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Studies of Acenaphthene Derivatives. XX.[1] The Reactions of Benzylideneacenaphthenones with Sulfonium Ylides

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The reactions of benzylideneacenaphthenones with sulfonium ylides were studied extensively. Although the reactions of benzylidene- and *p*-methylbenzylideneacenaphthenone with dimethylsulfonium methylide gave only resinous materials, the *p*-chlorobenzylidene derivative condensed with the ylide to afford the corresponding spiroxirane compound in a good yield. In the reactions with dimethyloxosulfonium methylide and carbonyl-stabilized sulfonium ylides such as ethyl (dimethylsulfuranilidene)acetate and dimethylsulfonium phenacylide, benzylideneacenaphthenones gave the corresponding spirocyclopropyl ketones in good yields. The products obtained in the latter reactions were established to be *cis*-cyclopropyl compounds on the basis of NMR spectral studies. On the other hand, ethoxycarbonylmethyleneacenaphthenone condensed with carbonyl-stabilized sulfonium ylides to give *trans*-cyclopropyl ketones. On the basis of these results, the reaction mechanism was discussed. Also, bis-2,2′-methyleneacenaphthenone reacted with ethyl (dimethylsulfuranilidene)acetate to give the bis-spirocyclopropyl ketone.

From the study of the reactions of benzylideneacenaphthenones (I)[2] with hydrazines[3] and Grignard reagents,[1,4] it has been established that I behaves differently from ordinary α,β-unsaturated ketones such as chalcones, and that the β-carbon atom in I acts as a strong Michael acceptor toward the above reagents. In connection with our current studies of the reactivity of I, we wish to obtain further information concerning the ability of the conjugate addition of I, which are cyclic α,β-unsaturated ketones possessing a cisoid arrangement of the conjugated double bond with the carbonyl group.

Recently, it has been reported that reactive dimethylsulfonium methylide (II) interacts with chalcones to afford oxiranes, while less reactive dimethyloxosulfonium methylide (III) and carbonyl-stabilized sulfonium ylides (IV) such as dimethylsulfonium phenacylide react to give cyclopropyl ketones exclusively.[5-7] However, there have been few investigations of the reactions of cyclic α,β-unsaturated ketones with sulfonium ylides.

In the present work, the reactions of I with sulfonium ylides II—IV were studied in order to prepare spiroxiranes and spirocyclopropanes, and

1) Part XIX: O. Tsuge, I. Shinkai and M. Tashiro, *Kogyo Kagaku Zasshi*, **72**, 1680 (1969).

2) O. Tsuge, M. Tashiro and I. Shinkai, This Bulletin, **42**, 181 (1969).

3) O. Tsuge, I. Shinkai and M. Tashiro, *ibid.*, **42**, 185 (1969).

4) O. Tsuge, I. Shinkai and M. Tashiro, *Tetrahedron Lett.*, **1968**, 3631.

5) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

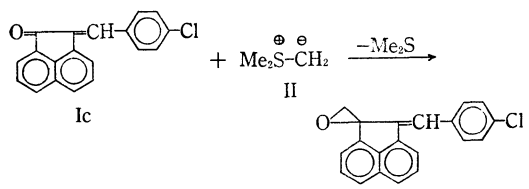
6) H. König, H. Metzger and K. Seelert, *Chem. Ber.*, **98**, 3712 (1965).

7) H. Nozaki, D. Tunemoto, S. Matubara and K. Kondo, *Tetrahedron*, **23**, 545 (1967).

the stereochemistry of the products were investigated on the basis of NMR spectral studies. In addition, the reactions of ethoxycarbonylmethyleneacenaphthenone (V) and bis-2,2′-methyleneacenaphthenone (VI) with sulfonium ylides were studied.

Results and Discussion

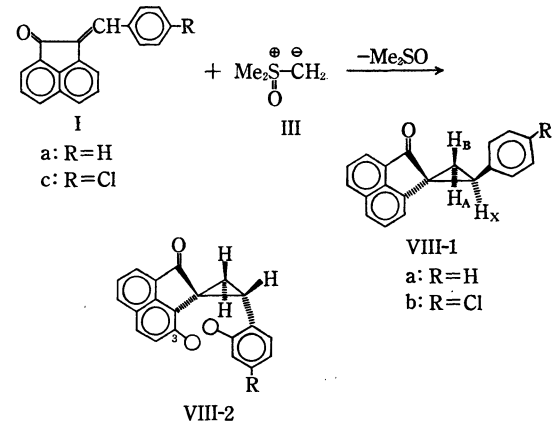
Although the reactions of benzylidene- (Ia) and *p*-methylbenzylideneacenaphthenone (Ib) with II which had been generated *in situ* by the treatment of trimethylsulfonium iodide with potassium *t*-butoxide in dimethylsulfoxide (DMSO) gave only resinous materials, the *p*-chlorobenzylidene analogue (Ic) condensed with II under similar conditions to give the expected spiroxirane (VII), mp 113—114°C (decomp), in an 85% yield. The structure of VII was confirmed by a study of the mass (M^+ *m/e* 304), infrared, and NMR spectra as well as by elemental analysis. The infrared spectrum did not show any bands due to the carbonyl group, while the NMR spectrum in deuterochloroform ($CDCl_3$) exhibited signals at τ 7.60 (2H, methylene-protons, singlet), 3.26 (1H, olefinic proton, singlet), and 2.0—2.9 (10H, aromatic protons, multiplet).



The compound VII was relatively unstable and decomposed on standing at room temperature for a few days. Although it is well known that epoxides rearrange to the corresponding aldehydes upon treatment with boron trifluoride, VII did not give the aldehyde, but only resinous materials.

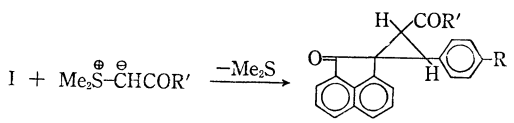
When Ia was allowed to react in tetrahydrofuran (THF) at room temperature with III which had been generated *in situ* from trimethyloxosulfonium chloride and sodium hydride, the expected spirocyclopropyl ketone (VIIIa), mp 118—119°C, was obtained in a 74% yield. Its structure was established by a study of the mass (M^+ *m/e* 270), infrared, and NMR spectra as well as by elemental analysis. The infrared spectrum showed the band ascribed to the carbonyl group at 1705 cm^{-1}, while the NMR spectrum in $CDCl_3$ did not reveal any signals for olefinic protons, but did show a typical ABX pattern for cyclopropyl-protons: double-doublets appeared at τ 6.65 (1H, H_X), 7.70 (1H, H_A) and 7.90 (1H, H_B) with J_{AX} (*cis*)=9.0, J_{BX} (*trans*)=8.7 and J_{AB} (*gem*)=3.3 Hz, and a multiplet at τ 1.8—2.9 (11H, aromatic protons).[8]

A similar reaction of Ic with III gave the spirocyclopropyl analogue (VIIIb), mp 141—142°C, in a 93% yield. Its infrared spectrum showed the carbonyl band at 1691 cm^{-1}, and the NMR spectrum in $CDCl_3$ exhibited double-doublets at τ 6.60 (1H, H_X), 7.71 (1H, H_A) and 7.93 (1H, H_B) with J_{AX} (*cis*)=9.0, J_{BX} (*trans*)=8.4 and J_{AB} (*gem*)=3.5 Hz, and a multiplet at τ 1.8—2.9 (10H, aromatic protons).[8]



Two geometrical isomers resulting from the conformation of the spiro-carbon atom are, then, possible for the structure of VIII: one (VIII-1) in which the phenyl group overlooks the carbonyl group, and the other (VIII-2) in which it sees the acenaphthenone ring.

An inspection of Dreiding models for VIII indicates that the hydrogen atom on the *ortho* position of the phenyl ring interacts with that on the 3-position of the acenaphthenone ring in VIII-2, but does not interact in VIII-1. Consequently,



IV		IX
a: R=H	a: R′=OEt	a: R=H, R′=OEt
b: R=Me	b: R′=Ph	b: R=Me, R′=OEt
c: R=Cl	c: R′=*p*-BrC_6H_4	c: R=Cl, R′=OEt
		d: R=H, R′=Ph
		e: R=H, R′=*p*-BrC_6H_4
		f: R=Cl, R′=Ph

8) J. D. Graham *et al.* observed that the values of $J_{cis}+J_{trans}+J_{gem}$ in 1,1,2-trisubstituted cyclopropanes are virtually constant (about 21 Hz), regardless of the nature of the substituents.[9] The values of $J_{cis}+J_{trans}+J_{gem}$ are 21 and 20.9 Hz in VIIIa and VIIIb respectively. These observations are also in agreement with the structures of 1,1,2-trisubstituted cyclopropane derivatives proposed for VIIIa and VIIIb.

9) J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962).

Table 1. *cis*-Spirocyclopropyl ketones (IX)

IX	R	R'	Yield (%)	Appearance[1]	Mp (°C)	Formula	Analysis (%) Found (Calcd) C	H	Mol wt (*m/e*)
a	H	OEt	77	colorless needles	150—151	$C_{23}H_{18}O_3$	80.87 (80.68)	5.15 (5.30)	342
b	Me	OEt	62	colorless prisms	140.5	$C_{24}H_{20}O_3$	81.08 (80.88)	5.29 (5.66)	356
c	Cl	OEt	57	colorless prisms	144—145	$C_{23}H_{17}O_3Cl$	73.57 (73.40)	4.26 (4.52)	376
d	H	Ph	82	colorless needles	168—169	$C_{27}H_{18}O_2$	86.81 (86.61)	4.71 (4.85)	374
e	H	*p*-BrC_6H_4	81	colorless grains	155—156	$C_{27}H_{17}O_2Br$	71.62 (71.52)	3.37 (3.75)	453
f	Cl	Ph	55	colorless prisms	157—158	$C_{27}H_{17}O_2Cl$	79.37 (79.41)	4.07 (4.12)	408

1) Recrystallized from methanol.

it may be deduced that VIII-1 is a more favorable configuration than that of VIII-2.

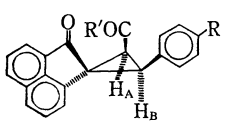
The treatment of Ia with ethyl (dimethylsulfuranilidene)acetate (IVa) which had been generated *in situ* from the corresponding sulfonium bromide and sodium hydride in THF gave the spirocyclopropyl ketone (IXa). Similar reactions of I with carbonyl-stabilized sulfonium ylides (IVa—IVc) gave the corresponding spirocyclopropyl ketones (IXb—IXf).

The yields, physical properties, elemental analyses, and spectral data are summarized in Tables 1 and 2.

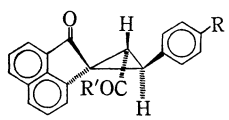
Table 2. Infrared and NMR data of IX[1]

IX	H_A (τ)	H_B (τ)	J_{AB} (Hz)	$\nu_{C=O}$ (cm^{-1})	
a	6.43	5.99	9.0	1712	1732
b	6.50	6.16	8.9	1705	1728
c	6.05	5.76	9.0	1715	1729
d	5.65	5.44	8.7	1675	1712
e	5.71	5.54	9.0	1675	1710
f	5.75	5.53	8.4	1670	1712

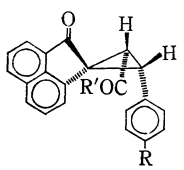
1) NMR spectra were measured in $CDCl_3$.



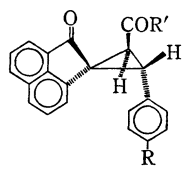
IX-1 (*cis*)



IX-2 (*trans*)



IX-3 (*cis*)



IX-4 (*trans*)

As a result of the conformation of the spiro-carbon atom and the *cis-trans* configuration of hydrogens in the cyclopropyl ring of IX, the following four isomers (IX-1—IX-4) are possible for the structure of IX.

As is illustrated in Fig. 1, the NMR spectrum of IXa in $CDCl_3$ exhibits peaks at τ 8.76 (3H, methyl-protons, triplet) 6.43 (1H, H_A, doublet), 5.99 (1H, H_B, doublet) (J_{AB}=9.0 Hz), and 5.75 (2H, methylene-protons, quartet), besides aromatic protons.

It is well known that *cis*-cyclopropanes exhibit higher coupling constants (8—10,[10] 7.9—9.3 Hz[9]) than those (4—7,[10] 5.3—6.6 Hz[9]) of the corresponding *trans* isomers.

As is shown in Table 2, the vicinal coupling constants (J_{AB}=8.4—9.0 Hz) of IX correspond to those of *cis*-cyclopropanes. In addition, the configurations, IX-3 and IX-4, in which the phenyl group sees the acenaphthenone ring may be disregarded as unreasonable because of the steric hindrance mentioned in the case of VIII-2.

Consequently, it may be deduced that the most reasonable structure for IX is the configuration IX-1, in which H_A and H_B are situated *cis*, and in which the phenyl group overlooks the carbonyl group in acenaphthenone. As will be described below, this conclusion is also supported by the fact that the shielding effect of the acenaphthenone ring does not exert any effect on the methyl resonance of the ethoxycarbonyl group in the respective NMR spectrum of IXa, IXb, or IXc.

The fragmentation on electron impact was compatible with the proposed structure for IX. For example, the mass spectrum of IXa shows peaks at *m/e* 342 (M^+), 298 ([M–MeCHO]$^+$), 270

10) K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, **85**, 2788 (1963).
11) B. M. Trost, *ibid.*, **89**, 138 (1967).
12) G. B. Payne, *J. Org. Chem.*, **32**, 3351 (1967).

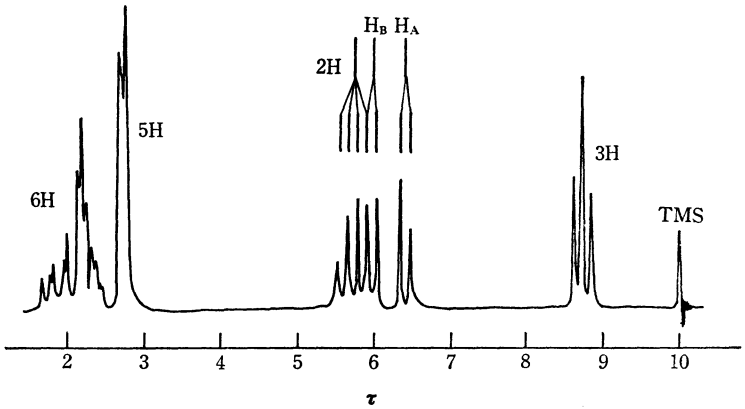


Fig. 1. NMR spectrum of IXa in $CDCl_3$.

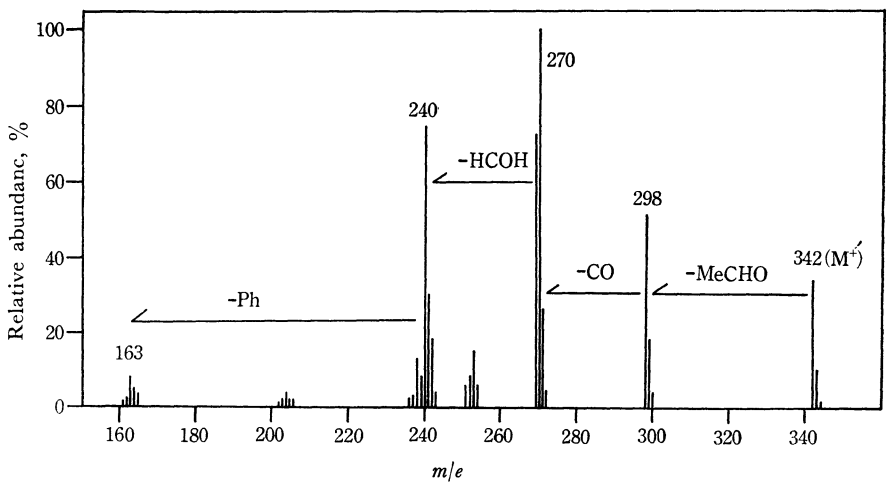
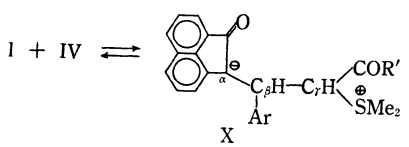


Fig. 2. Mass spectrum of IXa.

([298-CO]$^+$), 240 ([270-CH_2O]$^+$), and 163 ([240-Ph]$^+$), as is shown in Fig. 2.

It has been reported that dimethylsulfonium phenacylide (IVb) condensed with chalcone to afford a mixture of *cis*- and *trans*-cyclopropane in the ratio of 1 : 2.[11] Also, Payne[12] found that the corresponding *trans*-cyclopropanes were obtained predominantly in the reactions of IVa with α,β-unsaturated carbonyl compounds, such as acrolein and mesityl oxide.



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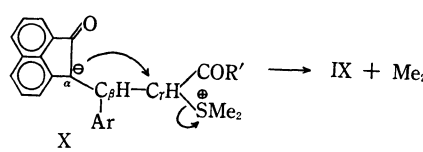


(2)

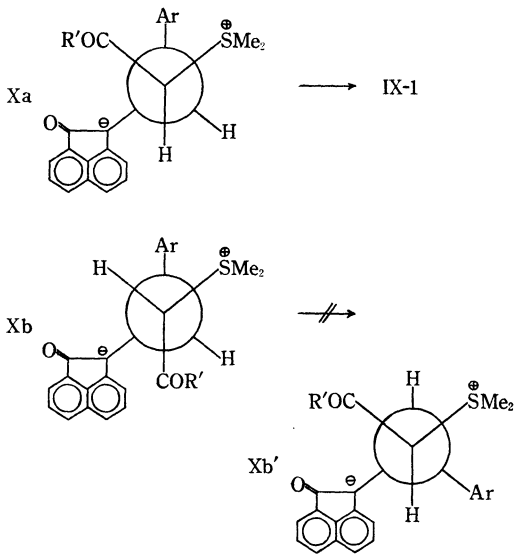
Although the exact course of the reaction of I with IV is not clear, it is thought to consist of step 1, a reversible nucleophilic attack by the ylide carbanion on the β-carbon atom in I to form a betain intermediate X, followed by step 2, an irreversible intramolecular ring closure with the *trans*-elimination of dimethyl sulfide.

As is shown in Table 1, all the reactions of I with IV gave the corresponding *cis*-cyclopropyl ketones exclusively. The relative amounts of *cis*-(IX-1) and *trans*-cyclopropyl ketone (IX-2) must be reflected by the relative energies of the *threo*-precursor (Xa) of IX-1 and the *erythro*-precursor (Xb) of IX-2; the betains which are precursors of IX-3 and IX-4 are excluded from our discussion.[13]

The Newman projections clearly indicate that Xa is a more unfavorable conformation than Xb, because the four bulky groups in Xa are in a *gauche* position relative to each other.

13) In this paper, the prefixes of *threo* and *erythro* are used assuming that the substituent COR' is larger than SMe_2.

However, an inspection of the Dreiding models indicates that the free rotation of the C_α-C_β bond in Xb to form Xb′ is hindered by the steric interaction between the acenaphthenone ring and the phenyl group, and that, in an intramolecular ring closure with a backside attack of the carbanion on the γ-carbon atom (step 2), there is a significant repulsion between the substituent COR′ and the acenaphthenone ring in Xb.



Accordingly, it will be very difficult for the ring-closure reaction of Xb to IX-2 to take place and Xb will return to the starting materials, I and IV. These situations result in the stereoselective formation of the *cis*-cyclopropyl ketone IX-1 from the precursor Xa.

If the free rotation of the C_α-C_β bond in a betain were possible, one might expect the formation of the *trans*-cyclopropyl ketone from the *erythro*-betain in a lower energy. In order to make this point clear, the reactions of two isomeric ethoxycarbonylmethyleneacenaphthenone, V[2] and V′[2], which have an ethoxycarbonyl group in place of a phenyl group in I, with sulfonium ylides were investigated.

The reaction of V, whose ethoxycarbonyl group overlooks the carbonyl group in acenaphthenone, with IVa afforded the expected *trans*-spirocyclopropyl ketone (XI), mp 110—111°C, in a good yield. In order to confirm whether or not the conformation of the ethoxycarbonyl group in V is maintained in XI, the reaction of the isomer V′, in which the ethoxycarbonyl group sees the acenaphthenone ring, with IVa was carried out; the same product, XI, was thus obtained in an excellent yield. This shows that the free rotation of the C_α-C_β bond in a betain takes place, as was expected.

The structure of XI was confirmed by the infrared, mass, and NMR spectra as well as by the results of the elemental analyses.

As is shown in Fig. 3, the NMR spectrum of XI in $CDCl_3$ exhibits signals at τ 8.82, 8.75 (each 3H, methyl-protons, triplet, J=4.2 Hz), 6.56 (2H, methine-protons H_A and H_B), 5.84, 5.77 (each 2H, methylene-protons, quartet, J=4.2 Hz), 1.8—2.5 (6H, aromatic protons). The vicinal coupling constant is very small ($J \fallingdotseq 0$); this indicates that H_A and H_B are situated *trans*. Furthermore, it is clear that the two ethoxycarbonyl groups in XI are in an unequivalent situation. This phenomenon can be understood in terms of the shielding effect of the acenaphthenone ring in

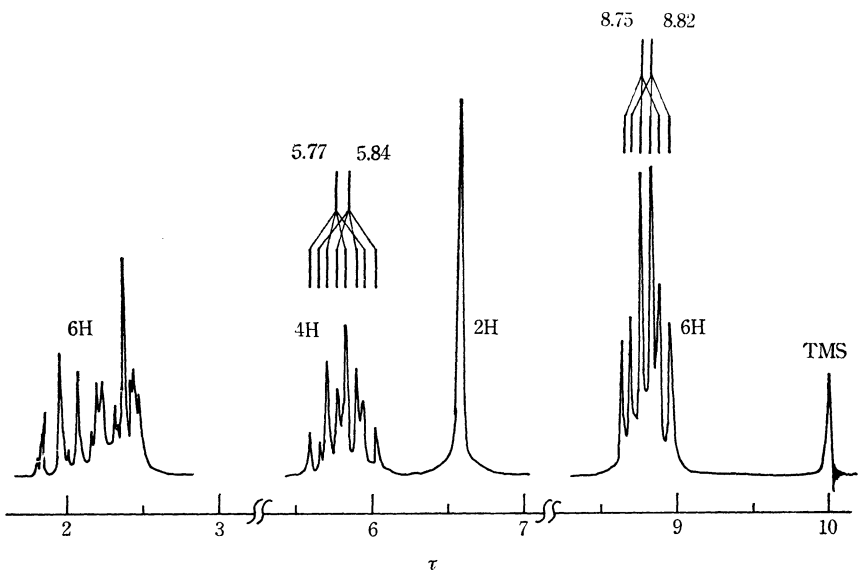


Fig. 3. NMR spectrum of XI in $CDCl_3$.

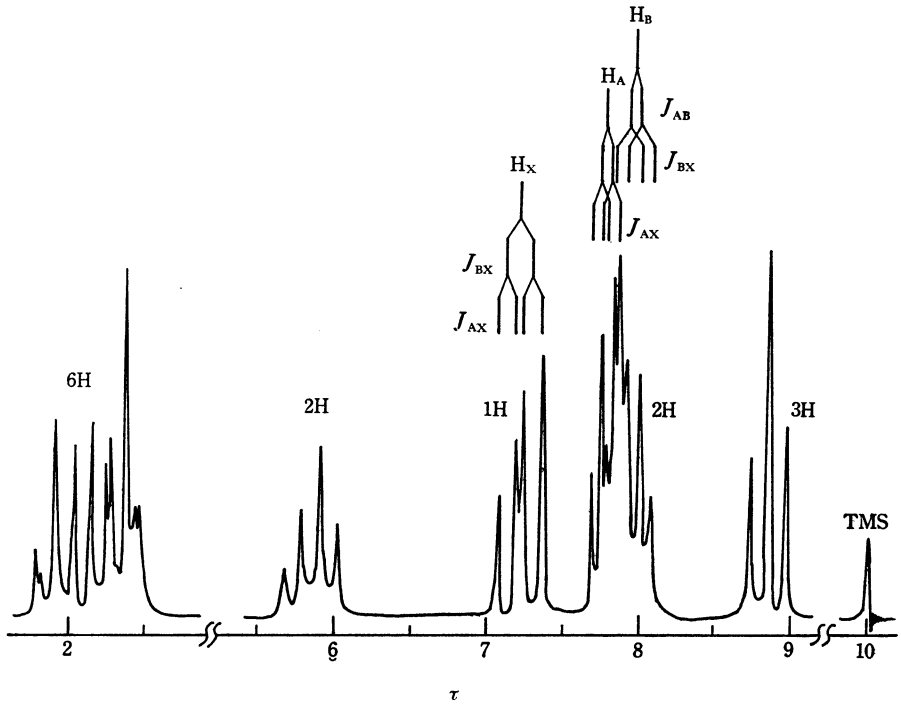


Fig. 4. NMR spectrum of XII in $CDCl_3$.

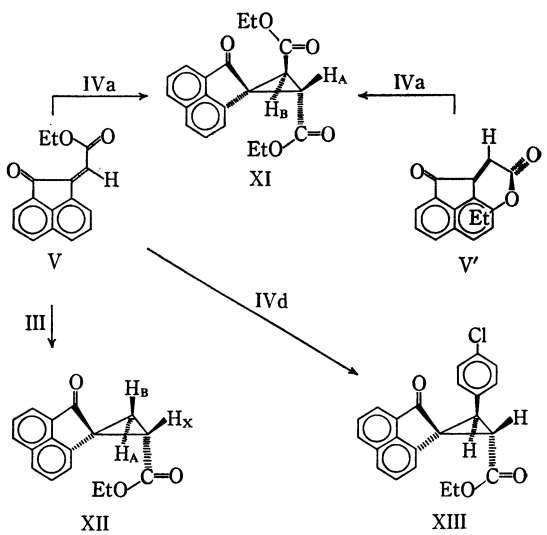
XI: one (methyl at τ 8.82) sees the acenaphthenone ring, and the other (methyl at τ 8.75) overlooks the carbonyl group in acenaphthenone.

Similar reactions of V with III and dimethylsulfonium *p*-chlorophenacylide (IVd) afforded spirocyclopropyl ketones, XII (mp 74—75°C) and XIII (mp 147—148°C) respectively. The structures for XII and XIII were established by spectral studies as well as by elemental analyses.

The NMR spectrum of XII in $CDCl_3$ is illustrated in Fig. 4. Signals appear at τ 8.82 (3H, methyl-protons, triplet), 5.86 (2H, methylene-protons, quartet), and 1.8—2.5 (6H, aromatic protons), besides a typical ABX pattern for cyclopropylprotons at τ 7.25 (1H, H_X), 7.75 (1H, H_A), and 7.95 (1H, H_B) with J_{AX} (*trans*)=6.5, J_{BX} (*cis*)=9.9 and J_{AB} (*gem*)=4.5 Hz. On the basis of the above observations, XII can be said to be consistent with the cyclopropyl ketone, in which the ethoxycarbonyl group sees acenaphthenone ring.[14]

On the other hand, the NMR spectrum of XIII in $CDCl_3$ showed signals at τ 8.81 (3H, methyl-protons, triplet), 6.25 and 6.17 (each 1H, methine-proton, doublet, J=5.8 Hz), 5.84 (2H, methylene-protons, quartet) and a lower field (10H, aromatic protons); XIII is compatible with the *trans*-cyclopropyl ketone, in which the ethoxycarbonyl group sees the acenaphthenone ring.

The original conformation of the ethoxycarbonyl group in V is not maintained in either XII or XIII.



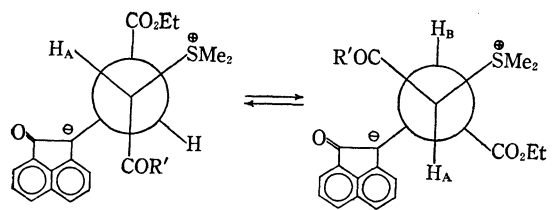
The methyl-protons signals of ethoxycarbonyl groups in IXa, IXb, and IXc appeared at τ 8.76, 8.75 and 8.77 respectively in the NMR spectra.

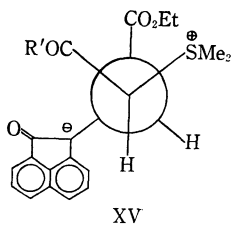
14) The value of $J_{cis}+J_{trans}+J_{gem}$ is 20.9 Hz.[8] In the reaction of diazoacenaphthenone with ethyl acrylate in refluxing benzene, XII and the isomeric spirocyclopropyl ketone in which the ethoxycarbonyl group overlooks the carbonyl group in acenaphthenone were obtained; these results will be reported shortly in more detail.

No ethoxycarbonyl group in IX is affected by the shielding effect of the acenaphthenone ring, but each overlooks the carbonyl group in acenaphthenone. This fact indicates that IX is compatible with the proposed structure, IX-1.

The formation of the *trans*-cyclopropyl ketone in the reaction of V with IV can, then, be understood in terms of the following considerations.

As has been pointed out in the discussion of the formation of IX, it must be determined by the relative energies of *erythro*- (XIV) and *threo*-betain (XV) which isomer, the *trans* or the *cis*, is formed predominantly in the reaction of V with IV.[13] The Newman projections indicate that the precursor, XIV, of the *trans*-isomer is a more favorable conformation than the precursor, XV, of the *cis*-isomer.

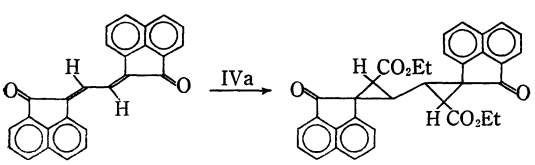




The exclusive formation of the *cis*-cyclopropyl ketone IX-1 in the reaction of I with IV may be attributed to the fact that the transformation of *erythro*-betain Xb to the *trans*-isomer IX-2 can not occur because of the steric repulsion between the acenaphthenone ring and COR′ at the step 2, but Xb reverts to the starting materials.

Contrary to the case of Xb, it becomes feasible of the C_α- C_β bond in XIV to rotate, as is shown by the fact that the reactions of both V and V′ with IVa gave the same product, XI. That is, XIV can convert to XIV′, in which the steric repulsion between the acenaphthenone ring and COR′ is absent in the ring-closure reaction.

Thus, the above situation leads to the formation of the *trans*-cyclopropyl ketone, whose ethoxycarbonyl group does not retain the original conformation in V, from the preferred betain, XIV′.



VI XVI

The reaction of bis-2,2′-methyleneacenaphthenone (VI)[2] with IVa afforded the bis-spirocyclopropyl ketone (XVI), mp 225°C (decomp), in a 57% yield. However, the stereochemistry of XVI is not yet clear.

Experimental

All the melting points are uncorrected. The infrared spectra were measured in KBr disks, while the NMR spectra were recorded on a 60 MHz Hitachi R-20 NMR spectrometer, using TMS as an internal reference. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer, using a direct inlet and an ionization energy of 70 eV.

Benzylideneacenaphthenones (I), ethoxycarbonylmethyleneacenaphthenone (V), and bis-2,2′-methyleneacenaphthenone (VI) were prepared by a previously-reported method.[2]

Trimethylsulfonium iodide,[5] trimethyloxosulfonium chloride[5] dimethylethoxycarbonylmethyl-,[15] dimethylphenacyl-[15], dimethyl-*p*-bromo-,[15] and -*p*-chlorophenacylsulfonium bromides[16] were prepared by methods described in the literature.

The Reaction of *p*-Chlorobenzylideneacenaphthenone (Ic) with Dimethylsulfonium Methylide (II). A solution of the ylide II was prepared by stirring a mixture of trimethylsulfonium iodide (1.0 g), potassium *t*-butoxide (0.56 g), and DMSO (20 m*l*) for 25 min under a nitrogen atmosphere. A solution of Ic (350 mg) in DMSO (10 m*l*) was then slowly added, drop by drop, to the solution of II, and the reaction mixture was stirred at room temperature for 1 hr. After the mixture had been poured into 15 m*l* of cold water, yellow crystals were collected by filtration, washed with water, and dried. Yield, 310 mg (85%). Recrystallization from petroleum benzine (bp 40—65°C) gave spiroxirane (VII), mp 113—114°C (decomp), as yellow needles.

Found: C, 78.60; H, 4.00%. Calcd for $C_{20}H_{13}OCl$: C, 78.95; H, 4.28%.

Similar reactions of benzylidene- (Ia) and *p*-methylbenzylideneacenaphthenone (Ib) with the ylide II gave only resinous materials.

The Reaction of Ic with Dimethyloxosulfonium Methylide (III). A solution of the ylide III was prepared by refluxing a mixture of trimethyloxosulfonium chloride (450 mg), sodium hydride (200 mg) as a 50% mineral oil dispersion, and THF (20 m*l*) for 3.5 hr under a nitrogen atmosphere. To a stirred solution of Ic (1.0 g) in THF (15 m*l*) was then slowly added, drop by drop, the solution of the ylide III at 0°C, after which the reaction mixture was stirred at room temperature for 2 hr. After the mixture had been concentrated *in vacuo*, methanol (10 m*l*) was added to the residue and the mixture was allowed to stand at room temperature for several hours, thus giving 974 mg (93%) of colorless crystals. Recrystallization from methanol gave the spirocyclopropyl ketone (VIIIb), mp 141—142°C, as colorless needles.

Found: C, 78.80; H, 4.19%. Calcd for $C_{20}H_{13}$-

15) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).

16) K. W. Ratts and A. N. Yao, *ibid.*, **33**, 70 (1968).

OCl: C, 78.95; H, 4.28%. M^+: *m/e* 304.

A similar reaction of Ia with III afforded the spirocyclopropyl ketone (VIIIa), mp 118—119°C, as colorless prisms (from methanol). Yield, 74%.

Found: C, 88.55; H, 5.06%. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22%.

The Reaction of I with the Carbonyl-stabilized Sulfonium Ylide (IV). The procedure used is illustrated with the reaction of Ia with ethyl (dimethylsulfuranilidene)acetate (IVa).

A solution of the ylide IVa was prepared by the following procedure. To a stirred suspension of dimethylethoxy-carbonylmethylsulfonium bromide (1.2 g) in THF (10 m*l*), sodium hydride (0.3 g) was added as a 50% mineral oil dispersion in one portion. After the mixture had then been stirred at room temperature for 3 hr, it was filtered to remove the sodium bromide, thus giving a yellow solution of IVa.

After the solution of IVa had been added to a solution of Ia (1.2 g) in THF (10 m*l*) at 0°C, the reaction mixture was stirred at room temperature for 12 hr and then at 70—80°C for 30 min. The mixture was concentrated *in vacuo*, and methanol (10 m*l*) was added to the residue. It was then allowed to stand at room temperature for several hours, giving 1.23 g (77%) of colorless crystals, mp 148—150°C. Recrystallization from methanol afforded the *cis*-spirocyclopropyl ketone (IXa) as colorless needles.

Similar reactions of Ia Ib, and Ic with IVa, dimethylsulfonium phenacylide (IVb), and dimethylsulfonium *p*-bromophenacylide (IVc) gave the corresponding *cis*-spirocyclopropyl ketones (IX-IXf).

The yields, physical properties, spectral data, and elemental analyses are summarized in Tables 1 and 2.

The Reaction of Ethoxycarbonylmethyleneacenaphthenone (V) with the Ylide IVa. A solution of the ylide IVa, prepared from the corresponding sulfonium bromide (250 mg) and sodium hydride (65 mg) as a 50% mineral oil dispersion in THF (15 m*l*), was slowly added to a solution of V (250 mg) in THF (10 m*l*) at 0°C, and then the reaction mixture was stirred at room temperature for 3.5 hr. After the mixture had been concentrated *in vacuo* to leave a residue, the addition of methanol (10 m*l*) to the residue gave 290 mg (88%) of colorless crystals. Recrystallization from methanol gave the *trans*-spirocyclopropyl ketone (XI), mp 110—111°C, as colorless prisms.

Found: C, 71.29; H, 5.27%. Calcd for $C_{20}H_{18}O_5$: C, 70.99; H, 5.36%. M^+: *m/e* 338. IR: $\nu_{C=O}$ 1735, 1724 and 1712 cm^{-1}.

The same spirocyclopropyl ketone, XI, was obtained in a 90% yield from a similar reaction of isomeric ethoxycarbonylmethyleneacenaphthenone (V′) with the ylide IVa.

The Reaction of V with the Ylide III. To a solution of V (250 mg) in THF (5 m*l*) added a solution of the ylide III, prepared from the corresponding sulfonium chloride (250 mg) and sodium hydride (90 mg) as a 50% mineral oil dispersion in THF (10 m*l*); the reaction mixture was then stirred at room temperature for 20 hr, and then at 70—80°C for 10 min. After the mixture had been concentrated *in vacuo*, petroleum ether (10 m*l*) was added to the residue, giving 145 mg (54%) of colorless crystals. Recrystallization from petroleum ether gave the spirocyclopropyl ketone (XII), mp 74—75°C, as colorless prisms.

Found: C, 76.78; H, 5.04%. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30%. M^+: *m/e* 266. IR: $\nu_{C=O}$ 1708 cm^{-1}.

The Reaction of V with Dimethylsulfonium *p*-Chlorophenacylide (IVd). A solution of the ylide IVd, prepared from the corresponding sulfonium bromide (310 mg) and sodium hydride (60 mg) as a 50% mineral oil dispersion in THF (15 m*l*), was added to a solution of V (250 mg) in THF (10 m*l*) at 0°C. After the reaction mixture had been stirred at room temperature for 3 hr and then at 70—80°C for 30 min, the mixture was concentrated *in vacuo* to leave a residue. To the residue then added methanol (10 m*l*), giving 230 mg (57%) of colorless crystals. Recrystallization from methanol afforded the *trans*-spirocyclopropyl ketone (XIII), mp 147—148°C, as colorless prisms.

Found: C, 71.43; H, 3.79%. Calcd for $C_{24}H_{17}O_4Cl$: C, 71.29; H, 4.21%. M^+: *m/e* 404. IR: $\nu_{C=O}$ 1730, 1710 and 1675 cm^{-1}.

The Reaction of Bis-2,2′-methyleneacenaphthenone (VI) with the Ylide IVa. After a solution of the ylide IVa, prepared from the corresponding sulfonium bromide (300 mg) and sodium hydride (75 mg) as a 50% mineral oil dispersion in THF (15 m*l*), was added to a solution of VI (180 mg) in THF (10 m*l*), the reaction mixture was stirred at room temperature for 3 hr and then at 70—80°C for an additional hour. The mixture was concentrated *in vacuo* to give a residue, to which methanol was then added, giving 150 mg (57%) of colorless crystals. Recrystallization from petroleum benzine afforded the *bis*-spirocyclopropyl ketone (XVI), mp 225°C (decomp), as colorless prisms.

Found: C, 76.99; H, 5.01%. Calcd for $C_{34}H_{26}O_6$: C, 76.97; H, 4.94%. M^+: *m/e* 530. IR: $\nu_{C=O}$ 1730 and 1710 cm^{-1}.