Preparation, spectral studies and X-ray crystal structure of 1,3,5-triphenyl-1,5-pentanedione, C₂₃H₂₀O₂

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1,3,5-triphenyl-1,5-pentanedione, $C_{23}H_{20}O_2$, has been prepared and characterized by spectroscopic methods and single crystal X-ray analysis. Crystals are monoclinic, space group $P2_1/n$, a = 28.124(4), b = 5.997(1), c = 10.434(1)Å, $\beta = 98.42(1)^\circ$, Z = 4. The structure has been refined to a final *R*-value of 0.040 for 1625 reflections with $F_o > 3\sigma(F_o)$. The compound contains the two carbonyl groups in a mutually *cis* arrangement.

KEY WORDS: C₂₃H₂₀O₂, diketone, *cis* arrangement.

Introduction

In connection with our work^{1,2} on the mechanism of the Latif reaction,^{3,4} we isolated, among other compounds, 1,3,5-triphenyl-1,5-pentanedione from the reaction of benzaldehyde, acetophenone and sodium sulphide in aqueous methanol. Herein we describe several methods for the preparation of this useful diketone, its spectral characteristics and X-ray crystal structure.

Experimental

Preparation

(A). From benzaldehyde, acetophenone and sodium sulphide in aqueous methanol. A mixture of benzaldehyde (0.01 mol), acetophenone (0.02 mol) and methanol (25 cm³) were placed in a three-necked round bottomed flask fitted with a reflux condenser, a pressure equalizing dropping funnel and a strong magnetic index. A solution of sodium sulfide (0.03 mol) in water (25 cm³) was then added dropwise over a period of 10 min. The temperature of the oil-bath was maintained at 60°C. A yellowish color developed. The mixture was refluxed (reaction temperature 70°C, the oil bath temperature 95-100°C) for 2 h with constant stirring and then cooled and extracted with ether. The ether extract was washed with distilled water, dried over anhydrous sodium sulphate, filtered and distilled to remove the solvent to give a yellow liquid. Column chromatographic separation {silica gel 60-120 mesh, 1:1 mixture of benzene-petroleum ether (b.p. 60-80°C)} of the liquid mass and subsequent recrystallization from the eluent mixture, gave among other compounds, 1,3,5-triphenyl-1,5-pentanedione, (I), m.p. 81.5-82.5°C, in 10% yield.

$$Ph_a - CH(CH_2COPh_b)_2$$
 (I)

The IR spectrum of the compound gave the following important absorption peaks, ν_{max} cm⁻¹: 3050, 3030 (aromatic C-H str), 1680 (C=O str), 1584, 1575 (aromatic skeletal), 1276, 1235, 1216, 1000, 978; and 757 and 698 (aromatic out-of-plane C-H bending). UV, λ_{max} (ethanol): 211, 244 (C=O) and 280.5. The ¹H NMR spectrum of the compound has the following signals, δ (ppm): 7.94 (d, 4H, ortho COPh_b), 7.54 (t, 2H, *para* COPh_b), 7.44 (t, 4H, meta COPh_b), 7.15-7.30 (m, 5H, Ph_a), 4.07 (quintet, 1H, benzylic, J 7.0 Hz) 3.49 (d, d, 2H, one proton of CH₂CO, J 7.0 and 16.8 Hz), and 3.36 (d, d, 2H, the other H of the CH₂CO, J

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7.0 and 16.8 Hz); ¹³C NMR, δ (ppm): 198.5 (C=O), 143.7 (*ipso* C of Ph_a), 136.8 (*ipso* C of Ph_b), 133.0, 128.6, 128.5, 128.1, 127.4, 126.6 (aromatic C), 44.9 (CH₂), and 37.1 (benzylic C). The mass spectrum of the compound has the following important peaks, m/z, 328 (M⁺), 209 (M-CH₂COPh)⁺, 105 (PhCO)⁺, 77 (Ph)⁺. Also formed in this reaction were 1,3-diphenyl-2-propen-1-one and 3-benzoyl-2,6-diphenyl-4-hydroxy-4-phenyltetrahydro-thiopyran, but these would be reported elsewhere.

The above reaction when conducted in aqueous ethanol rather than aqueous methanol the yield of (I) was 8%.

(B). From benzaldehyde, acetophenone and sodium hydroxide in water. Benzaldehyde (0.01 mol) and acetophenone (0.02 mol) were added to a solution of sodium hydroxide (0.03 mol) in water (25 cm^3) in a one necked-flask fitted with a reflux condenser and the mixture was refluxed for 2h while continuously being stirred magnetically. The reaction mixture was allowed to cool to room temperature, extracted with ether and worked up as described above to give (I) in 80% yield, m.p. $81-82^{\circ}C$, and 1,3-diphenyl-2-propen-1-one in 14% yield.

(C). From 1,3-diphenyl-2-propen-1-one, acetophenone and sodium hydroxide in aqueous ethanol. 1,3-Diphenyl-2-propen-1-one (0.01 mol) and acetophenone (0.01 mol) were added to a solution of sodium hydroxide (0.02 mol) in water (30 cm³) and the mixture was refluxed for 2h with continuous stirring. The reaction mixture was cooled, extracted with diethyl ether (3 \times 25 cm³), the ether extract dried over anhydrous sodium sulphate, filtered and solvents removed. Recrystallization from absolute ethanol gave (I), m.p. 81-82°C, in 44% yield.

X-ray Crystallography

Crystal data; $C_{23}H_{20}O_2$, M.W. 328.41, monoclinic, $P2_1/n$ (No. 14), a = 28.124(4), b = 5.997(1), c = 10.434(1)Å, $\beta = 98.42(1)^\circ$, V = 1740.74Å³, Z = 4, $D_c = 1.253$ g cm⁻³, F(000) = 696e, $\mu = 0.43$ cm⁻¹.

The crystallographic measurements were made on a colorless prismatic crystal $0.45 \times 0.40 \times 0.25$ mm using an Enraf-Nonius CAD4 diffractometer and graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). The unit-cell parameters and orientation matrix for data collection were obtained from least-squares refinement of 15 reflections ($12 < \theta < 14^{\circ}$). The intensity data were collected at room temperature (298K), ω -2 θ scan, scan width ($0.8 + 0.35 \tan \theta$)°, scan speed 0.07-0.27° s⁻¹, in a manner described previously.⁵ Reflections

(2900) were measured (1.5 < θ < 23°; h = -30, 30; k = 0, 6; l = 0, 11), processed and merged to give 2421 unique reflections ($R_{int} = 0.008$), of which 1625 were considered observed $[F_{\alpha} > 3\sigma(F_{\alpha})]$ and used in the refinement. Three standards measured every 100 reflections did not show any significant variations in intensities. The data were corrected for Lorentz and polarization effects but not for absorption or extinction. The structure was solved by direct methods using SHELX-86⁶ and refined by full-matrix least-squares using SHELX-80.⁷ The refinement based on F [non-Hatoms anisotropic, H atoms in calculated positions with C-H = 0.96 Å and a common U_{iso} free to refine which had a final value of 0.068(2)Å²] converged at $R = \Sigma(\Delta F)/\Sigma(F_o) \approx 0.0396$ and $Rw = [\Sigma w(\Delta F)^2/$ $\Sigma w(F_{o})^{2}$]^{1/2}} = 0.0388 for 1625 observed reflections and 227 variables; $(\Delta/\sigma)_{max} = 0.002$; final difference map showed maximum and minimum of +0.14 and -0.22 eÅ⁻³ which were of no stereochemical significance. The weighting scheme used was $w = 1/[\sigma(F_{\alpha})]$ + 0.0015 $(F_o)^2$], which gave reasonably flat analyses of variance with F_o/F_{max} and $(\sin \theta)/\lambda$. Neutral atom scattering factors were as in SHELX-80.⁷ The calculations were performed on a T800 transputer hosted by an IBM/ AT personal computer. Diagrams were drawn with SNOOPI.⁸ The positional and isotropic equivalent displacement coefficients for the nonhydrogen atoms, and the bond lengths and angles are given in Tables 1 and 2, respectively.

Results and discussion

The reaction of benzaldehyde, acetophenone and sodium sulphide in water-methanol gave 1,3,5-triphenyl-1,5-pentanedione (I) in 10% yield. Additionally, the reaction produced 1,3-diphenyl-2-propen-1-one and 3-benzoyl-2,6-diphenyl-4-hydroxy-4-phenyltetra-hydro-thiopyran.^{1,2} Compound (I) has also been prepared in excellent yield (80%) from the reaction of acetophenone, benzaldehyde and sodium sulphide in water. The identity of the compound (I) was suggested to be 1,3,5-triphenyl-1,5-pentanedione from spectroscopic results and confirmed by a single crystal structure analysis.

The X-ray structure of (I) is shown in Fig. 1. The corresponding bond lengths and angles within the two $-CH_2COC_6H_5$ moieties bonded to C(1) are equal within experimental errors, and have values as expected for this type of molecule. The C=O bond lengths 1.218(4) and 1.217(4) Å are comparable with the average value of 1.218(3) Å reported for other compounds.^{9,10} Although

Table 1. Fractional atomic co-ordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\dot{A}^2 \times 10^3$) for C₂₃H₂₀O₂

	x	у	z	$U_{eq}^{\ a}$
O(1)	4156(1)	491(3)	9155(2)	75(1)
O(1')	2756(1)	-760(3)	5808(2)	70(1)
C(1)	3412(1)	1998(4)	7339(2)	46(1)
C(2)	3616(1)	3450(4)	8496(2)	50(1)
C(3)	4043(1)	2413(4)	9336(2)	49(1)
C(4)	4323(1)	3754(4)	10383(2)	43(1)
C(5)	4761(1)	2929(4)	10994(2)	53(1)
C(6)	5035(1)	4153(5)	11935(2)	61(1)
C(7)	4878(1)	6204(5)	12293(2)	61(1)
C(8)	4448(1)	7032(5)	11700(2)	59(1)
C(9)	4173(1)	5821(4)	10749(2)	50(1)
C(2')	2914(1)	2795(4)	6736(2)	53(1)
C(3')	2674(1)	1230(5)	5714(2)	50(1)
C(4')	2334(1)	2099(4)	4609(2)	47(1)
C(5')	2217(1)	748(5)	3533(3)	63(1)
C(6')	1909(1)	1490(6)	2474(3)	79(1)
C(7')	1708(1)	3559(7)	2476(3)	79(1)
C(8')	1810(1)	4900(5)	3535(3)	73(1)
C(9')	2128(1)	4204(5)	4599(3)	60(1)
C(10)	3752(1)	1877(4)	6329(2)	41(1)
C(11)	4003(1)	-51(4)	6165(2)	50(1)
C(12)	4308(1)	-185(5)	5247(3)	61(1)
C(13)	4366(1)	1596(6)	4475(3)	66(1)
C(14)	4119(1)	3523(5)	4618(2)	66(1)
C(15)	3815(1)	3671(4)	5543(2)	54(1)

^{*a*} U_{eq} is defined as one-third of the orthogonalized U_{ii} tensor.



Fig. 1. X-ray Structure of C23H20O2 showing the atom labeling used.

Table 2. Bond lengths (Å) and angles (°) for $C_{23}H_{20}O_2$

C(3)-O(1)	1.218(4)	C(3')-O(1')	1.217(4)
C(2) - C(1)	1.531(5)	C(2')-C(1)	1.526(5)
C(3) - C(2)	1.511(5)	C(3')-C(2')	1.504(5)
C(4) - C(3)	1.487(4)	C(4')-C(3')	1.481(4)
C(5) - C(4)	1.392(4)	C(5')-C(4')	1.385(4)
C(9)-C(4)	1.382(4)	C(9')-C(4')	1.388(4)
C(6)-C(5)	1.369(4)	C(6')-C(5')	1.375(5)
C(7)-C(6)	1.376(5)	C(7')-C(6')	1.363(5)
C(8)-C(7)	1.370(4)	C(8')-C(7')	1.363(5)
C(9)-C(8)	1.373(4)	C(9')-C(8')	1.383(5)
C(10) - C(1)	1.523(5)	C(11)-C(10)	1.379(4)
C(15)-C(10)	1.380(4)	C(12) - C(11)	1.379(4)
C(13)-C(12)	1.362(4)	C(14)-C(13)	1.367(5)
C(15)-C(14)	1.384(4)		
C(3) - C(2) - C(1)	113.4(3)	C(3') - C(2') - C(1)	112.7(3)
C(2) = C(3) = O(1)	120.2(3)	C(2')-C(3')-O(1')	119.6(3)
C(4)-C(3)-O(1)	120.2(3)	C(4') - C(3') - C(1')	120.1(3)
C(4) - C(3) - C(2)	119.6(3)	C(4')-C(3')-C(2')	120.3(3)
C(5) - C(4) - C(3)	118.9(3)	C(5')-C(4')-C(3')	118.3(3)
C(9) - C(4) - C(3)	122.5(3)	C(9') - C(4') - C(5')	118.5(3)
C(9) = C(4) = C(5)	118.6(3)	C(9')-C(4')-C(3')	123.2(3)
C(6) = C(5) = C(4)	120.3(3)	C(6')-C(5')-C(4')	120.6(4)
C(7) - C(6) - C(5)	120.3(3)	C(7')-C(6')-C(5')	120.4(4)
C(8) - C(7) - C(6)	119.9(3)	C(8')-C(7')-C(6')	120.0(4)
C(9)-C(8)-C(7)	120.1(4)	C(9')~C(8')-C(7')	120.5(4)
C(8) = C(9) = C(4)	120.8(3)	C(8')-C(9')-C(4')	120.0(4)
C(10) - C(1) - C(2)	111.9(3)	C(2') - C(1) - C(2)	111.2(3)
C(10) - C(1) - C(2')	111.1(3)	C(11) - C(10) - C(1)	120.7(3)
C(15) - C(10) - C(1)	121.5(3)	C(15) - C(10) - C(11)	117.8(3)
C(12) - C(11) - C(10)	121.2(3)	C(13) - C(12) - C(11)	120.4(4)
C(14) - C(13) - C(12)	119.5(3)	C(15) - C(14) - C(13)	120.4(4)
C(14) - C(15) - C(10)	120.8(3)		

the sum of the inter-bond angles at the two carbonyl carbons C(3) and C(3') are each 360.0 showing their planar configurations, the C=O bonds are somewhat out of the C(1)-C(2)/C(2')-C(3)/C(3') planes as indicated by the torsion angles C(1)-C(2)-C(3)-O(1) = $-8.7(4)^{\circ}$ and C(1)-C(2')-C(3')-O(1') = 31.6(4)^{\circ}. Similarly, the C=O bonds are also noncoplanar with the neighboring phenyl rings, as indicated by the torsion angles $O(1)-C(3)-C(4)-C(5) = 11.1(4)^{\circ}$ and $O(1')-C(3')-C(4')-C(5') = 17.4(4)^{\circ}$. It is observed that the torsion angles involving C(3') = O(1') are larger than the corresponding values involving C(3)=O(1); this may be attributed to the intramolecular short $H(9') \cdot \cdot \cdot H(2'A)$ contact of 2.26 Å which is ~0.14Å less than the van der Waals' radii sum (2.40 Å). The $H(9) \cdot \cdot \cdot H(2A)$ and $H(9) \cdot \cdot \cdot H(2B)$ contacts are 2.45 and 2.42Å respectively. It also appears that the above $H \cdot \cdot \cdot H$ short contacts are responsible for the C(3)-C(4)-C(9) and C(3')-C(4')-C(9') angles [122.5(3) and 123.2(3)°] being larger than the corresponding C(3)-C(4)-C(5) and C(3')-C(4')-C(5') angles [118.9(3) and 118.3(3)°] by 3.6(4) and 4.9(4)°,



Fig. 2. Packing of the molecules in the unit cell viewed along b.

respectively. The phenyl rings are all planar [maximum atomic deviation 0.011(4)Å], and have C-C bonds 1.362(4) to 1.392(5)Å [average 1.376(4)Å] and C-C-C angles 117.8(3) to $121.2(3)^{\circ}$ [average $120.0(4)^{\circ}$]. The shortest intermolecular nonhydrogen contact is 3.254(5)Å [C(9)···O(1) at x, 1 + y, z] which indicates that the molecules are held together in

the crystal by van der Waals' forces. The packing of molecules in the unit cell is shown in Fig. 2.

Mechanism

Since sodium sulphide in water produces a highly basic medium, we propose the following mechanism for the formation of (I):

$$PhCOCH_{3} \stackrel{OH^{-}}{\Longrightarrow} PhCOCH_{2} + H_{2}O$$

$$O^{-}$$

$$PhCOCH_{2} + PhCHO \rightarrow PhCH--CH_{2}COPh \xrightarrow{H_{2}O}$$

$$OH$$

$$OH$$

$$Ph-CH-CH_{2}COPh \xrightarrow{-H_{2}O} PhCH=CHCOPh \xrightarrow{PhCOCH_{2}}$$

$$O^{-} CH_{2}COPh$$

$$PhCH-CH=CPh \xrightarrow{H_{2}O} PhCH$$

$$PhCO-CH_{2} CH_{2}COPh$$

$$(I)$$

Structure of 1,3,5-triphenyl-1,5-pentanedione

In support of this mechanism, we have found that 1,3diphenyl-2-propen-1-one is formed as by product in the two reactions described above. Further, the reaction of 1,3-diphenyl-2-propen-1-one with acetophenone in an aqueous alkaline medium produces (I) in 44% yield.

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