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Spectroscopic Studies on the Tautomers of Heptane-2,4,6-trione and Its Methylated Homologues[1]

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3,5-Dimethylheptane-2,4,6-trione and 3-methylheptane-2,4,6-trione are synthesized by methylationheptane of-2,4,6-trione *via* alkali metal enolates or an enamine intermediate of the mother compound. In keto-enol tautomerism, the latter two compounds take triketo-, monoenol-, and bisenol forms, while the first one exists in triketo- and monoenol forms, being unable to take a bisenol form. NMR spectra of the tautomers are assigned by combining with IR data. *Keto-enol* ratio in a range of solution phases at various temperatures are estimated by NMR method and effect of the branched methyl groups upon the keto-enol tautomerism is discussed.

A β,δ-tricarbonyl compound is a higher analogue of a β-dicarbonyl compound, and can take triketo-, monoenol- or bisenol forms in its tautomeric equilibrium. Accordingly, the tricarbonyl compound can behave as a bidentate- or terdentate ligand to form a metal chelate complex.

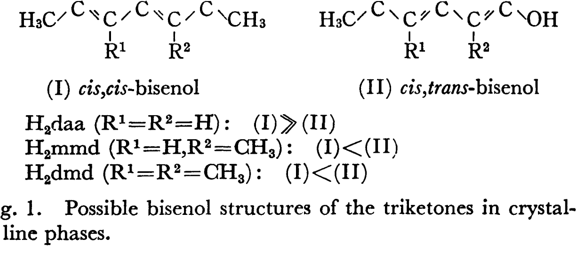
In the course of studies on chelating behavior of some β,δ-tricarbonyl compounds,[2] we were interested in their keto-enol tautomerism in relation to positions of the coordinating sites in the respective ligand molecules, especially in unsymmetric ones.

Tautomerism of compounds of this kind in aqueous media[3] have been studied extensively and recently NMR studies in a range of organic solvents were also reported.[4]

In this paper, we present synthesis and spectroscopic studies on keto-enol tautomerism of three triones; heptane-2,4,6-trione(H_2daa),[5] 3-methylheptane-2,4,6-trione (H_2mmd) and 3,5-dimethylheptane-2,4,6-trione (H_2dmd) in various phases by means of IR and NMR methods.

Results and Discussion

(1) Tautomeric Structures in Crystalline Phases. IR spectrum of H_2daa in a crystalline phase is somewhat different from those of crystalline H_2mmd and H_2dmd despite close similarity in their tricarbonyl skeletons. A band diffused over 3400 to 2200 cm^{-1}, combined together with a broad absorption at 1650 cm^{-1}, indicated the presence of a *cis-β*-ketoenol system with strong intramolecular hydrogen-bonding in crystalline H_2daa, while H_2mmd and H_2dmd exhibit an additional strong peak at 3400 cm^{-1}, which was apparently ascribable to intermolecularly hydrogen-bonded enolic hydroxyl groups in such a condensed phase. Presence of free keto groups is unlikely in the crystalline phases of the three tricarbonyl compounds, since such a keto group, if being present, would display an additional sharp ab-



(I) *cis,cis*-bisenol (II) *cis,trans*-bisenol

H_2daa ($R^1=R^2=H$): (I)$\gg$(II)
H_2mmd ($R^1=H, R^2=CH_3$): (I)$<$(II)
H_2dmd ($R^1=R^2=CH_3$): (I)$<$(II)

Fig. 1. Possible bisenol structures of the triketones in crystalline phases.

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1) Contribution No. 210 from the Department of Organic Synthesis, Kyushu University.

2) a) Preliminary communication: F. Sagara, H. Kobayashi, and K. Ueno, This Bulletin, **41**, 266 (1968). A detailed article in press in this Bulletin. b) Y. Taguchi, F. Sagara, H. Kobayashi, and K. Ueno, *ibid.*, **43**, 2470 (1970).

3) a) G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 576 (1944). b) A. J. Birch, P. Fitton, D. C. C. Smith, D. F. Steere, and A. R. Stelfox, *J. Chem. Soc.*, **1963**, 2209. c) J. Stuehr, *J. Amer. Chem. Soc.*, **89**, 2826 (1967).

4) a) C. W. Dudley, T. N. Huckerby, and C. Oldham, *J. Chem. Soc., A*, **1970**, 2605. b) E. Marcus, J. K. Chan, and C. B. Strow, *J. Org. Chem.*, **31**, 1369 (1966).

5) Abbreviation, H_2daa, comes from *di*acetyl*a*cetone, and prefixed H_2 shows that the trione contains two dissociable enol protons upon metal-chelate formation, according to usage in coordination chemistry. H_2mmd and H_2dmd correspondingly symbolize the *mono*methyl- and *di*methyl-*d*aa, both prefixed also with H_2 meaning two dissociable protons. Though the prefix, H_2, is no use as far as the present paper is concerned, we feel it more convenient to use consistent symbols with subsequent reports on various metal chelates of the ligands.

sorption near 1710 cm^{-1} as observed in oily H_2mmd or in molten H_2daa.

Above observations in IR absorptions lead reasonably to a presumption that a *cis,cis*-bisenol form with cyclic intramolecular hydrogen-bondings is a major component among the H_2daa tautomers, while a *cis,-trans*-bisenol form is predominant regarding H_2mmd and H_2dmd in their crystalline phases as shown in Fig. 1. The present spectral evidences, however, do not distinguish which two of the three carbonyl groups enolize in the bisenols of crystalline phases, two possible forms in respect to enol positions being equally probable, and neither suggest the detailed stereochemistry of the *cis,trans*-bisenol, which is remained to be elucidated. In any case, the introduction of additional methyl groups at the interposition between carbonyl groups does not favor the formation of *cis, cis*-bisenol tautomer with cyclic intramolecular hydrogen-bondings.

Table 1. NMR spectra of H_2daa (c=1.0M) at 38°C

Assignment	Chemical shifts δ(ppm) in solvent			
	Methanol	$CDCl_3$	CCl_4	Benzene
Bisenol CH_3	1.97	1.97	1.94	1.63
C=C–H	—	5.12	5.02	4.88
Monoenol				
CH_3 (enol side)	2.05	2.07	2.04	1.63
CH_3 (keto side)	2.19	2.23	2.19	1.82
CH_2	—	3.38	3.27	2.97
C=C–H	—	5.53	5.45	5.15
Triketo CH_3	—	2.23	2.19	1.73
CH_2	—	3.67	3.57	3.20
Enol OH		14.10[a]	14.20[a]	14.53
Bisenol fraction (mol %)	18[b]	21	54	57

a) A diffused enol proton signal at room temperature is splitted into two signals at 14.05 and 15.13 ppm at −41°C in $CDCl_3$, and 13.83 amd 15.00 ppm at −21°C in CCl_4, respectively. The sharp peak at a higher field being assigned to that of bisenol and the broad one at a lower field to that of monoenol.

b) Value determined from the respective methyl signal intensities.

(2) Tautomeric Structures in Solution Phases. *(2-a) Tautomerism of H_2daa*: Table 1 summarizes the NMR spectra of H_2daa in various solvents, including the assignments of signals and bisenol content in solution phases. The assignments are virtually in agreement with those reported by the previous workers[4] except the assignment of the enolic hydroxyl protons. Since the intramolecular hydrogen-bonding in the monoenol would be stronger than those in the bisenol in which two enol protons are chelated to the common central carbonyl oxygen, enol protons in the *cis,cis*-bisenol are conceivably much more shielded than that of the monoenol, and correspondingly the former signal would appear in a higher field than the latter one. Although the conclusion being different from the assignment, by Marcus *et al.*,[4b] this reasoning is confirmed by comparisons of relative intensities of enol protons of the tautomers in H_2daa, and in H_2mmd of variable temperature NMR measurements, which are described below, especially at lower temperatures. Presence of a monoenol form in the solution phases is consistently indicated in IR spectra which show a sharp intense peak at 1720 cm^{-1}.

Table 2. *Keto-enol* ratio of H_2daa at various temperatures (c=1.0M)

Temp. (°C)	Monoenol (%)	Bisenol (%)	Triketo (%)
	in $CDCl_3$		
48	74	17	9
36	73	21	6
5	68	27	5
−41	68	25	5
	in CCl_4		
56	54	43	3
36	45	54	2
5	36	62	2

Table 2 shows the temperature dependence of keto-enol equilibrium of H_2daa in solution phases, indicating that a higher temperature favors the monoenol form among the tautomeric isomers. This tendency is consistent with the fact that both molten H_2daa and H_2mmd at an elevated temperature reveal a free carbonyl band at 1720 cm^{-1}. Fraction of the triketo form, though being minor, also increases with the elevation of temperature.

On the other hand, as shown in Table 1, bisenol content of H_2daa increases with decrease in polarity of the solvent used. This tendency, being in good agreement with those observed in related pentane-2,4-diones, indicates highly polar character of keto form than an enol form with intramolecular hydrogen-bonding.[6]

Table 3. NMR spectra of H_2mmd at room temperature

Chemical shifts δ(ppm)		Assignment and coupling constants
in CCl_4	in $CDCl_3$	
1.25	1.30 1.32	3j; D, J(jm)=7 Hz 1g; D, J(gl)=7 Hz
1.73	1.73	4k
1.80	1.80	2h
1.98	2.03	4f
2.03	2.07	3e
2.12	2.14 2.18	2d 3c
2.17	2.20—2.24	1a; 2b
3.30	3.40	3m; Q, J(mj)=7 Hz (1l; Q, J(1g)=7 Hz)
3.40	3.50	2p
3.50	3.62	1n
5.37	5.42	4r
5.48	5.52	3q; multiplet
14.42		4v; broad
14.85		4u; multiplet
15.10	(15.10)[b]	3t; diffused
16.03	16.00	2s

a) Numerals and alphabetical letters indicate the formula number and the positions of protons in Fig. 2 respectively.

b) appeared at −41°C, not observable at room temperature.

D: doublet, Q: quartet

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[6] a) M. I. Kobachnik, S. T. Ioffe, E. M. Popov, and K. V. Vatsuro, *Tetrahedron*, **12**, 76 (1961). b) S. T. Yoffe, E. M. Popov, K. V. Vatsuro, E. K. Tulikova, and M. I. Kobachnik, *ibid.*, **18**, 923 (1962).

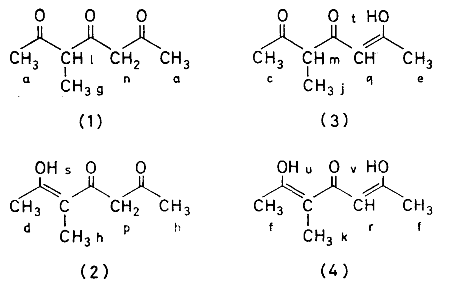

Fig. 2. Tautomeric structures of H_2mmd: (1) triketo, (2) monoenol (B), (3) monoenol (A) and (4) bisenol forms.

TABLE 4. NMR SPECTRA OF H_2dmd AT ROOM TEMPERATURE

Chemical shifts δ(ppm) in CCl_4	Chemical shifts δ(ppm) in $CDCl_3$	Assignment[a] and coupling constants
1.07 1.13	1.13 1.20	2h; D, J(hq)=7 Hz 3j; D, J(jr)=7 Hz
1.25 1.27 1.28	1.32 1.33 1.35	1g(*rac* and *meso*); D, J(gp)=7 Hz 4k, 5k; D, J(kr)=7 Hz
1.40 1.55	1.47 1.62	2l 3m
1.63	1.68	2f, 3f; broad
1.85	1.90	4n
	1.92	5n
1.96	1.98	2b, 3c; broad
2.07	2.17	1a
2.10	2.20	4d
	2.27	5e
2.42 2.48	2.58 2.62	2q; Q, J(qh)=7 Hz 3r; Q, J(rj)=7 Hz
4.64	3.62	all free hydroxyl
3.59 3.70	3.68 3.80	1p(*rac* and *meso*); Q, J(pg)=7 Hz 4r, 5r; Q, J(rk)=7 Hz
16.18	16.25	4s

D: doublet, Q: quartet

a) Numerals and alphabetical letters indicate the formula number and the positions of protons in Fig. 3 respectively.

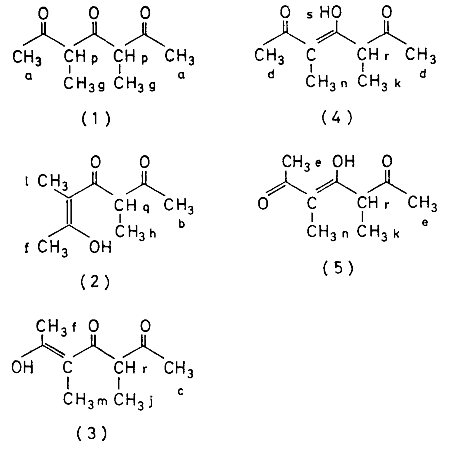

Fig. 3. Tautomeric structurs of H_2dmd: (1) triketo (racemic and meso), (2) *cis*-side-monoenol (A), (3) *trans*-side-monoenol (B), (4) *cis*-central-monoenol and (5) *trans*-central-monoenol forms.

(2-b) Assignments of NMR Signals of H_2mmd and of H_2dmd: Based upon chemical shifts, relative intensities, and spin-spin splitting patterns, NMR signals of H_2mmd and H_2dmd are assigned tentatively as summarized in Tables 3 and 4 accompanied by Figs. 2 and 3. Useful informations are obtained from the results of variable temperature measurements, decoupling measurements, deuterium exchange experiments, and comparisons with IR data in the same solvents.

TABLE 5. *Enol* SIGNALS OF SUBSTITUTED PENTANE-2,4-DIONES (c=1.0M in CCl_4)

1,5-Substituted		3-Substituted	
Substituent	Chemical shifts, δ(ppm)	Substituent	Chemical shifts, δ(ppm)
H- (pentane-2,4-dione)	14.8	methyl-	16.0
1,5-diethyl-	14.9	ethyl-	16.1
1,5-diisopropyl-	15.1	*n*-propyl-	16.1
1,1,1,5,5,5-hexamethyl-	16.7	*n*-butyl-	16.2
(dipivaloylmethane)		benzyl-	16.7[a]

a) Private communication from Prof. Y. Murakami.

The NMR signal of a monoenol proton of H_2dmd appears as a sharp peak at a lower field by 1 ppm as compared with that of H_2daa. Comparisons of chemical shifts of enol protons in some β-dicarbonyl compounds as shown in Table 5, indicate that introduction of an alkyl group to the central carbon causes a deshielding effect upon an enolic hydroxyl signal by about 1 ppm and gives a narrower peak, whereas substitution on side carbons, except with *t*-butyl group does not very much affect the chemical shift, remaining as a broad signal. The deshielding effect observed here is conceivably due to increased hydrogen-bonding of the enol proton which becomes closer to the β-carbonyl oxygen by steric repulsion between methyl groups on the both sides and the alkyl group on the central carbon. Enol proton chemical shift of dipivaloylmethane at an exceptionally lower field may be also explained in a similar manner by steric repulsion between the central hydrogen and bulky *t*-butyl groups on the both sides.

These observations on the enol protons lead that two hydroxyl signals observed at 16.00 and 15.10 ppm in H_2mmd can be assigned to two kinds of enol protons, one carrying an additional methyl group and the other not methylated respectively. Correspondingly the hydroxyl signals at 14.85 and 14.25 ppm of the bisenol form of H_2mmd are also assigned to the two kinds of enol protons in a similar manner.

Measurements on H_2dmd in 100 MHz in deuteriochloroform[7] shows the overlapped doublets centered at 1.33 ppm consisting of three doublets separated by about 0.01 ppm. By deuteration of H_2dmd, the doublet signals of the branched methyl protons coalesce respectively into three broad peaks and signals at a lower field than 2.3 ppm disappear. Combined with the

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[7] Measured with a JNM-PS-100 by courtesy of Mr. A. Kito in the Government Industrial Research Institute, Osaka, to whom the authors are very grateful.

decoupling data, the above results indicate that the missing signals upon deuteration are undoubtedly due to active protons such as an enolic hydroxyl and methine group interposed between two carbonyls and the coalesced signals are those of the methyl groups on the 3- and 5-carbons of H_2dmd. Also the overlapped doublet signals assigned to three kinds of methyl groups, suggest the presence of two diastereomeric triketo forms, one being a *meso*- and another a racemic form, and a monoenol form at the central oxygen, which is not found among monoenol forms of H_2daa and H_2mmd.

Signals assignable to a bisenol form of H_2dmd can not be found in the NMR spectra either in deuteriochloroform nor in carbon tetrachloride. As reported by Kobachinik *et al.*,[6] the methyl group interposed between two carbonyl groups in a *β*-diketone does not prevent the formation of a *cis*-enol with cyclic intramolecular hydrogen-bonding. Absence of a *cis,cis*-bisenol form in H_2dmd would be, therefore, conceivably due to steric repulsion between two methyl groups on the 3- and 5-carbons of H_2dmd. A study with molecular model shows that the coplanar *cis,cis*-bisenol form is accompanied by a strong steric hindrance due to the overlapping of the two methyl groups as illustrated in Fig. 4.

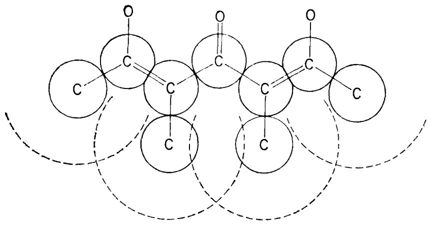

Fig. 4. Coplanar *cis, cis*-bisenol form of H_2dmd, broken semi-circles showing van der Waals radii of the methyl groups.

(2-c) Tautomerism of H_2mmd: H_2mmd in a carbon tetrachloride solution exhibits a widely diffused IR band over the range of 3600 to 2200 cm^{-1}, a sharp absorption at 1720 cm^{-1} and a broad, more intense band from 1650 to 1550 cm^{-1}. In a deuteriochloroform solution the carbonyl band at 1720 cm^{-1} increases in its intensity.

Combined with NMR data, these results indicate that H_2mmd in a solution phase takes in a major portion a *cis*-monoenol as well as a *cis,cis*-bisenol with intramolecular hydrogen-bonding, and that decrease in solvent polarity seemingly favor the *cis,cis*-bisenol form in agreement with a case of H_2daa.

As shown in Table 6, temperature causes substantial effect on the tautomeric composition of H_2mmd in a carbon tetrachloride solution, whereas causing little effect in deuteriochloroform, the keto-enol contents being virtually invariable within the experimental error in so far as a temperature range used (from 55 to 0°C).

Table 6. *Keto-enol* ratio of H_2mmd at various temperatures in mol % (c=0.8M)

Temp. (°C)	Monoenol (A)	Monoenol (B)	Bisenol	Triketo
		in CCl_4		
59	77	8	13	2
36	30	25	46	0
6	13	30	58	0
		in $CDCl_3$		
36	76	9	12	3

(2-d) Tautomerism of H_2dmd: IR spectrum of H_2dmd in deuteriochloroform reveals a prominent hydroxyl band and a free carbonyl band at 3400 and 1720 cm^{-1} respectively, the former absorption indicating evidently the presence of a substantial concentration of a *trans*-enol form. In carbon tetrachloride, the free carbonyl band is splitted into three peaks at 1730, 1715 and 1700 cm^{-1}, which indicate the presence of some configurational isomers in respect to the carbonyl groups.

Consistent with IR data on the hydroxyl group, NMR spectra exhibit a broad signal ascribable to the *trans*-enol proton at 5.90 ppm in deuteriochloroform at −46°C, shifting to a higher field with elevation of temperature as a more sharpened peak, at 3.35 ppm at 46°C. In carbon tetrachloride, the signal appears as a much more diffused band centered at 4.65 and 3.78 ppm at 36 and 55°C respectively.

Table 7. *Keto-enol* ratio of H_2dmd at various temperatures in mol % (c=0.5M)

Temp. (°C)	Side monoenol	Central monoenol	Triketo
	in $CDCl_3$		
50	33	48	19
36	40	45	16
0	51	41	8
	in CCl_4		
56	35	54	11
36	54	30	16

Table 7 shows the temperature dependence of the tautomer content. The presence of a considerable fraction of the triketo form shows a striking contrast to H_2daa and H_2mmd. However, the effect of temperature here seems not so simple as in the other tricarbonyl compounds.

Comparisons of the total enol content of H_2daa, H_2mmd, and H_2dmd suggest that enolizability decreases in the above order and the interposed methyl group seems to hinder enolization. However, the effect of the interposed methyl group seems to be somewhat complicated by combination of both electronic and steric effects. On the other hand, solvents also influence the tautomeric equilibrium in agreement with those observed in *β*-dicarbonyl compounds, polar solvents favoring the abundance of a keto form and less polar solvents an enol form.

Experimental

Materials. Heptane-2,4,6-trione was prepared according to Bethel and Maitland.[8] Mp 41.0—41.5°C (lit. mp 49°C). Found: C, 58.99; H, 7.27%.

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[8] J. R. Bethel and P. Maitland, *J. Chem. Soc.*, **1962**, 3751.

3-Methylheptane-2,4,6-trione: (a) Heptane-2,4,6-trione (10.0 g, 0.0703 mol) was dissolved in ethanolic potassium ethoxide which was prepared from absolute ethanol (30 m*l*) and potassium metal (4.10 g, 0.105 mol). After an addition of methyl iodide (80.0 g, 0.563 mol), the solution was kept at 40—50°C for 20 min. The resulting mixture was evaporated under reduced pressure, giving a slurry, which was filtered to remove potassium iodide. A viscous filtrate was dissolved in chloroform (100 m*l*) and treated with an aqueous cupric acetate (14.0 g of the monohydrate in 300 m*l* of water). The resulting blue chloroform solution containing copper complexes was separated by filtration from precipitates, which was mainly the 2 : 2 (metal ion : ligand) copper complex of H_2daa, being insoluble in chloroform. The filtrate was evaporated to give blue solid, which was dissolved in an aqueous methanol solution of cupric acetate (7.2 g of the monohydrate in 760 m*l* of 10% aq. methanol). The solution, when heated at 50—55°C for 6 hr, gave green precipitates, which, being a 2 : 2 copper complex of H_2mmd, were collected by filtration and dissolved in 1 N hydrochloric acid. Chloroform extract from the above acid solution was evaporated, giving an oil boiling at 45—49°C/5×10^{-3} mmHg. Yield was 3.84 g (35%). Found: C, 61.32; H, 7.92%. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74%. The oil crystallized either spontaneously, but very slowly at room temperature, or from a petroleum ether solution on cooling, to give colorless granular crystals melting at 56.0—56.6°C.

The same compound could be obtained by using sodium or lithium metal in place of potassium in a similar manner as above, but in poorer yields.

In the last methanolic filtrate, there remained the 1 : 2 complex of H_2dmd, being readily soluble in methanol and not convertible into a form of 2 : 2 complex.

(b) A mixture of pyrrolidine (10.0 g, 0.141 mol), heptane-2,4,6-trione (20.0 g, 0.141 mol) and ethyl acetate (100 m*l*) was left standing overnight at room temperature. The resulting yellow crystals, which were collected and dried under reduced pressure, were heated with dried methyl iodide (68.4 g, 0.481 mol) under reflux for 24 hr. The resulting solution was evaporated off, giving a semisolid mass which was heated together with water (100 m*l*) at boiling point. The aqueous mixture was extracted with chloroform (50 m*l*). The chloroform extract was shaken with aqueous cupric acetate thoroughly, and a separated chloroform layer was evaporated, giving blue crystalline residue, which was purified by eluting from a silica gel (WAKOGEL Q-23) column with acetonitrile, to give the 1 : 2 complex of H_2mmd (2.64 g, 20.2%). The free ligand was obtained as described in procedure (a).

The position to which a methyl group was introduced, was confirmed by acid-catalyzed intramolecular condensation of H_2mmd into 2,3,6-trimethyl-γ-pyrone as well as by the following NMR studies on this trione.

3,5-Dimethylheptane-2,4,6-trione: H_2daa (10.0 g, 0.0703 mol) was treated in a similar manner as above, using absolute ethanol (160 m*l*), potassium (8.10 g, 0.210 mol) and methyl iodide (94 g, 0.68 mol). The reaction took 2 hr at 55°C to afford 1.53 g of the 2 : 2 complex of H_2mmd and 5.8 g of the 1 : 2 complex of H_2dmd. Decomposition of the H_2dmd complex with 1 N hydrochloric acid followed by extraction with chloroform and subsequent evaporation gave colorless oil, which was solidified when treated with petroleum benzine. Recrystallization from a benzene-petroleum benzine (1 : 1) mixture afforded fibrous needles melting at 81.5—82.5°C. Yield was 2.30 g (19.2%). Bp 105—110°C/4 mmHg. Found: C, 63.23; H, 8.54%. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29%. The methylated positions on the heptanetrione were confirmed by derivation of H_2dmd into 2,3,5,6-tetramethyl-γ-pyrone as well as the NMR studies on this trione.

2,3,6-Trimethyl-γ-pyrone from H_2mmd. A chloroform solution of H_2mmd was heated together with a catalytic amount of 0.1 N hydrochloric acid for 5 hr. The resulting solution was evaporated to dryness and solid residue was sublimed. Mp 82.0—84.0°C, yield being 84%. Found: C, 69.58; H, 7.37%. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.30%. NMR (1.0 M in $CHCl_3$): Four singlets at 1.93 (3H), 2.30 (3H), 2.35 (3H), and 6.64 ppm (1H). IR (Nujol mull): $\nu_{C=O}$ 1675 cm^{-1}.

The structure of the product was characterized by spectral comparisons with 2,6-dimethyl-γ-pyrone⁹⁾ (Mp 135.5—137°C. Found: C, 67.47; H, 6.51%. NMR (1.0 M in $CHCl_3$): Two singlets at 2.25 (6H) and 6.00 ppm (2H). IR (Nujol mull): $\nu_{C=O}$ 1675 cm^{-1}) and 2,3,5,6-tetramethyl-γ-pyrone¹⁰⁾ (Mp 91.0—92.0°C. Found: C, 70.46; H, 8.06%. NMR (1.0 M in $CHCl_3$): Two singlets at 1.92 (6H) and 2.23 ppm (6H). IR (Nujol mull): $\nu_{C=O}$ 1660 cm^{-1}) which were obtained from H_2daa and H_2dmd respectively in a similar manner described above.

Deuteration of H_2dmd. H_2dmd (86 mg) was dissolved in a mixture of methanol-d_4 (328 mg) and heavy water (183 mg). Exchange reaction was traced by NMR measurements immediately after an addition of a drop of pyridine. The reaction was completed in 2 hr at 35°C. The resulting solution was evaporated to dryness under high vacuum (10^{-4} mmHg) at room temperature, to give colorless solid melting at 85—87°C. Treatment with methanol and successive drying afforded the original H_2dmd, which was identified by the infrared spectral comparison.

The β-dicarbonyl compounds quoted in Table 5 were either commercially available or synthesized in our laboratory unless otherwise described.

IR spectra were measured on a JASCO 403-G in both KBr disc and Nujol mull phases for crystalline samples. Of solution phases, the concentrations of samples were prepared so as to be equal to those of NMR samples respectively. NMR spectra were recorded on a Varian A-60 instrument. All chemical shifts from tetramethylsilane were calibrated by use of chloroform proton chemical shift to be 7.27 ppm, both used as internal references. Contents of tautomeric isomers were determined by the least squares calculation from the respective peak areas unless otherwise stated.

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10) J. N. Collie, *J. Chem. Soc.*, **77**, 962 (1900).