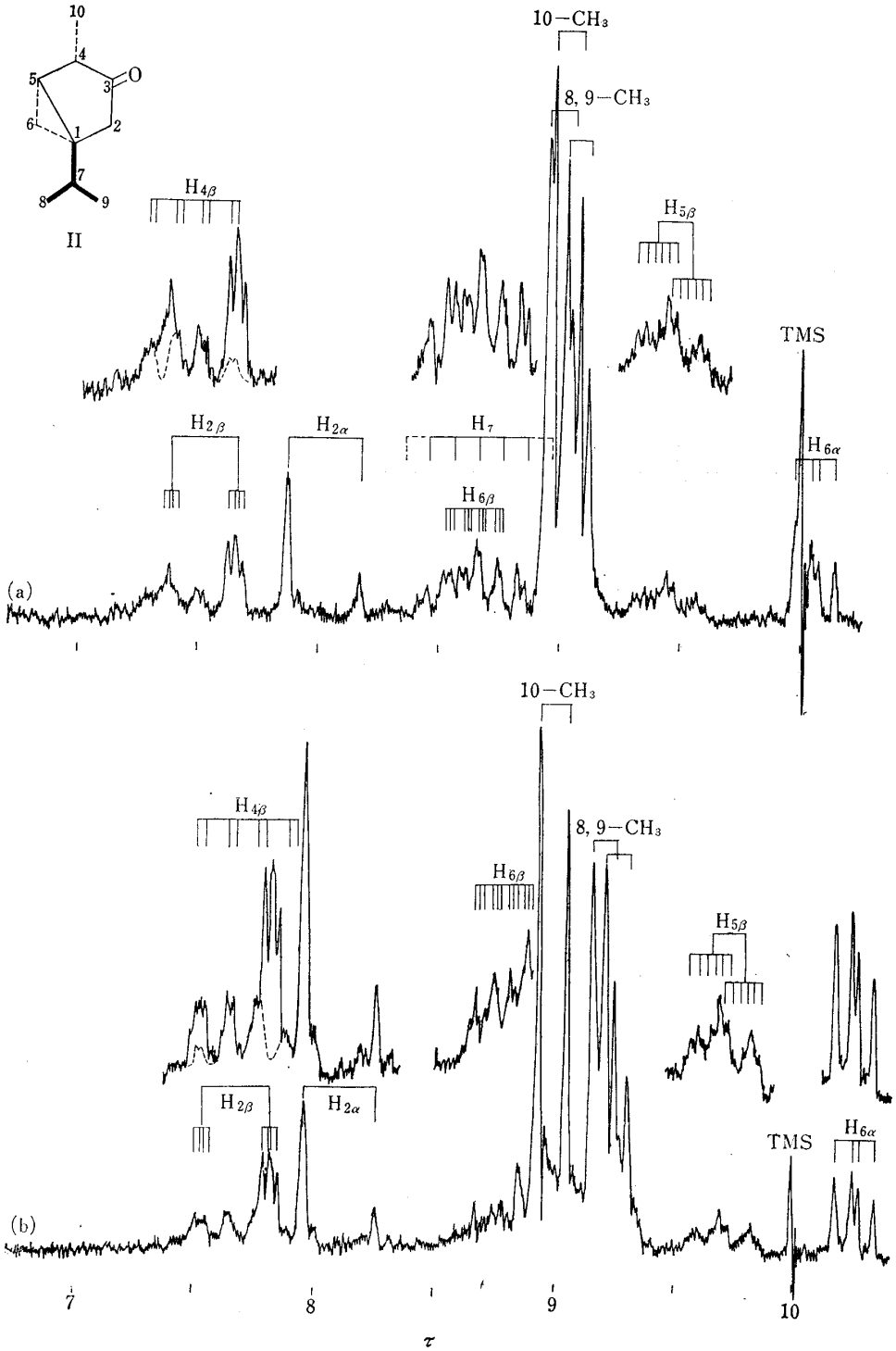
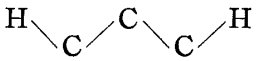


Fig. 3. The Proton Magnetic Resonance Spectra of β-Thujone (II) in Carbon Tetrachloride (a) and in Benzene (b) at 60 Mc.p.s.

Signal peaks of the three methyl groups are expected to appear as a doublet for the 10-methyl group and as a pair of doublets for the magnetically nonequivalent methyl protons in the isopropyl group. Comparison of the spectra in the four solvents made possible the assignment of the methyl peaks as shown in Figs. 2 and 3 and in Table I. The signal peaks corresponding to three protons at the lower-field part of the spectra consist of an AB-type quartet (J=18.5 c.p.s.), each lower field half of which is further split into quartets, and a quartet (J=7.0 c.p.s.) of narrow multiplets, which was disclosed by alteration of the solvent. The latter quartet is assignable to the C_4-proton coupled to the 10-methyl group. Each signal peak arising from the C_4-proton in I are only slightly coupled to other protons, whereas in the spectrum of II this quartet is mainly doubled by the coupling to the $C_{5\beta}$-proton (J=2.0 c.p.s.). This fact is quite useful for estimating the conformations as described later. The AB-type quartet is readily assignable to the C_2-methylene protons, one of which must be coupled to two other protons. Recent NMR studies have frequently revealed the presence of long-range spin couplings through four single bonds.[6] This long-range spin coupling is generally recognized when two protons are of the transoid relationship as shown below :



Inspection of Dreiding models of I and II shows that only three pairs of protons, $H_{2\beta}$-$H_{5\beta}$, $H_{2\beta}$-$H_{6\beta}$, and $H_{4\beta}$-$H_{6\beta}$, are of the above relationship under all considered conformations. Therefore, the two quartets at the lower field can be ascribed to the $C_{2\beta}$-proton.

In general, the magnitude of coupling constants related to protons in alkyl-substituted cyclopropanes is known to be in the order, $J_{cis} > J_{trans} > |J_{gem}|$.[7] Bearing this order and the possible long-range spin couplings of the $C_{5\beta}$- and $C_{6\beta}$-protons mentioned above in mind, we proceed to the assignment of cyclopropyl proton signals. A clear quartet signal of one cyclopropyl proton at an extraordinarily high field can be assigned to the $C_{6\alpha}$-proton from the absence of long-range spin couplings. Thus, the J_{trans} and $|J_{gem}|$ obtained were 5.2 and 4.0 c.p.s., respectively. Another cyclopropyl proton signal in I is fully disclosed in benzene to be a quartet of doublets (9.57 τ), whereas this signal in II appears as a quartet of triplets, as shown in Figs. 2 and 3. The coupling constants obtained from these signals in I were 7.8, 5.1, and 2.1 c.p.s., which correspond to J_{cis}, J_{trans}, and a long-range spin coupling, respectively. This fact implies that the signal is due to the $C_{5\beta}$-proton. The possibility of the long-range spin coupling between the $C_{5\beta}$- and $C_{6\beta}$-protons and the negligible vicinal coupling between the $C_{4\alpha}$- and $C_{5\beta}$-protons supports this assignment. The slight tripling of the quartet in II can arise from the vicinal coupling between the $C_{4\beta}$- and $C_{5\beta}$-protons (J=2.0 c.p.s.) mentioned above and the long-range spin coupling between the $C_{2\beta}$- and $C_{5\beta}$-protons. If the magnitude of J_{trans} and $|J_{gem}|$ were determined reversely, this signal should be assigned to the $C_{6\beta}$-proton. This ambiguity may be excluded by examining the remaining region of the spectra around 8.5~9.0 τ. Signal peaks in this region are expected to arise from the C_7-proton and one cyclopropyl proton. However, the cyclopropyl proton signal in the spectra of I in all the solvents used is obscured by the methyl peaks, and that in the spectra of II overlaps with the C_7-proton signal. Fortunately, only the spectrum of II in benzene shows this cyclopropyl proton signal as a quartet of triplets at 8.78 τ separately, as shown in Fig. 3 (b). The coupling constants were obtained to be 8.0, 4.0, and 1~1.5 c.p.s.

6) D.R. Davis, J.D. Roberts: *Ibid.*, **84**, 2252 (1962); J. Meinwald, A. Lewis: *Ibid.*, **83**, 2769 (1961); J. Meinwald, Y.C. Meinwald: *Ibid.*, **85**, 2514 (1963); J.I. Musher: Mol. Phys., **6**, 94 (1963); D. Gagnaire, E. Payo-Subiza: Bull. soc. chim. France, **1963**, 2627; A. Rassat, C.W. Jefford, J.M. Lehn, B. Waegell: Tetrahedron Letters, No. 5, 233 (1964); K. Tori, Y. Takano, K. Kitahonoki: Chem. Ber., **97**, 2798 (1964).

7) D. J. Patel, M. E. H. Howden, J. D. Roberts : J. Am. Chem. Soc., **85**, 3218 (1963), and references cited therein.

for J_{cis}, $|J_{gem}|$, and the long-range spin couplings, respectively. Clearly, the tripling of this quartet is narrower than that of the quartet at 9.75 τ (in benzene). This fact forces us to assign the former quartet of triplets to the $C_{6\beta}$-proton and the latter to the $C_{5\beta}$-proton, and accordingly, the same assignments can be made for the case of I. Further, the remaining C_7-proton signal can readily be distinguished.

The chemical shifts and the coupling constants thus obtained are listed in Table I. The coupling constants vary scarecely with alteration of the solvent.

Evidence for the Conformations of the Thujones

Only two conformations are possible for bicyclo[3.1.0]hexane system, a chair-like envelope and a boat-like envelope shown in Fig. 1 [(a) and (b), respectively]. An approximate conformational analysis by using Dreiding models for the thujones shows that there are strong 1,3-diaxial interactions between the $C_{2\alpha}$- and $C_{6\alpha}$-hydrogens and the $C_{4\alpha}$-hydrogen or methyl and the $C_{6\alpha}$-hydrogen in the chair-like conformer. Therefore, the boat-like envelope type is preferable for the thujones. However, a probable interaction of the 10-methyl group with the $C_{2\beta}$-hydrogen in I may resist the boat-like conformation.

Recently, Bhacca and Williams[8] have demonstrated in an NMR study that the signal of an axial proton or methyl group on the carbon atom adjacent to a carbonyl group is shifted upfield by the solvent effect of benzene, whereas the signal of an equatorial proton or methyl group moves downfield. This solvent effect probably results from the anisotropic shielding effects of a benzene molecule perpendicularly coordinating to the carbonyl group, and is quite applicable to the present problem. Thus, in Table I are also listed the difference between the chemical shifts in carbon tetrachloride and those in benzene. In the case of I, the solvent effect of benzene shifts the signals of the $C_{2\beta}$- and C_{10}-protons by 0.15 p.p.m. to higher fields, whereas minor upfield shifts are exerted on the $C_{2\alpha}$- and $C_{4\alpha}$-proton signals. Interestingly, considerably larger upfield shifts are observed on the $C_{2\beta}$- and $C_{4\beta}$-proton signals (+0.25 and +0.34 p.p.m., respectively) in the case of II, whereas the $C_{4\alpha}$-methyl signal is hardly shifted by the benzene effect. These facts suggest that the $C_{2\beta}$-hydrogen and the $C_{4\beta}$-hydrogen or methyl group in the molecules of I and II are axially oriented in boat-like envelope conformations, and that the molecule of II is more puckered than the molecule of I, as anticipated above.

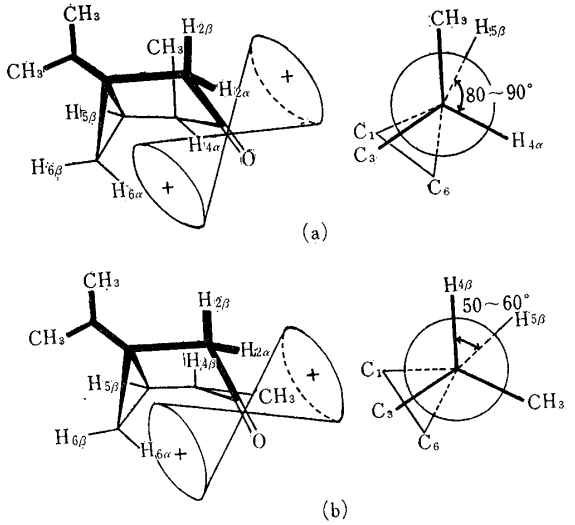


Fig. 4. The Conformations and the Dihedral Angle Views of α-Thujone (I, a) and β-Thujone (II, b)

Although the danger to applications of the well known Karplus equation[9] without any criticism has frequently been pointed out,[10] the angular dependence of the coupling constants between two vicinal protons

8) N. S. Bhacca, D. H. Williams: Tetrahedron Letters, No. 42, 3127 (1964); N. S. Bhacca: private communication.
9) M. Karplus: J. Phys. Chem., **30**, 11 (1959).
10) *Idem*: J. Am. Chem. Soc., **85**, 2870 (1963); R. J. Abraham, J. S. E. Holker: J. Chem. Soc., **1963**, 806; K. L. Williamson: J. Am. Chem. Soc., **85**, 516 (1963); K. Tori, T. Komeno, T. Nakagawa: J. Org. Chem., **29**, 1136 (1964); D. H. Williams, N. S. Bhacca: J. Am. Chem. Soc., **86**, 2742 (1964); R. J. Abraham, K. G. R. Pachler: Mol. Phys., **7**, 165 (1963~4).

is believed to be valid. The dihedral angles between the C_4- and $C_{5\beta}$-protons measured in Dreiding models and the coupling constants calculated by the original Karplus equation[9] are as follows: in I, 95~65° (0.2~1.1 c.p.s.) for the boat-like conformer and 95~125° (0.2~6.1 c.p.s.) for the chair-like one; in II, 30~60° (6.1~1.8 c.p.s.) for the boat-like conformer and 30~0° (6.1~8.2 c.p.s.) for the chair-like one. Therefore, the observed coupling constants between these two protons (about 0 in I and 2.0 c.p.s. in II) also support the estimating conformations,*4 as shown in Fig. 4.

Under these conformations, the appearance of the $C_{6\alpha}$-proton signal at an extraordinarily high field is readily understandable in terms of the anisotropic shielding effect of the C_2-carbonyl group. Furthermore, the more puckered form for II can be justified by the fact that this $C_{6\alpha}$-proton signal appears at a higher field in II than in I.

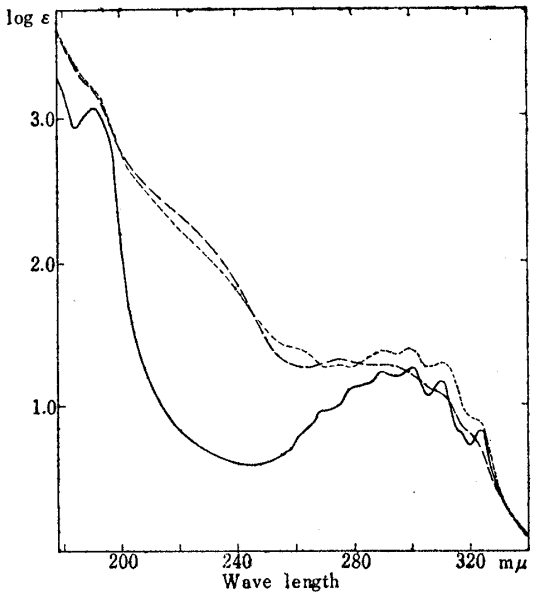


Fig. 5. The Ultraviolet Spectra of Cyclopentanone and the Thujones in Heptane

——— cyclopentanone
– – – – – α-thujone (I)
— — — β-thujone (II)

Other evidence for the boat-like envelope conformation was obtained from ultraviolet absorption spectroscopy. In the boat-like conformer, a weak transannular interaction[11] can be expected between the cyclopropane ring and the carbonyl group. Such interaction can generally be confirmed by the ultraviolet spectra. Fig. 5 shows the spectra of I, II, and cyclopentanone as a reference compound. In the spectra of I and II, a new absorption band at about 220~230 mμ appears and the *R*-band shows a hypsochromic shift, particularly in II. The spectra of cyclopropanes are known to be transparent above 190 mμ.[12] Therefore, the bands at about 220~230 mμ in the spectra of I and II result from the weak conjugation between the cyclopropane ring and the carbonyl group. Furthermore, this absorption band is more intense in II than in I. The both groups are thought to be more strongly conjugated in II. Consequently, the estimated conformations for I and II are also ascertained.

The ORD spectra of I and II are also consistent with the boat-like conformations, as has already been described by Bergqvist and Norin.[3,4]

Experimental

The NMR spectra were taken with a Varian A-60 spectrometer on about 10% (w/v) solutions in carbon tetrachloride, deuteriochloroform (Varian Associates), pyridine (Eastman Kodak Co., Spectro Grade), and benzene containing tetramethylsilane (TMS) as an internal reference. Calibration of the spectrometer was checked by the side-band technique using Hewlett-Packard 200-CD audio ascillator and 521-C frequency counter. Chemical shifts are expressed in τ-values (accuracies, $\pm 0.02\,\tau$) and coupling constants in c.p.s. (accuracies, ± 0.3 c.p.s.). The UV spectra (region 180~350 mμ) were recorded on a Beckman DK-2A ratio recording spectrophotometer by using heptane as the solvent.

α- and β-Thujones are commercially available (Mann Research Laboratories, Inc., New York, N. Y.) and purified by gas chromatography.[13] α-Thujone (I); $[\alpha]_D^{26}$ −15.3° (±2°) (c=1.104, $CHCl_3$); ORD (c=1.100, CH_3OH), $[\phi]_{318}^{trough}$ −795, $[\phi]_{272}^{peak}$ +991, a=−18; UV $\lambda_{max}^{heptane}$ mμ (ε): 291 (23.4), 300 (24.9), 311 (19.2).

11) S. Winstein, L. de Vries, R. Orloski: *Ibid.*, **83**, 2020 (1961), and references cited therein.
12) J. R. Platt, H. B. Klevens: Rev. Mod. Phys., **16**, 182 (1944).
13) I. Ishizuka, K. Okuno, Y. Sato, S. Sumimoto: Ann. Repts. Shionogi Research Lab., **14**, 96 (1964).

β-Thujone (II); $[\alpha]_D^{26.5}$ +68.0 (±2°) (c=1.000, $CHCl_3$); ORD (c=0.636, CH_3OH), $[\phi]_{311}^{peak}$ +1152, $[\phi]_{272}^{trough}$ −431, a=+16; UV: $\lambda_{max}^{heptane}$ 274 mμ (ε 20.5).

The author is very grateful to Dr. K. Takeda, Director of this laboratory, and Dr. H. Minato for their advice and to Dr. T. Nakagawa for his interest on this work. He wishes to thank Dr. S. Sumimoto and coworkers for the gas chromatographic separation of the samples used and also Dr. K. Kuriyama and Mr. M. Yamakawa for their kind measurements of the ORD and UV spectra and helpful discussion.

Summary

Full interpretation of the proton magnetic resonance spectra of α- and β-thujones by using the solvent effect revealed that they take a boat-like envelope conformation. This conclusion was also supported by ultraviolet spectroscopy.

(Received September 7, 1964)

[Chem. Pharm. Bull. 12(12)1446~1451(1964)]

UDC 547.538.2.07

197. Issei Iwai, Tadahiro Iwashige, Yasuo Yura, Norio Nakamura,*1 and Kiyoshi Shinozaki*2 : Studies on Acetylenic Compounds. XXXIX.*3 The Addition Reaction of Cyanogen Bromide to Acetylenic Compounds.

(*Research Laboratories, Sankyo Co., Ltd.*1 and Technical Research Laboratory, Nihon Nyukazai Co., Ltd.*2*)

Addition of cyanogen halide to a double bond has been studied by Cowen and Dixon.[1] They carried out the reaction in the solution of carbon disulfide to obtain β-halonitriles using mixture of aluminum chloride and nitromethane as a catalyst. However, only one paper on the addition of cyanogen halide to a triple bond has been published : Dutcher obtained 3-chloroacrylonitrile by the reaction of cyanogen chloride with acetylene in the presence of cuprous ammonium chloride in the acidic aqueous medium.[2]

It has been known that a triple bond is more active than a double bond as concerns addition reaction of nucleophilic reagents. The difference between these unsaturated bonds is considerably great, especially in the addition reaction. On the other hand, it has been reported that acid chlorides easily adds to a triple bond in the presence of aluminum chloride.[3] Then, cyanogen halide would be expected to add to a triple bond in the similar way.

In this paper authors wish to report the addition reaction of cyanogen bromide to a triple bond activated by an adjacent phenyl group. Phenylacetylene reacted with a mixture of cyanogen bromide and aluminum bromide in tetrachloroethane or in carbon

---

*1 Nishishinagawa, Shinagawa-ku, Tokyo (岩井一成, 岩重忠博, 由良靖雄, 中村紀雄).
*2 Kawasaki-shi, Kanagawa-ken (篠崎 清).
*3 Part XXXVIII : This Bulletin, **12**, 1094 (1964).

1) F. M. Cowen, J. K. Dixon : Brit. Pat., 686,692 (C. A., **48**, 8251 (1953)).
2) H. A. Dutcher : U. S. Pat., 2,419,488 (C. A., **41**, 5145f (1947)).
Recently, it was reported that only *cis*-3-chloroacrylonitrile was obtained by this method. F. Scotti, E. J. Frazza : J. Org. Chem., **29**, 1800 (1964).
3) M. Julia : Ann. chim. (Paris), **5**, 595 (1950); *Idem* : Bull. soc. chim. France, **18**, c 13 (1951); C. C. Price, J. A. Pappalardo : J. Am. Chem. Soc., **72**, 2613 (1950); J. W. Kroeger, F. J. Sowa, J. A. Nieuwland : J. Org. Chem., **1**, 163 (1936).