

Structural Assignment to (*E*)- and (*Z*)-2-Methyl-1,3,5-triphenyl-2-pentene-1,5-diones and Configurational Studies on some 1,5-Enedione Enolates

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Structures were assigned to the *E*- and *Z*-methyl-1,3,5-triphenyl-2-pentene-1,5-diones by one- and two-dimensional NMR spectroscopy. The activation energy, ΔG^\ddagger (11.0–14.3 kcal mol⁻¹), for the rotational barrier of the 1,3,5-triphenyl-2-pentene-1,5-dione anion and related 1,5-enedione enolates was determined by dynamic ¹³C NMR spectroscopy and discussed in terms of the interconversion between two (identical) *sickle*-like configurations.

The ring opening of pyrylium salts by hydroxide ion to 1,5-enediones (acyclic pseudo-bases) has been illustrated by numerous examples.¹ In principle, such 1,5-enediones can exist in two stereoisomeric forms (*E/Z*), but as a rule only one isomer was obtained and its configuration not studied in detail. Only in a few cases were both stereoisomers obtained,² or isolated³ and characterized.⁴

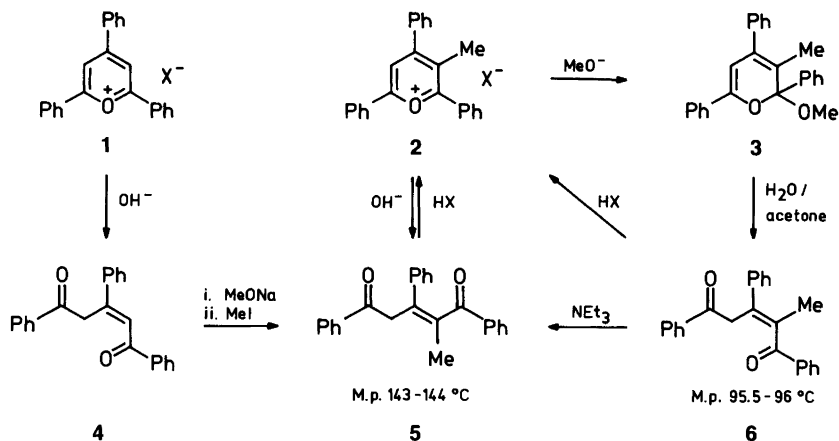
In this paper we report structural assignment to the (*E*)- and (*Z*)-isomers of 2-methyl-1,3,5-triphenyl-2-pentene-1,5-dione, which is the acyclic pseudo-base of 3-methyl-2,4,6-triphenylpyrylium salts. Furthermore, the configurational interconversion of the 1,3,5-triphenyl-2-pentene-1,5-dione anion and related 1,5-enedione enolates has been studied.

Formation and structure of 2-methyl-1,3,5-triphenyl-2-pentene-1,5-dione stereoisomers

Ring opening of 2,4,6-triphenylpyrylium salts (**1**) by OH⁻ ion yielded the (*E*)-configured 1,3,5-triphenyl-2-pentene-1,5-dione (**4**) with an *s-cis* situated carbonyl group.⁵ Sodium methoxide

transformed **4** into a sodium enolate,⁶ which recently has been isolated and spectroscopically characterized.^{7,8} The reaction of this enolate with methyl iodide gave a methyl derivative of m.p. 143–144 °C which initially was assumed to be an *O*-alkylation product,^{5,6} whereas later investigations showed that *C*-alkylation occurred, leading to a 2-methyl-1,3,5-triphenyl-2-pentene-1,5-dione of unknown configuration.^{4,8,9} The same product is formed by base-induced ring opening of 3-methyl-2,4,6-triphenylpyrylium salts (**2**).^{4,10} On the other hand, on treating 2-methoxy-3-methyl-2,4,6-triphenyl-2*H*-pyran (**3**), prepared from **2** and sodium methoxide in absolute methanol,¹¹ with aqueous acetone, an isomeric 2-methyl-1,3,5-triphenyl-2-pentene-1,5-dione of m.p. 95.5–96 °C was formed.¹² The latter isomerized completely on heating with triethylamine in acetone to give the higher melting form. On treating with mineral acids (e.g. perchloric acid), both isomers recyclyzed to the starting pyrylium system **2**, but the lower-melting isomer in a fast, and the higher-melting isomer in a slow reaction. Since precyclic configurations generally favour ring closure reactions, we assumed that the higher-melting product was the (*Z*)-isomer (**5**) and the lower-melting one the (precyclic) (*E*)-

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Scheme 1.

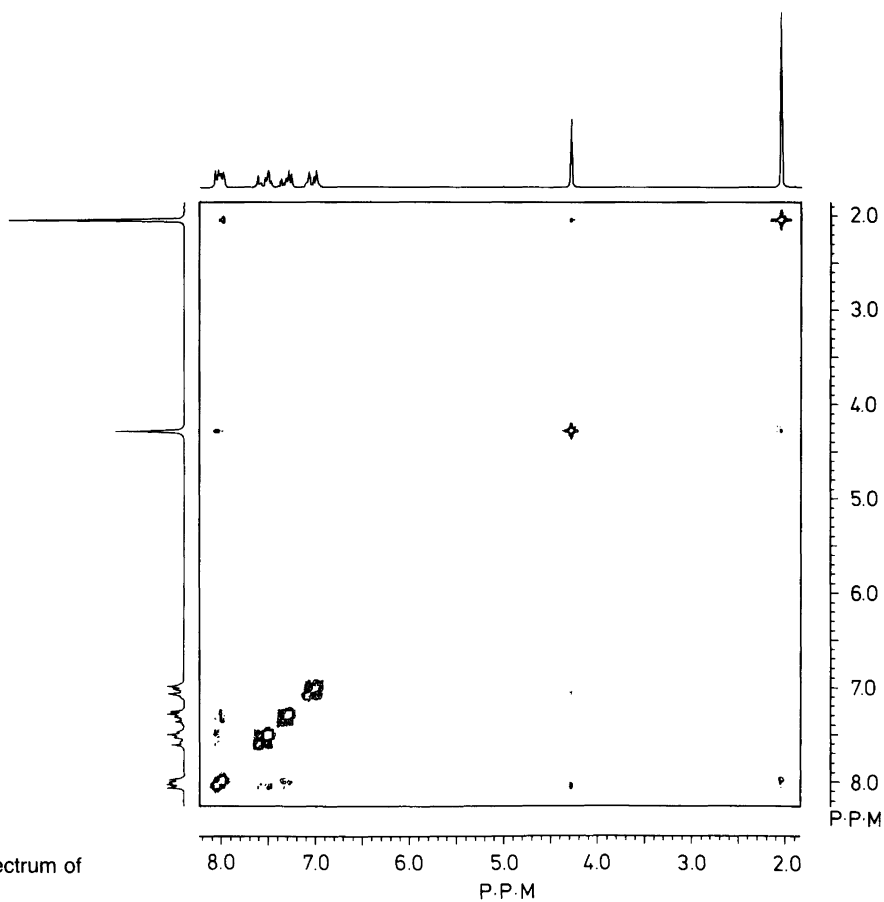


Fig. 1. NOESY spectrum of compound 5.

isomer (**6**) (Scheme 1). Unequivocal evidence for this assignment has now been obtained by one- and two-dimensional NMR spectroscopy.

The ^1H and ^{13}C NMR spectra of **5** and **6** have been recorded. Only minor differences were observed between the two isomers. The nuclear Overhauser effect (NOE) between the protons in the CH_3 and CH_2 groups is *a priori* expected to be quite different in the two isomers. In order to distinguish **5** from **6** by use of this difference we have recorded the two-dimensional nuclear Overhauser effect spectroscopy (NOESY) spectra of both isomers. The NOESY spectrum (Fig. 1) of **5** exhibited a clear off-diagonal peak between the CH_3 and CH_2 protons. This was not the case for isomer **6**. The conclusion obtained in this way was further confirmed by one-dimensional NOE difference spectroscopy, where a clear NOE effect between CH_3 and CH_2 was observed in **5**, whereas such an effect was absent in the case of **6**. Consequently, the NOE experiments confirm that **5** is in fact the (*Z*)-isomer and **6** the (*E*)-isomer.

Long-range ^1H - ^1H spin-spin coupling constants for coupling between CH_3 and CH_2 have been observed for both **5** and **6**. The value of this coupling constant was 0.5 Hz for **5** and 1.0 Hz for **6**. A comparison of these values in terms of the zig-zag rule¹³ for long-range coupling constants underlined the assignment to the two isomers of structures **5** and **6**.

Interconversion of 1,5-enedione anions

The successful isolation of alkali enolates of **4** and related 1,5-enediones under anhydrous conditions enabled us to study not only their chemical reactivity* (e.g. towards organic isothiocyanates^{7,15} or alkylating agents)^{8,9} but also their spectroscopic properties in more detail. Thus, we noted^{7,8} that ^1H and ^{13}C NMR spectra of the 1,5-enedione anions exhibited broad lines for the proton and carbon resonance at C-2 and C-4; this effect was explained in terms of a fast interconversion between two different configurations.⁷

Complete electronic delocalization in the 1,3,5-trisubstituted enol anions limits the number of possible configurations, as steric requirements of the substituents render the planar all-*trans*

configuration **7** (*W*-form) as well as the all-*cis* configuration **8** impossible. Furthermore, CNDO/2 (complete neglect of differential overlap, version 2) calculations^{16,8} indicated that the *U*-form (**10**) was energetically more favourable than the corresponding *W*-form (**7**).

However, *sickle*-forms of type **9** can be planar and therefore are responsible for the dynamic process according to the equilibrium $\mathbf{9} \rightleftharpoons \mathbf{10} \rightleftharpoons \mathbf{9}$ (Scheme 2), where only the *sickle* form is appreciably populated although the average structure in this dynamic equilibrium is equivalent to the *U*-form (**10**). In the case of enolate **10a**, i.e. the sodium salt of 1,3,5-triphenyl-2-pentene-1,5-dione (**4**), the ^{13}C NMR spectrum in the region near 103 ppm showed distinct lines from C-2 and C-4 at low temperature, but only one common line at high temperature. We have investigated this dynamic process by a temperature study of the ^{13}C NMR spectrum and explained it in terms of the interconversion between the two (identical) *sickle*-forms (**9a**). Fig. 2 shows the important part of the spectra in these experiments.

In order to determine the free energy (ΔG^\ddagger) for a rotational barrier by dynamic NMR, two methods are mainly used, namely a total line-shape analysis or the simple approximative method^{17,*} in which ΔG^\ddagger can be found when the coalescence temperature T_c and the peak separation at low temperature are known; here, the approximative method was used.

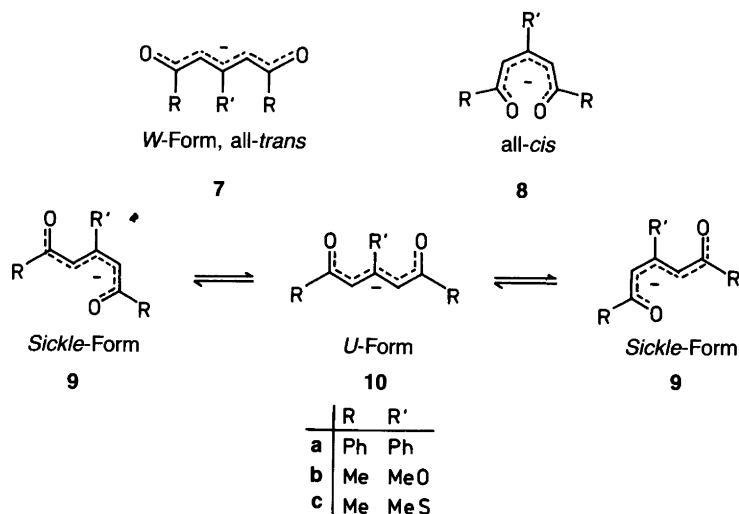
The result for **10a** is given in Table 1 and is compared with the data for the 1,5-dimethyl-3-methoxy-2-pentene-1,5-dione anion (**10b**) and the 1,5-dimethyl-3-thiomethoxy-2-pentene-1,5-dione anion (**10c**) obtained by the same type of experiment. The values found here are of the same order of magnitude as those found for hindered

*The CNDO/2 method gives the following results:

Anion	Energy/au		$E_U - E_W/\text{kcal mol}^{-1}$
	<i>U</i> -form (10)	<i>W</i> -form (7)	
a	-212.9461	-212.8970	-30.8
b	-120.2976	-120.2923	- 3.3
c	-112.2571	-112.2331	-15.1

*For a review on the reactivity of the parent glutaldehyde anion see Ref. 14.

*According to Ref. 17:
 $\Delta G_c^\ddagger = 4.57 T_c [9.97 + \log(T_c/\delta\nu)]$ in kcal mol^{-1} .



Scheme 2.

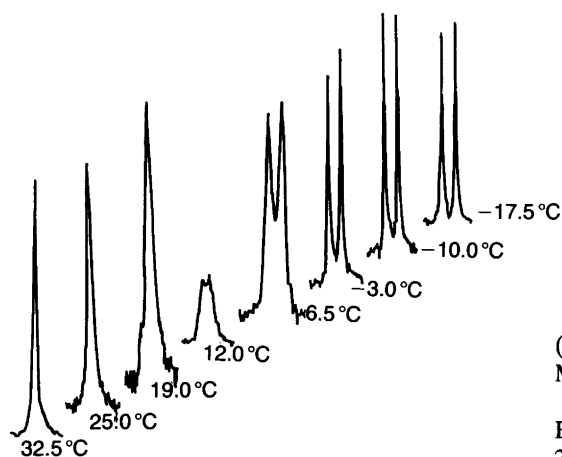


Fig. 2. Coalescence temperature T_c for the rotational barrier in the anion **10a**. The band at $\delta = 103.03$ ppm in the ^{13}C NMR spectrum was used.

rotation in enol anions of the acetylacetonone type.¹⁸

Experimental

Melting points were determined on a BOËTIUS apparatus. IR spectra (KBr) were recorded on a Perkin-Elmer 225 spectrophotometer and UV/Vis spectra on a Unicam SP 8000 instrument

(25°C). Mass spectra were recorded on a Varian MAT CH 6 spectrometer (70 eV).

The ^1H NMR spectra were obtained on a Bruker AC 250 NMR spectrometer operating at 250.13 MHz for protons. The NOESY experiments were performed in CDCl_3 as solvent by using the pulse sequence: $90^\circ-t_1-90^\circ-\tau-90^\circ\text{-aq}$. Values of τ varying between 0.5 s and 1.5 s were used to maximize the NOE effects. The dynamic ^{13}C NMR spectra were obtained with a Jeol FX 60Q spectrometer with a standard variable tem-

Table 1.

Compound	T_c/K	$\delta\nu/\text{Hz}$	$\Delta G_c^\ddagger/\text{kcal mol}^{-1}$
10a	287	34.5	14.3
10b	237	153.3	11.0
10c	264	117.0	12.5

perature regulator (15.03 MHz, pulse width 8 μ s, 60°, 8 K datapoints).

The ^{13}C NMR spectra of **5** and **6** were recorded on a Bruker AC 250 NMR spectrometer (62.90 MHz, power-gated, pulse width 7 s, 90°, repetition rate 4 s, 32 K datapoints).

Compounds **5**,⁴ **10a**,⁷ **10b**¹⁵ and **10c**¹⁵ were prepared according to procedures given in the literature. DMF-*d*₇ was used as solvent for **10a-c** in the dynamic NMR experiments.

(*Z*)-2-Methyl-1,3,5-triphenyl-2-pentene-1,5-dione (**5**). M.p. 143–144°C (ethanol). IR (KBr): C=O 1681, COCH=CH 1665 cm^{-1} . ^1H NMR (CDCl_3): δ CH_3 1.96 (s), CH_2 4.21 (s), H_{aryl} 6.9–8.1 ppm (m). ^{13}C NMR (CDCl_3): δ CH_3 18.08, CH_2 44.48, conjugated CO 196.27, CH_2CO 200.89 ppm. UV (cyclohexane): λ_{max} (log ϵ) 242 (4.48), 275 sh nm (4.03). MS (70 eV): *m/z* (rel. int. %) 340 M^+ (2), 235 ($\text{M}-\text{C}_6\text{H}_5\text{CO}$)⁺ (9), 105 $\text{C}_6\text{H}_5\text{CO}^+$ (100), 77 C_6H_5^+ (60).

(*E*)-2-Methyl-1,3,5-triphenyl-2-pentene-1,5-dione (**6**). 2-Methoxy-3-methyl-2,4,6-triphenyl-2*H*-pyran (**8**)⁸ (1.77 g, 5 mmol) was heated with 20 ml acetone and 5 ml water for 5 h under reflux. Cooling and addition of water gave 1.45 g (85%) of **6**; colourless needles from acetone/water, m.p. 95.5–96°C. IR (KBr): C=O 1683, COCH=CH 1653 cm^{-1} . ^1H NMR (CDCl_3): δ CH_3 1.86 (s), CH_2 4.04 (s), H_{aryl} 7.8–8.0 (m). ^{13}C NMR (CDCl_3 , TMS): δ CH_3 18.31, CH_2 44.81, conjugated CO 196.23, CH_2CO 200.57 ppm. UV (cyclohexane): λ_{max} (log ϵ) 243 (4.49), 271 sh nm (4.04). MS (70 eV): *m/z* (rel. int. %) 340 M^+ (2), 235 ($\text{M}-\text{C}_6\text{H}_5\text{CO}$)⁺ (10), 105 $\text{C}_6\text{H}_5\text{CO}^+$ (100), 77 C_6H_5^+ (41). Anal. $\text{C}_{24}\text{H}_{20}\text{O}_2$: C, H.

Isomerization of the (E)-enedione (6) to the (Z)-enedione (5). Enedione **6** (0.34 g, 1 mmol) and triethylamine (0.10 g, 1 mmol) were heated under reflux in 10 ml of acetone for 1 h. Cooling and addition of water gave 0.32 g (94%) of **5** as colourless crystals, m.p. 143–144°C, identical with the compound obtained from the pyrylium salt **2**.⁴

Recyclization of the enediones 5 and 6. Equimolar amounts of **5** and **6** were treated dropwise with concentrated (70%) perchloric acid. From the solution of **6**, 3-methyl-2,4,6-triphenylpyrylium perchlorate (**2**) crystallized immediately, whereas **5** gave the same salt **2**, but only after prolonged standing at room temperature.

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