Notes

Chem. Pharm. Bull.
24(4) 813—815 (1976)

UDC 547.442.04 : 547.291'233.3.04

Formic Acid Reduction. XXIV.[1] Path of the Reductive Fission of the Centered β-Carbon Bond of Alkylidenebisketones

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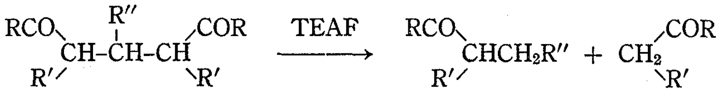
(Received June 14, 1975)

The reductive fission, previously realized at one of the centered β-carbon bond of alkylidenebisketones by the formate, triethylammonium formate, has been mechanistically revealed to be initiated by retro-Michael addition and followed by reduction of the resulting α,β-unsaturated carbonyl compound.

In the previous works[3–7] of this series the reductive carbon-carbon bond fission induced by the formate, TEAF,[8] which is the distillable liquid of bp 98° (18 mmHg), given by $5HCO_2H \cdot 2NEt_3$, has been exhibited in the two patterns, one is the reductive fission of one of the centered β-carbon bonds of alkylidenebisketones (**1**)



$$\underset{\mathbf{1}}{(RCO)(R')CH\text{-}\overset{R''}{CH}\text{-}CH(COR)(R')} \xrightarrow{TEAF} \underset{\mathbf{2}}{(RCO)(R')CHCH_2R''} + CH_2(COR)(R')$$

and the other is that of the *p*- and *o*-(N,N-dimethylamino)phenyl carbon bond of *p*- and *o*-(N,N-dimethylamino)-substituted triphenylmethane derivatives[7] and of 9-(*p*-N,N-dimethylaminophenyl)-1,8-dioxo-1,2,3,4,5,6,7,8-octahydroxanthene.[5] The latter has been stated to involve the cleavage into the corresponding diphenylmethyl carbonium ion, but the former has remained vague in distinction from the latter. It is a mechanistic investigation of the former fission reaction that the present paper describes.

The preceding papers[1,3,9–11] have reported the reduction of carbon-carbon double bond conjugated with carbonyl which is effected by heating with TEAF.

$$\underset{\mathbf{3}}{(RCO)(R')C{=}CHR''} \xrightarrow{TEAF} \underset{\mathbf{2}}{(RCO)(R')CH\text{-}CH_2R''}$$

When considered pathway of the reductive fission, if a retro-Michael addition of **1** as shown in the following scheme could be effected in TEAF medium, the formed **3** should be successively reduced into the product **2** equal to the reductive fission product.

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[1] Part XXIII: K. Suzuki, H. Fukawa, T. Okugawa, and M. Sekiya, *Chem. Pharm. Bull.* (Tokyo), **24**, 607 (1976).

[2] Location: *2-2-1 Oshika, Shizuoka-shi 422, Japan.*

[3] M. Sekiya and C. Yanaihara, *Chem. Pharm. Bull.* (Tokyo), **17**, 738 (1969).

[4] M. Sekiya and K. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **19**, 1531 (1971).

[5] M. Sekiya and K. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **19**, 1540 (1971).

[6] M. Sekiya and K. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **20**, 343 (1972).

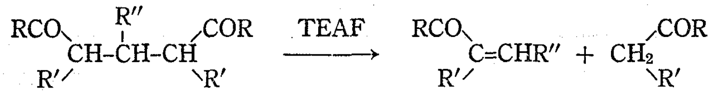
[7] M. Sekiya and K. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **22**, 1788 (1974).

[8] K. Ito, *Yakugaku Zasshi*, **86**, 1166 (1966).

[9] M. Sekiya and C. Yanaihara, *Chem. Pharm. Bull.* (Tokyo), **17**, 747 (1969).

[10] M. Sekiya and K. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **18**, 1530 (1970).

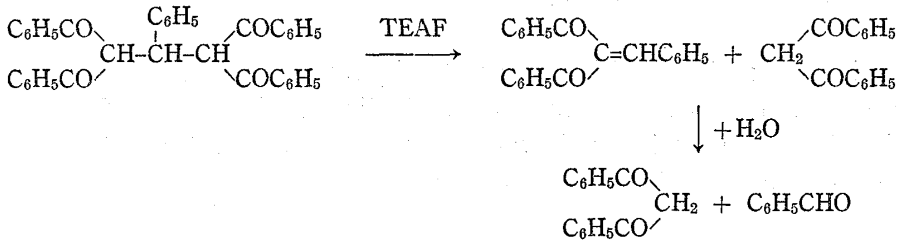
[11] T. Okugawa, K. Suzuki, and M. Sekiya, *Chem. Pharm. Bull.* (Tokyo), **22**, 448 (1974).



$$(RCO)(R')CH\text{-}CH(R'')\text{-}CH(COR)(R') \xrightarrow{TEAF} (RCO)(R')C{=}CHR'' + CH_2(COR)(R')$$

1 3

In order to demonstrate the retro-Michael addition an attempt was made to carry out an experiment by heating benzylidenebisdibenzoylmethane, selected as a model substrate, together with TEAA,[12,13] which is an azeotropic mixture of acetic acid and triethylamine in nearly 7:2 molar proportion, bp 74° (16 mmHg). With understanding of the resemblance of TEAA to TEAF in solvent features, the substitution of the former may permit avoidance of the reducing action of the latter. The retro-Michael addition was realized to give benzylidenedibenzoylmethane and dibenzoylmethane. Yield of the former was 71% and that of the latter was 107% which was assumed to include the same product formed by a successive hydrolysis.

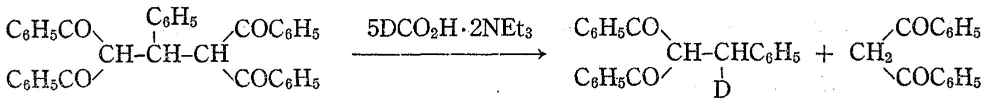


$$(C_6H_5CO)_2CH\text{-}CH(C_6H_5)\text{-}CH(COC_6H_5)_2 \xrightarrow{TEAF} (C_6H_5CO)_2C{=}CHC_6H_5 + CH_2(COC_6H_5)_2$$

$$(C_6H_5CO)_2C{=}CHC_6H_5 \xrightarrow{+H_2O} (C_6H_5CO)_2CH_2 + C_6H_5CHO$$

It has been previously reported that TEAF effects the reductive fission reaction of benzylidenebisdibenzoylmethane[6] and the reduction of benzylidenedibenzoylmethane[10] into benzyldibenzoylmethane. Therefore the reductive fission is deduced mechanistically to be initiated by the retro-Michael addition, which may be induced by triethylamine base, and followed by the reduction of the resulting α,β-unsaturated carbonyl compound.

Relating to this mechanism we describe a result of the reductive fission reaction with deuterated TEAF composed of DCO_2H using benzylidenebisdibenzoylmethane as a substrate. The reductive fission of benzylidenebisdibenzoylmethane with TEAF has been shown[6] to give benzyldibenzoylmethane and dibenzoylmethane. Nuclear magnetic resonance (NMR) measurement as to the corresponding products showed no deuterium content in the latter but in the former. The NMR spectrum of benzyldibenzoylmethane in $CDCl_3$ exhibited a doublet at $\delta=3.45$ ($J=7$ Hz) for the methylene protons and a triplet at $\delta=5.60$ ($J=7$ Hz) for the methine proton, while in the NMR spectrum of the product, the peak corresponding to the methylene protons showed decrease in intensity and that corresponding to the methine proton appeared as a doublet. Calculation of proton contents of these two signals in comparison with that of the aromatic proton signals showed one proton content in each disclosing one deuterium possession at β-carbon of the product. From this result the reaction with deuterated TEAF can be expressed by the following scheme.



$$(C_6H_5CO)_2CH\text{-}CH(C_6H_5)\text{-}CH(COC_6H_5)_2 \xrightarrow{5DCO_2H\cdot 2NEt_3} (C_6H_5CO)_2CH\text{-}CHDC_6H_5 + CH_2(COC_6H_5)_2$$

This result is not in conflict with the above proposed path, because in the TEAF reduction of carbon-carbon double bond conjugated with carbonyl it has been realized[1] that formyl hydrogen of formic acid is introduced into β-carbon.

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[12] M. Sekiya, K. Mori, K. Ito, and K. Suzuki, *Tetrahedron*, **29**, 57 (1973).

[13] H.S. Klooster and W.A. Douglas, *J. Phys. Chem.*, **49**, 67 (1945).

Experimental

Reaction of Benzylidenebisdibenzoylmethane with TEAA——A mixture of 2.7 g (5 mmoles) of benzylidenebisdibenzoylmethane and 8.9 g (50 mmols basede on CH_3CO_2H) of TEAA was heated at 145—150° for 3 hr with stirring. TEAA is an azeotropic mixture of acetic acid and triethylamine. After removal of excess TEAA by evaporation under reduced pressure, a solid distillate boiling at 125—173° under 0.03 mmHg was collected which contained benzylidenedibenzoylmethane and dibenzoylmethane. Separation of these was made by silica gel column chromatography using benzene as an eluent. Evaporation of benzene from the first fraction gave dibenzoylmethane (1.2 g, 107%) and from the second fraction gave benzylidenedibenzoylmethane (1.1 g, 71%). The infrared (IR) spectra of these two products were well consistent with those of the authentic samples prepared. From the solid distillation residue 0.3 g (11%) of the starting material was recovered.

Reaction of Benzylidenebisdibenzoylmethane with $5DCO_2H \cdot 2NEt_3$——A mixture of 2.0 g (3.7 mmoles) of benzylidenebisdibenzoylmethane and 3.2 g (37 mmoles based on DCO_2H) of TEAF composed of formic-*d* acid was heated at 145—150° for 3 hr with stirring. The reaction solution was concentrated under reduced pressure to remove excess TEAF. By distillation of the resulting residue under reduced pressure, dibenzoylmethane was obtained as a distillable solid fraction which recrystallized from Et_2O to give colorless prisms of mp 77—78°. The NMR spectrum of this product was well consistent with that of a nondeuterated authentic specimen. Recrystallization of the above solid distillation residue from dry Et_2O gave colorless needles of benzyldibenzoylmethane-*β-d*, mp 98—101°. In NMR spectrum of this product, the signal corresponding to methylene protons appeared as a doublet at $\delta=3.45$ ($J=7$ Hz) and the peak area of this showed one proton content by comparison with those of methine (1H, $\delta=5.60$, doublet, $J=7$ Hz) and aromatic protons (15H, $\delta=7.10$—8.05, multiplet) owing to deuterium substitution. Appearance of a doublet signal at $\delta=5.60$ for the methine proton in contrast to a triplet of the same of nondeuterated one was consistent with deuterium of the adjacent methylene.

[Chem. Pharm. Bull. 24(4) 815—817 (1976)]

UDC 547.814.5.02 : 581.192

Studies on Constituents of Genus *Iris*. VII.[1] The Constituents of *Iris unguicularis* Poir. (1)[2]

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(Received July 3, 1975)

Kanzakiflavone-1(III), $C_{17}H_{12}O_7$, mp 291—293°, a new flavone, has been isolated from the rhizomes of *Iris unguicularis* Poir. (Japanese name: Kanzakiayame) together with irigenin (I) and iristectorigenin A(II).

The structure of kanzakiflavone-1(III) has been determined as 5,8-dihydroxy-4'-methoxy-6,7-methylenedioxyflavone by chemical and spectral means.

In this series,[1,4] we have shown several new compounds from *Iris tectorum* Maximowiz,[4a,b] *I. florentina* Linne[1,4c–e] and *I. japonica* Thunbergii.[1] We now wish to report the structural elucidation of a new flavone, which have been named kanzakiflavone-1 (III), and isolation of two known isoflavones from the rhizomes of *Iris unguicularis* Poir. (Japanese name: Kanzakiayame).

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[1] Part VI: M. Arisawa, N. Morita, Y. Kondo, and T. Takemoto, *Yakugaku Zasshi*, 93, 1655 (1973).

[2] The 40th Meeting of Hokuriku Branch, Pharmaceutical Society of Japan, Kanazawa, June, 1975.

[3] Location; *Gofuku 3190, Toyama.*

[4] *a)* N. Morita, M. Shimokoriyama, M. Shimizu, and M. Arisawa, *Chem. Pharm. Bull.* (Tokyo), **20**, 730 (1972); *b) Idem, Yakugaku Zasshi*, **92**, 1052 (1972); *c)* N. Morita, M. Arisawa, Y. Kondo, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **21**, 600 (1973); *d)* M. Arisawa, N. Morita, Y. Kondo, and T. Takemoto, *ibid.*, **21**, 2323 (1973); *e) Idem ibid.*, **21**, 2562 (1973).