The Acid-catalyzed Reaction of the 2-Oxabicyclo[4.1.0]hept-3-en-5-one System: Isomerization from Homo-4-pyrones into 2-Furylacetone Derivatives

Hiroshi YAMAOKA, Ikuhiro MISHIMA, Mitsuko MIYAMOTO, and Terukiyo HANAFUSA*

Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-senda-machi, Hiroshima 730

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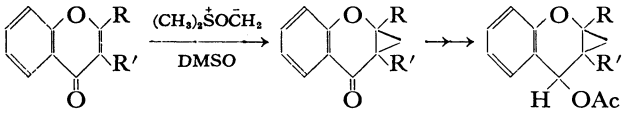
The monocyclopropanation of 4-pyrones with dimethyloxosulfonium methylide, using a dimethyl sulfoxide–hexamethylphosphoric triamide medium in place of neat dimethyl sulfoxide, gave homo-4-pyrone derivatives, which were then rearranged into the 2-furylacetone derivatives, along with hydrated triketones or the dehydrated naphtho[2,1-*b*]furan derivative, by means of strong acid catalysis at room temperature.

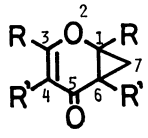
In 1965 Corey *et al.* reported that dimethyloxosulfonium methylide is a convenient reagent for preparing cyclopropyl ketones starting from the corresponding α,β-unsaturated ketones.[1] Thus, the treatment of chromones (**1**), regarded as α,β-unsaturated carbonyl compounds, with the above ylide in dimethyl sulfoxide (DMSO), which has been preferentially used in cyclopropanation,[2] affords 3,4-benzo-2-oxabicyclo[4.1.0]-hept-3-en-5-one(homochromone) derivatives (**2**).[3,4] We have been investigating their mass spectra[5] and the solvolytic behavior of the corresponding secondary ester, **3**,[3] in connection with homoconjugation or homoaromaticity, two of the most interesting concepts in organic chemistry.[6]



	R	R′
1a	CH_3	CH_3
1b	$-(CH_2)_3-$	

	R	R′	
2a	CH_3	CH_3	
2b	$-(CH_2)_3-$		
			3

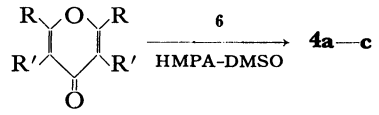
The parent 2-oxabicyclo[4.1.0]hept-3-en-5-one (homo-4-pyrone) (**4**), free from a condensed benzene ring, may be one of the best substrates for use in order to procure further information about the structural characteristics of homochromones **2**. As homo-4-pyrones have not been mentioned to date, we now wish to report the preparation and the acid-catalyzed reactions of **4**.



	R	R′
4a	CH_3	Ph
4b	CH_3	CH_3
4c	CH_3	H

Results and Discussion

Syntheses. Cyclopropanation of 4-Pyrones: According to the previously reported manner, 2,6-dimethyl-3,5-diphenyl- (**5a**), 2,3,5,6-tetramethyl- (**5b**), and 2,6-dimethyl-4-pyrone (**5c**) were prepared.[7] While the treatment of benzo-condensed 4-pyrones, **1**, with dimethyloxosulfonium methylide (**6**) for several hours gave cyclopropyl ketones (homochromones), **2**, in a fairly good yield,[3,4,8] the choice of solvent was found to be critical for the reaction when parent 4-pyrones, **5a**—**5c**, free from a condensed benzene ring, were subjected to cyclopropanation. As is shown in Table 1, tetramethyl-4-pyrone (**5b**), corresponding to the benzo-condensed compound **1a**, was intact after having been in contact with **6** in DMSO at 60 °C for many hours. When the reaction was carried out in mixtures of hexamethylphosphoric triamide (HMPA) and DMSO (1 : 1 by volume), time studies of aliquots by means of either NMR or TLC exhibited the formation of homo-4-pyrone, **4**. A change in the HMPA/DMSO ratios brought about no appreciable alterations in the yields of **4** within the region from 0.3 to 3.0, although DMSO was essential for the generation of **6** *in situ* because no evolution of hydrogen accompanied by the formation



	R	R′
5a	CH_3	Ph
5b	CH_3	CH_3
5c	CH_3	H

TABLE 1. ENTRY FOR CYCLOPROPANATION FROM 4-PYRONES WITH **6**

Run	Pyrone	Ylide **6** (mol)	Solvent[a]	Temperature (time)	Product (yield/%)	Ref.
1	**1a**	1.1	D	r. t. (0.5 h)	**2a** (28)	4
2	**1a**	1.1	D	r. t. (2 h)	**2a** (90)	8
3	**1b**	1.1	D	r. t. (2.5 h)	**2b** (70)	3
4	**5a**	2.5	H–D (1 : 1)	40 °C (6 h)	**4a** (53)[c]	b)
5	**5b**	Excess(>4)	D	60 °C (2 d)	No reaction	b)
6	**5b**	Excess[d]	H–D (1 : 1)	40 °C (4 d)	**4b** (40)	b)
7	**5c**	2.5	H–D (1 : 1)	40 °C (1 h)	**4c** (15)	b)
8	**4a**	2.5	H–D (1 : 1)	40 °C (1 d)	No reaction	b)

a) D: DMSO, H: HMPA. b) Present work. c) 15% Recovery of **5**. d) Additional **6** was necessary in order to promote the formation of **4b** at several-hour intervals.

of **6**[1] occurred when neat HMPA was chosen as the reaction medium.

The purification of the crude product was done by means of column chromatography on either deactivated neutral alumina or silica gel, using ether–light petroleum as the eluent. Thus, the diphenyl derivative **4a** was isolated as colorless prisms (mp 101—102 °C), while both **4b** and **4c** were less stable. Therefore, the structural assignments of the latter compounds may be elucidated by a comparison of the spectral data with those of **4a**.

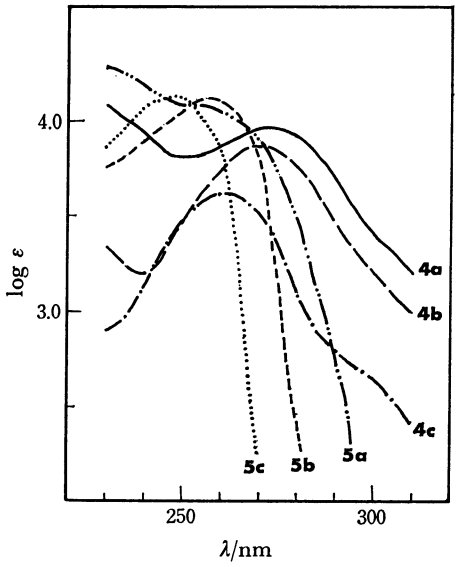


Fig. 1. UV spectra of **4a**—**c** and **5a**—**c** in methanol.

The UV spectra of **4a**—**4c** are shown in Fig. 1, along with those of the corresponding 4-pyrones, **5a**—**5c**. The change in the wave numbers for maximum absorption ($\nu_{C=O}$) according to the variation in the properties of the carbonyl function from **5** to **4** was not so remarkable as that in the benzo-condensed compounds, **2**.[3] Unlike the ambiguous information given concerning the production of cyclopropyl ketones, the mass spectra indicated an expulsion of the CHO radical from the molecular ion, M−29, which has been found to be a characteristic fragmentation in homochromones, **2**,[5] as well as in the parent ion (M^+) (see Table 2).

Table 2. Data of the mass spectra of homo-4-pyrones **4**

Compd	M^+(*m/e*)	M−15	M−28	M−29[b]	M−43
4a	290(100)[a]	275(28)	262(20)	261(15)	247(40)
4b	166(100)	151(73)	138(4)	137(18)	123(68)
4c	138(100)	123(13)	110(8)	109(19)	95(65)

a) Relative intensity. b) Expulsion of the CHO radical.

In the NMR spectrum of **4a**, protons belonging to the cyclopropane were not obvious because of the duplication with the signal of a methyl group (δ, 1.80), but a typical AB quartet (J=6 Hz) peculiar to cyclopropyl methylene protons (δ, 1.56 and 1.82) was revealed by the treatment of **4a** with alkaline 1,2-dimethoxyethane (DME)–D_2O, in analogy with that of 2,3-dimethylchromone (**1a**), which could be deuterated at the 2-methyl group, in the β-position to the α,β-unsaturated carbonyl group, to give **1a'** in our preliminary experiment. 4-Pyrone **5a** could be converted into 2,6-bis(trideuteriomethyl)-3,5-diphenyl-4-pyrone (**5a'**) under the same conditions. However, no deuterium exchange took place in the case of the homochromone **2a**. Taking these results into account, it seems that trideuteriomethylation on **4a** cannot proceed on the methyl group attached to cyclopropane (the C-1 position at δ, 1.28), while it can on the other methyl group (δ, 1.80 for the 3-methyl group adjacent to β-carbon for the α,β-unsaturated carbonyl function). The experimental results agreed exactly with this expectation, and the chemical shifts of all the aliphatic protons suggested a monocyclopropyl ketone, **4a'**, in comparison with those of related compounds, as is shown below.

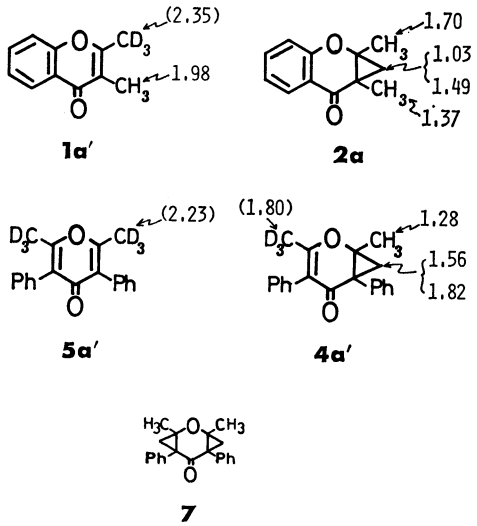


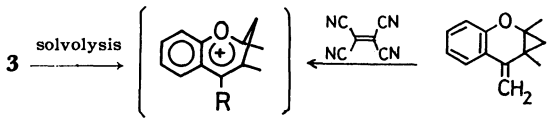
Fig. 2. ^1H NMR chemical shifts for aliphatic protons on 4-pyrones and homo-4-pyrones (δ, ppm).

Although deuterium exchange for either **4b** or **4c** failed to yield decomposition products, structural assignments could be made on the basis of their ^1H NMR spectra as well as the mass spectra. For example, the NMR spectrum of **4c** included two methyl signals, at δ=1.93 (3-methyl) and 1.63 ppm (attached to cyclopropane); a vinyl proton at δ=5.03 ppm for the singlet, and a methine proton at δ=*ca.* 1.8 ppm for the multiplet (C-6 position). Methylene protons of cyclopropane were observed at δ=1.43—1.03 ppm for the multiplet. Three different homo-4-pyrones were prepared; the most stable, **4a**, was employed for the further reactions.

An attempt to prepare the dicyclopropyl ketone (bishomo-4-pyrone), **7**, from **4a** with **6** in HMPA–DMSO was unsuccessful to be recovered so far.

Acid-catalyzed Reaction of Homo-4-pyrone 4a by Means of Trifluoroacetic Acid: Since it has been reported that the cationic intermediate may be highly stabilized by the homoaromatic conjugation depicted in **8** in either the solvolysis of the secondary cyclopropylmethyl ester, **3**,[3] or the electrophilic addition of tetracyanoethylene to

the 4-methylene-4*H*-homochromene derivatives, **9**,[9] we attempted to isolate secondary alcohols or vinylcyclopropanes corresponding to **3** or **9** starting from **4**, but we could not do so because of the cleavage of cyclopropane.[8] Therefore, we studied the protonation to the carbonyl function of homo-4-pyrone, **4a**, by means of acid catalysis as another way for investigating the cationic intermediate from **4a**.



8 **9**

R=H (from **3**)
R=CH_2-C(CN)$_2$-$\bar{C}$(CN)$_2$ (from **9**)

When **4a** was dissolved in trifluoroacetic acid (TFA) at room temperature for 1 d, followed by the usual work-up process, the column chromatography of the crude product on silica gel afforded three products in 6, 32, and 30% yields; they are recognized as a dehydrated, an isomeric, and a hydrated compound of **4a** respectively on the basis of both microanalyses and mass spectrometry.

*Reaction of Homo-4-pyrone, **4a**, by Means of an Other Acid Catalysis*: The same products, a dehydrated, an isomeric, and a hydrated one, were isolated in trace, 12, and 34% amounts respectively by the treatment of **4a** with *p*-toluenesulfonic acid in benzene at room temperature for 1 d, although **4a** was fairly stable in acetic acid. An acid-catalyzed reaction by the use of three polychloroacetic acids, CH_2ClCO_2H, $CHCl_2CO_2H$, and CCl_3CO_2H, afforded the hydrated product in 16, 30, and 36% yields respectively; moreover, the **4a** was recovered, judging from the NMR spectra of the mixture. As an isomeric compound could not be detected in either case, the production of an isomeric compound seems to occur by means of strong acid catalysis.

Structural Assignment of the Dehydrated Product: The IR absorptions obviously demonstrated the existence of neither hydroxyl nor carbonyl group, so this compound may possess an ether linkage. The NMR spectrum included signals for two methyl protons (δ, 2.43 and 2.57), a vinyl proton (δ, 6.80), and nine aromatic protons (δ, 7.33 to 8.25), in which the existence of a solitary multiplet (δ, 7.92 to 8.25 for 2H) in a fairly low field may be conjectured upon *peri*-(5, 8) protons in the naphthalene ring, which is probably crowded with substituents upon at least the 1,4-positions, judging from the NMR data for related naphthalenes in the literature as is shown in Table 3.[10]

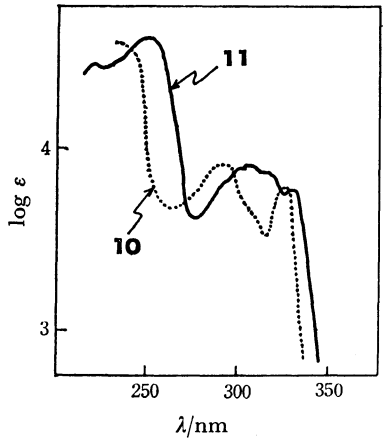
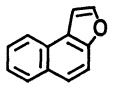


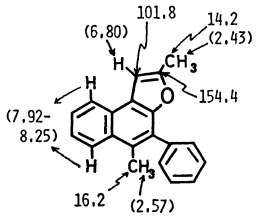
Fig. 3. UV spectra of naphtho[2,1-*b*]furans.

The ^{13}C NMR data at δ=154 and 102 ppm suggest the furan moiety,[11] although the other set of signals due to the furan ring cannot be found because of complicated signals between at δ=137 ppm and 122 ppm. Therefore, the structure of the ether may be speculated to be condensed furan, a so-called naphthofuran. On the basis of this speculation, the presence of α-methyl (δ_C, 14; δ_H, 2.43) and β-proton (δ_H, 6.80) on the furan moiety may be well interpreted; also the signal at 122 ppm for β-carbon shows a doublet under the off-resonance conditions in the ^{13}C NMR spectrum. The other methyl signal at δ=16 ppm was assigned to a substituent of the naphthalene; the *peri*-position is more plausible than the other positions, judging from the chemical shift of the ^1H NMR spectrum at δ=2.43 ppm (see Table 3).[10]

The UV spectrum showed maxima at 330, 304, and 249 nm (log ε 3.78, 3.94, and 4.63 respectively), nicely in accord with those of the parent naphtho[2,1-*b*]furan, **10**, reported in the literature,[12] as is illustrated in Fig. 3. On the basis of these data, the structure of the dehydrated product was identified as dimethylphenylnaphthofuran, **11**.



10



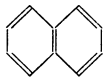
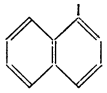
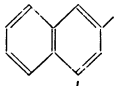
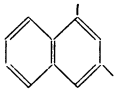
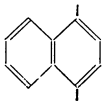
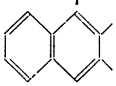
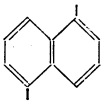
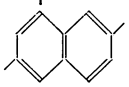
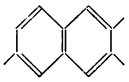
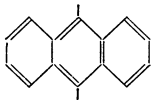
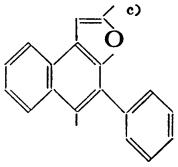
11

Chemical shifts; δ_C (δ_H)

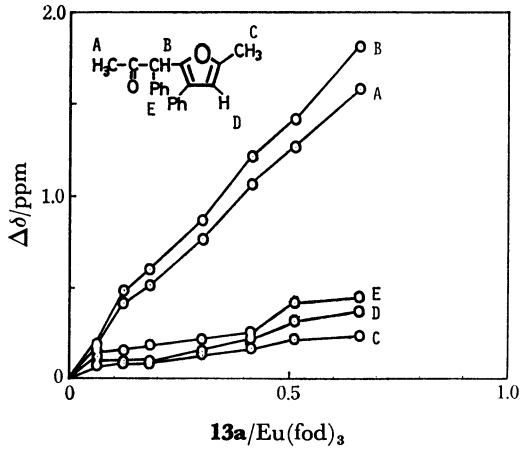
Structural Problem of the Isomeric Product: Because of a monooxime formation as well as the IR absorption at 1720 cm^{-1}, and its freedom from a hydroxyl group, the other oxygen atom of the isomeric product probably performs an ether function. That a cleavage of the cyclopropane ring had occurred was indicated by the ^1H NMR spectrum of the product, which had signals at δ=4.92 and 6.05 ppm for each singlet instead of the AB quartet for cyclopropyl methylene (δ, 1.56 and 1.82) in **4a**. Methyl signals were transferred into somewhat lower fields (δ, 2.02 for the sharp singlet and 2.33 for the broad singlet) in comparison with those of **4a**. Then, $Eu(fod)_3$ was added in portions to the substrate dissolved in deuteriochloroform, and the ^1H NMR spectra were recorded under various molar ratios in order to ascertain structural information. If the substrate is a methyl ketone, a remarkable lanthanoid-induced downfield shift may be expected for the methyl group adjacent to the carbonyl group.[13] The experimental results of the downfield shifts are presented in Fig. 4.

The relative extents of the induced shifts for both the sharp singlet for the methyl group (δ, 2.02) and the

TABLE 3. CHEMICAL SHIFTS IN NAPHTHALENES AND RELATED COMPOUNDS

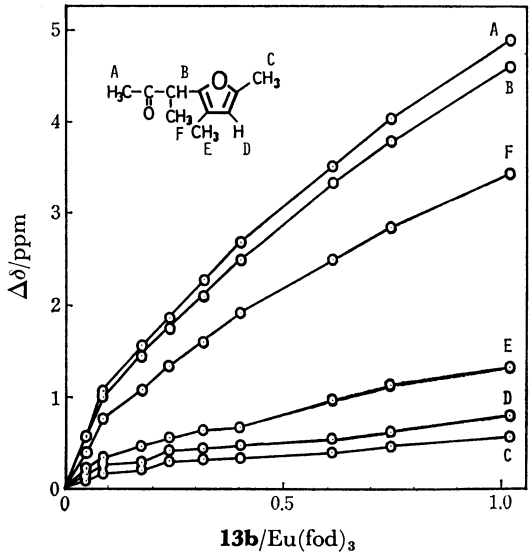
Compd	Chemical shifts (δ, ppm)[a]		
	Aromatic protons		Methyl protons
	peri-	Others	
	7.75—7.5	7.2—7.4	—
		7.9—7.2	2.63[b]
		7.9—7.2	2.47
		7.85—7.0	2.40, 2.57[b]
	8.05—7.9	7.55—7.35, 7.14	2.67[b]
		7.7—7.15	2.40
	7.9—7.7	7.45—7.15	2.63[b]
		7.7—7.2	2.47
		7.6—7.05	2.45, 2.38
	8.4—8.25	7.6—7.4	3.10[b]
	8.25—7.92	7.67—7.33, 6.80	2.43, 2.57[b]

a) $CDCl_3$ was used as the solvent unless otherwise noted.
b) Chemical shift assigned to α-methyl. c) In CCl_4.



13a/Eu(fod)$_3$

Fig. 4-1. Eu(fod)$_3$-induced shifts for **13a**.

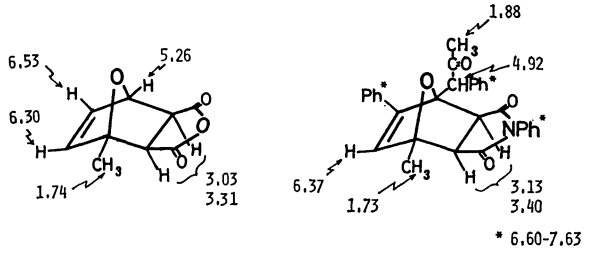


13b/Eu(fod)$_3$

Fig. 4-2. Eu(fod)$_3$-induced shifts for **13b**.

singlet for the methine proton (δ, 4.92) were much larger than any other proton signals. Accordingly, the product may possess a CH_3–C(=O)–CH(Ph)– moiety, an idea which is also supported not only by the facile disappearance of the methine signal (δ, 4.92) adjacent to the carbonyl group in its ^1H NMR spectrum after hydrogen-deuterium exchange upon treatment with alkaline DME–D_2O, but also by an intense fragment at *m/e* 247 (M−43) which may be readily accounted for by an expulsion of the acetyl group in the mass spectrum.

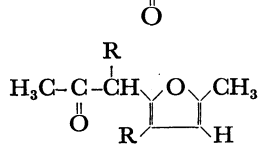
The formation of a one-to-one adduct with *N*-phenylmaleimide may be proof of the furan skeleton of the product. The stractural assignment of the adduct was carried out by means of a comparison with the adduct, **12**, which had been prepared from 2-methylfuran with maleic anhydride as reported in the literature[14] and as is demonstrated in Fig. 5. In the ^1H NMR spectrum of the *N*-phenylmaleimide adduct, one methyl signal of the isomeric product of **4a** (δ, 2.33) underwent an extraordinary upfield shift to δ=1.73 ppm, so that the methyl group changed into the substituent at α-carbon in the furan which had been obtained by the acid catalysis of **4a**.



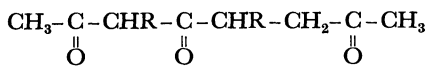
12 **adduct**

Fig. 5. ^{1}HNMR chemical shifts for Diels-Alder adducts (δ, ppm).

The conclusive information concerning the structural assignment of the isomeric product of **4a** was given by means of ^{13}C NMR measurement. In accordance with the data on the chemical shifts in the literature,[11] the singlets at both δ=152 and 145 ppm (α-carbons), and both the singlet at 125 ppm and the doublet at 108 ppm (β-carbons) under the off-resonance conditions, confirm the presence of the furan moiety. Although not all the signals could be assigned because of the duplication of signals in the region of the phenyl carbons (δ, 126 to 137), the signals at δ=203 ppm for the singlet and δ=29 ppm for the quartet (off-resonance spectrum) also showed CH_3–C(=O) function.



13



14

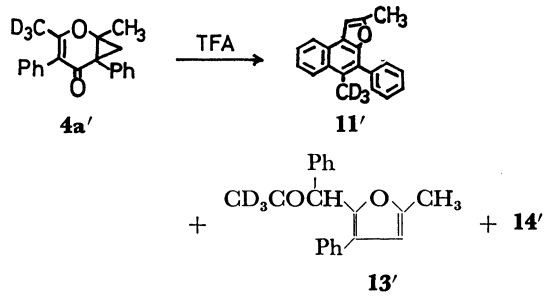
(**a**; R=Ph, **b**; R=CH_3, **c**; R=H)

As a long-range coupling of the allyl type was found between the signals of the methyl group (δ, 2.33) and the vinyl proton (δ, 6.05), the –CH=C(–)–CH_3 moiety should be included in the furan ring. After all, then, the structure of the isomeric product could be deduced to be that of the 2-furylacetone derivative, **13a**.

The Structure of the Hydrated Product: This was assigned by means of its spectroscopic data to **14a**; it was dissolved in TFA for several hours to give a dehydrated compound, **11**, in about a 10% yield, accompanied by the recovery of **14a**. For the purpose of obtaining further information about the reaction pathway, the exposure of either deuterium-labelled **4a′** or other homo-4-pyrones in TFA was carried out; also, the decisive structural assignment of the isomeric product, **13**, will be made.

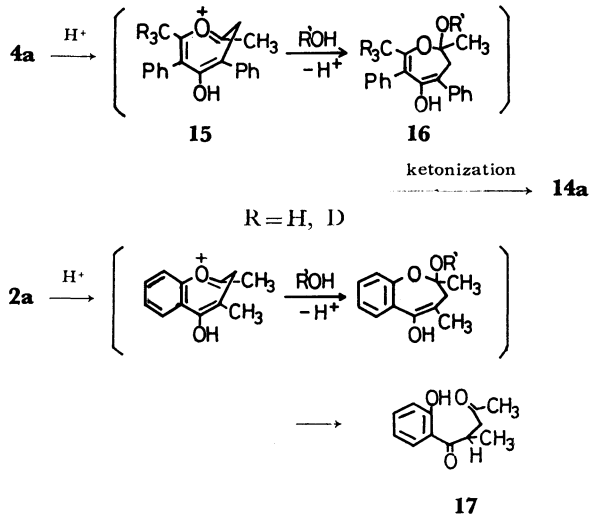
*Acid-catalyzed Reaction of Trideuteriomethyl-substituted **4a′** in TFA*: By using the procedure mentioned above, three products were isolated analogously. The ^1H NMR spectrum of the dehydrated one showed only one methyl signal (δ, 2.43) which could be identified as α-methyl in the furan, while the signal for the naphthylmethyl group (δ, 2.57) scarcely appeared at all. Therefore, the CD_3 group on the C-3 position in homo-4-pyrone, **4a′**, can be said to have been specifically transferred into the *peri*-position on the naphthalene ring of **11**.

On the other hand, the signal for the methyl group at a lower field (δ, 2.02) identified as acetyl protons completely disappeared, and the signal for α-methyl in the furan ring (δ, 2.33) was observed exclusively in the ^1H NMR spectrum of the isomeric product. Consequently, the α-methyl group belonging to the furan ring seems to be derived from the bridgehead methyl group (C-1 position) in 2-oxabicyclo[4.1.0]hept-3-en-5-one derivatives, **4a**, in either **11** or **13a**. In the case of 2-furylacetone, **13a**, further evidence was provided by the mass spectrum of **13a′**. Thus, accompanying the parent peak at *m/e* 293 ($C_{20}H_{15}D_3O_2$), there was a peak at *m/e* 247 (M−46, base) corresponding to the loss of the CD_3CO moiety; this peak appeared entirely cut off from any surrounding peaks, so upon acid catalysis that the CD_3 group in **4a′** seems move into the acetyl group as the side chain of the furan ring in **13a′**.

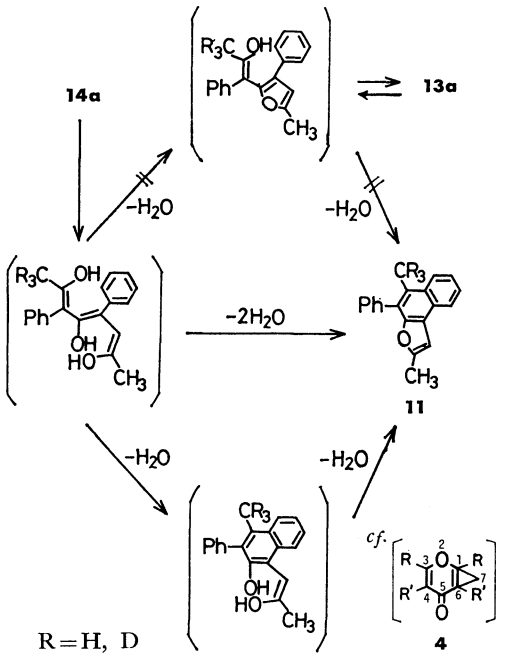


Mechanism: On the basis of the above experimental results, a plausible mode of formation that we favor for **11**, **13a**, and **14a** is illustrated below. Protonation onto the carbonyl group of **4a** occurs to give a cationic intermediate such as **15** by strong acid catalysis, *e.g.*, TFA,[15] followed by nucleophilic attack by a solvent

on the C-1 position adjacent to ether oxygen coexisting with a ring enlargement due to the cleavage of the cyclopropane. Then, the acetal **16** thus produced undergoes ketonization to yield 3,5-diphenyl-2,4,7-octanetrione (**14a**). Such a product was also obtained when the benzo-condensed compound **2a** was submitted to an acid-catalyzed reaction; in this case, one of the carbonyl groups was enolated to **17** as a phenol, as is depicted below.[4]



As it is a convenient route for furan synthesis for the dehydration of 1,4-diketones to take place under appropriate conditions, *e.g.*, in the presence of sulfuric acid (the so-called Paal-Knorr-type reaction),[16] the formation of the 2-furylacetone derivative, **13a**, may be expected in a similar manner. Support for this reaction mechanism was provided by the deuterium-labelled experiment. Thus, the 3-methyl group of **4a** was changed into acetonyl function in **13a**, while the other methyl group (the C-1 position of **4a**) was changed into the 2-furylmethyl function, as has been described above; therefore, it may be speculated that carbons belonging to the furan in **13a** originate as carbons at the 1, 5, 6, and 7 positions in **4a**.

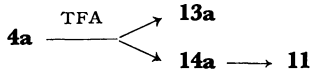


Taking this postulation into account, the conversion from triketone, **14a**, into naphthofuran, **11**, can be explained: (i) the furan moiety was made from the carbons of the C-1, 5, 6, 7 positions in **4a**; (ii) the carbons of the C-3, 4, 5, 6 positions in **4a** belong to the new benzene ring, which condenses with the phenyl group at the C-6 position in **4a** to give a naphthalene in which the CD_3 group may be assigned as a substituent at the *peri*-position in the case of the deuterium-labelled experiment, as is shown below.

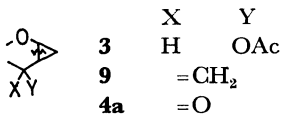
Nevertheless, the correct mechanism of 2-furylacetone **13a** formation seems to be somewhat different from the above deduction, judging from the following experimental results:[19] (i) when the reaction of **14a** with TFA was followed by means of either ^1H NMR spectroscopy or TLC at intervals, the formation of **13a** was undetectable, and (ii) interconversion from **13a** into **11** did not occur in TFA at room temperature.

Accordingly, **13a** is not given from **14a** by means of a Paal-Knorr reaction in the present case, but was directly formed from the starting material, although it seems, on the basis of the above deuterium-labelled experiment, likely that the C-1, 6 bond fission of **4a** occurred during the production of **13a**.

Thus, the interconversions among **4a**, **11**, **13a**, and **14a** may be finally expressed as below. This scheme may be well interpreted by the fact that the product ratio, **13a**/(**11**+**14a**), for the treatment of **4a** with TFA was found to be inevitably constant for at least six entries:



It is noteworthy that a similar mode of the cleavage of the cyclopropane ring has been deduced from the product studies of either the solvolysis of the secondary ester, **3**,[3] or the electrophilic addition of tetracyanoethylene to the *exo*-methylene compound, **9**,[9] and that the same characteristic cleavage of cyclopropane may also be involved in the acid-catalyzed reaction of homo-4-pyrone, **4a**.



Mode of cleavage of the cyclopropane ring

Reaction of Other Homo-4-pyrones with TFA: An isomerization of both **4b** and **4c** by means of acid catalysis took place analogously with the case of **4a** to give **13b** and **13c** in 40 and 15% yields respectively, along with a triketone **14c** (20% yield, starting from **4c**), although TFA was diluted with an equal volume of carbon tetrachloride or chloroform for the purpose of relieving a vigorous reaction moderately. The structural assignments of the products were made by means of both their ^{13}C NMR spectra, in which a furan moiety was clearly indicated, as is shown in Table 4, and their other spectral characteristics in comparison with those

Table 4. The ^{13}C NMR chemical shifts for 2-furylacetones **13**

Compd	C=O					$-C(=O)-\overset{*}{C}HR-$	$\overset{*}{C}H_3C(=O)-$		CH_3
13a	203	152	145	125	108 (d)	57 (d)	29 (q)	14 (q)	
13b	206	151	146	117	109 (d)	46 (d)	28 (q)	14 (q) 13 (q)	10 (q)
13c[a)]	205	152	147	109	107	43	29	14	

a) Only an off-resonance spectrum was obtained.

of **13a**. The proton NMR data of **13b** including $Eu(fod)_3$ were closely analogous with those of **13a**, as is shown in Fig. 4.

In connection with reports on the chemistry of flavors, 2-furylacetone **13c** has been identified as one of the components in molasses aroma, bread aroma, meat flavor, and so on,[17)] and antibiotic nonactic acid, which has been noted to have structural characteristics[18)] analogous to the carbon skeleton of **13**. The production of 2-furylacetone starting from homo-4-pyrone in our present study is interesting because of the versatile utility of the product as well as the finding that aromatization into five-membered heterocycle may be one of the most suitable pathways for the cleavage of the cyclopropane of homo-4-pyrones under strong acid catalysis.

Experimental

General. All the melting and boiling points are uncorrected. The IR spectra were measured using a Hitachi 215 spectrometer; the UV spectra, on a Hitachi 124 spectrometer; the mass spectra, on a Hitachi RMU-6L spectrometer, and the ^1H NMR spectra, on a Varian T-60 spectrometer. The chemical shifts on both ^1H and ^{13}C NMR spectra are given in δ, with tetramethylsilane as the internal standard.

Materials. The preparation of 2,6-dimethyl-3,5-diphenyl-4-pyrone (**5a**) was carried out according to the procedure reported by Letsinger *et al.*[7)] Mp 208—211 °C (lit, 202—206 °C)[7)] (40% yield; flaky crystals, from benzene–ligroin). Analogously 2,3,5,6-tetramethyl-4-pyrone (**5b**) was synthesized from 3-pentanone in a 13% yield. Bp 154 °C/25 mmHg, mp 90—91 °C (lit, 90 °C)[7)] (colorless prisms, from light petroleum). Starting from commercially available dehydroacetic acid, 2,6-dimethyl-4-pyrone (**5c**) was obtained. Mp 132—134 °C (lit, 130 °C),[7)] bp 155 °C/35 mmHg (65% yield, colorless needles, from chloroform–hexane). Dimethyloxosulfonium methylide (**6**) was generated *in situ* by the treatment of sodium hydride with trimethyloxosulfonium iodide in dimethyl sulfoxide which had been distilled on calcium hydride under reduced pressure. Hexamethylphosphoric triamide was also distilled *in vacuo* before use and dried on molecular sieves.

General Procedure for the Cyclopropanation of 4-Pyrones. Dimethyldiphenylhomo-4-pyrone(1,3-dimethyl-4,6-diphenyl-2-oxabicyclo[4.1.0]hept-3-en-5-one) (4a): To mineral oil-free sodium hydride, prepared from commercial NaH (5.5 g, 0.14 mol; 61% in mineral oil) by means of triple decantation with light petroleum, we added trimethyloxosulfonium iodide (30 g, 0.14 mol) in one portion, after which we stirred in freshly distilled dimethyl sulfoxide (DMSO) (60 ml) over a period of 15 min, at first very carefully, at 20 °C. After the cessation of the violent evolution of hydrogen, the milky-white solution was kept in a nitrogen atmosphere. Into the dimethyloxosulfonium methylide generated in DMSO we poured hexamethylphosphoric triamide (HMPA) (60 ml), after which we added **5a** (15 g, 0.054 mol) in several portions, because of the poor solubility of **5a** in the medium. The solution was then allowed to stand at room temperature for 3 h under nitrogen, warmed at 40 °C for 6 h, and then cooled in an ice-bath; anhydrous ether (100 ml) was then added to the solution. The mixture was then poured into ice water and separated; the aqueous layer was extracted thoroughly with ether, and at last it was extracted once with benzene. The combined organic layer was satisfactorily washed with water and then dried on anhydrous sodium sulfate. The solution was evaporated *in vacuo*; a brown syrup (16.3 g) thus obtained was chromatographed on neutral alumina (80 g, deactivated by the addition of 10% water (w/w)) using ether–light petroleum (1: 10 by volume) as the eluent, and the solvent was evaporated *in vacuo* to give 8.31 g (53%) of **4a**. Mp 101—102 °C (colorless prisms, from light petroleum). IR (Nujol): 1655, 1515 cm^{-1}. ^1H NMR (CCl_4): 7.3—7.0 (10H, m, aromatic), 1.80 (3H, s, methyl), 1.28 (3H, s, methyl), 1.82, 1.56 (2H, AB quartet, $J=6$ Hz, cyclopropane). Found: C, 82.69; H, 6.29%. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%. MS and UV data (see Table 2 and Fig. 1). About 15% of the **5a** was recovered in the column chromatography as a more polar fraction than **4a**.

Tetramethylhomo-4-pyrone(1,3,4,6-tetramethyl-2-oxabicyclo[4.1.0]hept-3-en-5-one) (4b): According to the general procedure, **4b** was obtained as a colorless oil (see Table 1). IR (neat): 1640, 1625, 1440, 1400, 1195, 1035, 805 cm^{-1}. ^1H NMR (CCl_4): 1.89 (3H, s, methyl), 1.65 (3H, s, methyl), 1.57 (3H, s, methyl), 1.22 (3H, s, methyl), 1.22, 0.78, (2H, AB quartet, $J=7$ Hz, cyclopropane). MS and UV data (see Table 2 and Fig. 1).

Dimethylhomo-4-pyrone(1,3-dimethyl-2-oxabicyclo[4.1.0]hept-3-en-5-one) (4c): The synthetic procedure was analogous to those used for the other homo-4-pyrones mentioned above. (see Table 1). IR (neat): 1650, 1610, 1400, 1170, 965, 840 cm^{-1}. ^1H NMR (CCl_4): 5.03 (1H, s, vinyl), *ca.* 1.8 (1H, m, methine), 1.93 (3H, s, methyl), 1.63 (3H, s, methyl), 1.4—1.0 (2H, m, cyclopropane). MS and UV data (see Table 2 and Fig. 1).

General Procedure for Deuterium Exchange: A solution of the substrate (**4a**; 0.10 g) in DME (3 ml) was added to a stirred solution of a catalytic amount of sodium hydroxide in DME–D_2O (1: 1 by volume, 6 ml). After having been stirred overnight at room temperature, the solvent was evaporated *in vacuo* without heating; then the residue was extracted twice with dry ether (20 ml). The extracts were combined, washed with water, and dried over anhydrous sodium sulfate. The solution was condensed *in vacuo* to give a residue (**4a'**; 0.09 g), whose spectroscopic data have been discussed above.

General Procedure on the Treatment of Homo-4-pyrones 4 with Trifluoroacetic Acid: A wine-red solution of homo-4-pyrone **4a** (0.50 g) in trifluoroacetic acid (TFA) (5 ml) was subjected to ^1H NMR measurement, but a complicated pattern was observed. The solution was stirred at room temperature for 1 d, diluted with dry ether (50 ml), poured into an ice-cold

aqueous sodium hydrogencarbonate solution, and extracted three times with ether (100 ml); the combined organic layer was washed thoroughly with cold aqueous sodium hydrogencarbonate and with water, and then dried over anhydrous sodium sulfate. A yellow syrup (0.49 g) obtained by the subsequent evaporation of the ether was chromatographed on silica gel (15 g), using ether–light petroleum (1: 9) as the eluent, to give three crystalline products: **11**, 30 mg (6%), mp 115—117 °C (from light petroleum). IR (nujol): 1600, 1580, 1360, 1230, 1180, 1010 cm^{-1}. ^1H NMR (CCl_4): 8.25—7.92 (2H, m, aromatic), 7.67—7.33 (7H, m, aromatic), 6.80 (1H, broad s, vinyl), 2.57 (3H, sharp s, methyl), 2.43 (3H, broad s, methyl). ^{13}C NMR ($CDCl_3$): 154.4 (s), 136.7 (s), 130.7, 130.2, 128.2, 127.5, 127.2, 126.5, 125.6, 124.5, 123.9, 122.4, 101.8 (d), 16.2 (q), 14.2 (q) (see also text). MS (*m/e*): 272 (M^+, base), 229. UV data (see Fig. 1). Found: C, 87.65; H, 5.94%. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92%. **13a**, 160 mg (32%), mp 35—37 °C (from light petroleum). IR (neat): 1720, 1600, 1570, 1450, 1150, 760, 690 cm^{-1}. ^1H NMR (CCl_4): 7.20 (10H, aromatic), 6.05 (1H, broad s, vinyl), 4.92 (1H, s, methine, disappeared when alkaline DME–D_2O) was used, 2.33 (3H, broad s, methyl), 2.02 (3H, sharp s, methyl), ^{13}C NMR ($CDCl_3$): 203.7 (s), 151.9 (s), 144.6 (s), 137.2 (s), 133.8 (s), 130.8, 130.5, 130.2, 129.0, 128.7, 128.0, 127.4, 127.1, 125.5 (s), 108.1 (d), 57.7 (d), 28.5 (q), 13.5 (q) (see also Table 4). MS (*m/e*): 290 (M^+), 247 (base). Found: C, 82.44; H, 6.34%. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%. Monooxime, mp 154—156 °C (from methanol). Found: C, 78.28; H, 6.25; N, 4.50%. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59%. **14a**, 160 mg (30%), mp 75—77 °C (from light petroleum). IR (Nujol): 1715, 1600, 1160, 760, 730, 690 cm^{-1}. ^1H NMR ($CDCl_3$): 7.7—6.7 (10H, m, aromatic), 4.3—3.3 (4H, m), 2.13 (3H, s, methyl), 1.78 (3H, s, methyl). MS (*m/e*): 308 (M^+), 290 (base), 247. Found: C, 78.09; H, 6.61%. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.5%. In addition to these products, an almost one-to-one mixture of **13a** and **14a** was also isolated (130 mg; 25%).

*Reaction of **4a** by Means of* p-*Toluenesulfonic Acid*: Homo-4-pyrone, **4a** (0.50 g), and an equal amount of *p*-toluenesulfonic acid were dissolved in benzene (5 ml) at room temperature for 1 d. The mixture was then washed with aqueous sodium hydrogencarbonate and with water, and dried on anhydrous sodium sulfate. The solution was evaporated, and the residue was subjected to chromatography to yield **11** (trace), **13a** (60 mg, 12%), and **14a** (180 mg, 34%).

*Treatment of **4a** with Polychloroacetic Acids*: To each solution of **4a** (50 mg) in $CDCl_3$ (0.4 ml), equimolar polychloroacetic acid, CCl_3CO_2H (28 mg), $CHCl_2CO_2H$ (22 mg), or CH_2ClCO_2H (16 mg), was added, after which the mixture was kept at 40 °C for 1 d. Since **14a** was the sole isolable product in each case, the yields were estimated by ^1H NMR spectroscopy on the basis of the ratio for the characteristic signals identified as **14a** to the recovered **4a**. When the reaction was carried out in neat $CHCl_2CO_2H$, **14a** was the single isolable product in addition to the reactant. The yields have been shown above.

Preparation of N-*Phenylmaleimide Adduct*: a) Homo-4-pyrone **4a** (0.50 g, 1.72 mmol), *N*-phenylmaleimide (0.30 g, 1.72 mmol), and TFA (3 ml) was stirred at room temperature for 30 h, and then diluted with dry ether (100 ml), and poured into ice-cold sodium hydrogencarbonate; the mixture was extracted twice with ether (50 ml), and the combined organic layer was thoroughly washed with aqueous sodium hydrogencarbonate, washed with water, and dried over anhydrous sodium sulfate. The subsequent evaporation of the solution gave a syrup (0.80 g) which was subjected to preparative TLC on silica gel, using methyl acetate–light petroleum (1: 6) as the eluent, to yield pale yellow needles. (290 mg, 45%, from ether). Mp 125 °C. IR (Nujol): 1710, 1500, 1200, 1180, 750, 715, 690 cm^{-1}. ^1H NMR data (see the text). Found C, 77.46; H, 5.48; N, 2.91%. Calcd for $C_{30}H_{25}NO_4$: C, 77.74; H, 5.44; N, 3.02%.

b) The same product was obtained by the reaction of **13a** with equimolar *N*-phenylmaleimide in $CDCl_3$ at room temperature for several days; it was confirmed on the basis of both ^1H NMR spectrometry and the TLC analysis of the standard sample as has been described in Method a.

*Isomerization from Homo-4-pyrone **4b** into 2-Furylacetone **13b** by Means of Trifluoroacetic Acid*: Trifluoroacetic acid was diluted with chloroform (1: 1 by volume). Analogously with the procedure of the reaction starting from **4a**, **13b** was isolated in a 40% yield from **4b**, along with the recovery of **4b** in an 8% yield. Purification was accomplished by column chromatography (silica gel, with ether–light petroleum (1: 4) as the eluent). **13b**; colorless oil. IR (neat): 1730, 1590, 1450, 1360 cm^{-1}. ^1H NMR ($CDCl_3$): 5.65 (1H, broad s, vinyl), 3.55 (1H, q, J=6 Hz, methine), 2.20 (3H, s, methyl), 1.92 (3H, s, methyl), 1.90 (3H, s, methyl), 1.30 (3H, d, J=6 Hz, methyl). MS (*m/e*): 166 (M^+), 123 (M−43, base). Monooxime, mp 48—49 °C. MS (*m/e*): 181 (M^+).

*Acid-catalyzed Reaction of Homo-4-pyrone **4c***: Trifluoroacetic acid–carbon tetrachloride (1: 1 by volume) was used as the medium. After 1 d-reaction at room temperature, the mixture was worked up as has been described above; purification was carried out by column chromatography on silica gel, using ether–light petroleum (1: 3) as the eluent. **13c**; colorless oil (15%). IR (neat): 1720, 1570, 1355, 1220, 1025, 780 cm^{-1}. ^1H NMR (CCl_4): 6.03 (1H, d, J=3 Hz, vinyl), 5.90 (1H, d, J=3 Hz, vinyl), 3.57 (2H, s, methylene), 2.30 (3H, broad s, methyl), 2.10 (3H, sharp s, methyl). MS (*m/e*): 138 (M^+), 111, 95 (M−43, base). ^{13}C NMR data (see Table 4). **14c**; colorless oil (20%). IR (neat): 1710, 1610, 1400, 1360 cm^{-1}. ^1H NMR (CCl_4): 5.50 (s), 3.63 (s), 2.93—2.20 (m, total 6H), 2.20 (3H, s, methyl), 2.02 (3H, s, methyl). MS (*m/e*): 156 (M^+), 138, 123, 113 (M−43), 99, 85, 71.

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15) The possibility of the intervention of the highly delocalized cationic species, the so-called homopyrylium ion, is now being studied. **4a** was found to be much more stable for TFA than *trans*-2-phenoxycyclopropyl phenyl ketone, whose synthetic route has been discussed previously (see Ref. 9). Protonation to cyclopropyl ketones by the use of a strong acid has afforded homoaromatically stabilized cationic intermediates; *e.g.*, H. A. Corver and R. F. Childs, *J. Am. Chem. Soc.*, **94**, 6201 (1972).

16) C. Paal, *Ber.*, **18**, 367 (1885); L. Knorr, *ibid.*, **18**, 299 (1885).

17) For example: M. Winter, F. Gutschi, I. Flament, and M. Stoll, U. S. Patent, 3952026 (1976) (*Chem. Abstr.*, **85**, p94216e); U. S. Patent, 3989713 (*Chem. Abstr.*, **86**, 43556d); U. S. Patent, 3924015 (1975) (*Chem. Abstr.*, 84, p164364g); K. Watanabe and Y. Sato, *J. Agric. Food Chem.*, **20**, 174 (1972); M. Yokota and I. S. Fagerson, *J. Food Sci.*, **36**, 1091 (1971); E. J. Mulders, M. C. de Brauw, and S. V. Straten, *Z. Lebensm. Unters. Forsch.*, **150**, 306 (1973) (*Chem. Abstr.*, **78**, 70418b).

18) H. Gerlach and H. Welter, *Helv. Chim. Acta*, **57**, 2306 (1974), and the references cited therein.

19) These additional experiments were done in the referee's recommendation, which seemed appropriate.