obtained in a yield of 0.276 g. as a sirup and oxidized by bromine in presence of barium carbonate to yield 3,4-di-*O*-methyl-D-xylono-δ-lactone with m.p. and mixed m.p. 65–67°, $[\alpha]^{25}D$ −51° (10 min.) → −21° (48 hours, *c* 2, water), after recrystallization from ether.

Further Examination of Fractions III, IV and V.—Five-mg. samples of fractions III, IV and V were heated at 100° with 1-ml. portions of 1 *N* sulfuric acid for 16 hours, then neutralized with barium carbonate, filtered and shaken with Amberlite resin IRA-45(OH). Paper chromatography in solvent B, spray A, then indicated xylose as the major neutral product from each fraction. In addition, components corresponding to the following sugars also were detected in much smaller amounts; III, galactose (R_x 0.43) and mannose (R_x 0.67); IV, galactose, glucose (R_x 0.54), mannose and rhamnose (R_x 1.44); V, galactose, glucose and mannose.

Further samples of III, IV and V were esterified, reduced and hydrolyzed as described earlier[24] and the products examined by paper chromatography in solvent B. Components corresponding to the following sugars were detected and the approximate relative amounts are given; III, galactose, xylose, 4-*O*-methylglucose (R_x 1.20) (1:1:1); IV, galactose, xylose, 4-*O*-methylglucose, rhamnose, glucose, mannose (3:5:2:1:trace:trace); V, galactose, glucose, xylose, 4-*O*-methylglucose (1:1:3:2).

Hydrolysis Constant of 2-*O*-(4-*O*-Methyl-D-glucopyranosyluronic Acid)-D-xylose.—A solution of 0.1010 g. of aldobiouronic acid in 20 ml. of 1.07 *N* sulfuric acid was heated on the steam-bath under reflux. At intervals the solution was cooled and 2-ml. samples added to a mixture of Amberlite resin IRA-400 (5 ml., carbonate form) and 10 ml. of water and stirred for 3 hours. The solution was filtered, and the resin washed with water until the combined filtrate and washings totaled 50 ml. The xylose present in this solution was determined by the ferricyanide method[26] and the results are shown in Table II, the "constant" being calculated from the expression $k = 1/t \times \log C_0/C_t$.

Hydrolysis Constant of Maltose.—A solution of 0.2467 g. of maltose monohydrate in 50 ml. of 1.07 *N* sulfuric acid was heated under reflux on the steam-bath and the following changes in $[\alpha]^{25}D$ observed: +107° (15 min.), +90° (30 min.), +77° (45 min.). Using the expression

$$k = 1/t \times \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

the mean value for the hydrolysis constant is $k = 1.09 \times 10^{-2}$ min.$^{-1}$.

Action of Lime-water on 4-*O*-Methyl-D-glucuronic Acid.—A solution containing 0.142 g. of the acid in 50 ml. of oxygen-free 0.04 *N* lime-water was kept at 25° for 10 days. During this time a white precipitate separated and the solution became non-reducing to Fehling solution. Amberlite resin IR-120(H) (10 ml.) was added and the mixture shaken for 10 min. to break down and dissolve the calcium salt. The solution was then filtered and the resin washed with water. Titration with alkali of an aliquot of the combined filtrate and washings indicated the presence of 1.39 meq. of acid (2.04 equiv./mole starting material). The neutralized aliquot was again treated with Amberlite resin IR-120(H), combined with the remainder of the acid solution and evaporated to 0.130 g. of a colorless sirup. Paper chromatography of this product in solvent A showed an acid spot (R_x 1.12) (sprays B and C) and an elongated zone (approx. R_x 2.1) which gave a weak lactone reaction (spray D) and probably corresponded to monolactones of the dibasic acid.

The above product was combined with material from a similar reaction (total 0.230 g.) and heated 4 hours on the steam-bath with water and excess brucine. The mixture was cooled, filtered, washed twice with chloroform and concentrated to about 10 ml. On standing at 0° for 18 hours 0.148 g. of crystals separated and when recrystallized from aqueous acetone showed m.p. 189–194°, $[\alpha]^{25}D$ −29.3 ± 0.5° (*c* 2, 50% aqueous ethanol).

Anal. Calcd. for $C_{52}H_{62}O_{15}N_4$: C, 63.5; H, 6.4; N, 5.7. Found: C, 63.1; H, 6.4; N, 5.4.

Mother liquors from the original crystallization were evaporated to a colorless sirup (0.738 g.) and retreated with brucine as above to yield a further quantity (0.31 g.) of the same brucine salt.

Action of Lime-water on 2-*O*-(4-*O*-Methyl-D-glucopyranosyluronic Acid)-D-xylose.—A solution containing 0.0776 g. of the disaccharide in 25 ml. of oxygen-free 0.039 *N* lime-water was kept at 25° and at intervals aliquots were added to excess hydrochloric acid and back titrated with sodium hydroxide. These acid yields were obtained: 1.01 (0.05 hour), 0.995 (24 hours), 1.00 (48 hours) equiv./mole.

LAFAYETTE, IND.

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(26) H. C. Hagedorn and B. N. Jensen, *Biochem. Z.*, **135**, 46 (1923).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY]

Bis-(β-Diketones). I. Synthesis of Compounds of the Type $RCOCH_2CO$–Y–$COCH_2COR$[1,2]

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RECEIVED APRIL 7, 1958

A number of new bis-(β-diketones) of the type $RCOCH_2CO$–Y–$COCH_2COR$ have been prepared: R = C_6H_5, Y = $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$, $(CH_2)_7$, 1,3-C_6H_4, 1,4-C_6H_4 and 4,4′-$C_6H_4 \cdot C_6H_4$; R = *p*-$CH_3OC_6H_4$, Y = 1,4-C_6H_4; R = CH_2=$CHCH_2CH_2$, Y = 1,3-C_6H_4 and $(CH_2)_8$. The first two were prepared by the condensation of a bis-(acyl chloride) with the sodium salt of a ketone and the remainder by Claisen condensations. The infrared and ultraviolet absorption spectra indicate that these bis-(β-diketones) exist predominantly in the enolic form both in the solid state and in 95% ethanol.

Introduction

In continuation of an investigation into the chelation behavior of bis-(β-diketones),[3] several new compounds of the type $RCOCH_2CO$–Y–$COCH_2COR$ have been prepared. Previous investigators have reported the synthesis of the compounds where Y = nothing, R = CH_3[4]; R = C_2H_5[5]; R = C_6H_5[6]; R = 2,4-$(CH_3)_2C_6H_3$ and R = 4-$CH_3OC_6H_4$[7]; Y = $(CH_2)_2$, R = C_6H_5[8]; Y = $(CH_2)_3$, R = C_6H_5[9]; Y = $(CH_2)_8$, R = CH_3 and C_6H_5[3]; Y = 1,4-C_6H_4, R = CH_3[10]; and Y = 1,5-[2,4-$(CH_3O)_2C_6H_2$], R = CH_3, $C_6H_5CH_2$ and 4-$CH_3OC_6H_4$.[11] There are reported

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[1] This research was supported in whole by the United States Air Force under Contract AF33(616)-2742, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] Based upon a portion of the doctoral dissertation of Dean F. Martin, The Pennsylvania State University, 1958.

[3] E. H. Holst, Ph.D. dissertation, The Pennsylvania State University, 1955.

[4] L. Claisen and N. Stylos, *Ber.*, **21**, 1141 (1888).

[5] O. Diels, J. Sielisch and E. Müller, *ibid.*, **39**, 1328 (1906).

[6] E. Brôme and L. Claisen, *ibid.*, **21**, 1131 (1888).

[7] O. Widman and E. Virgin, *ibid.*, **42**, 2794 (1909).

[8] G. H. Daub and W. S. Johnson, THIS JOURNAL, **72**, 501 (1950).

[9] H. Wieland and I. Drishaus, *Ann.*, **474**, 102 (1929).

[10] L. Berend and P. Herms, *J. prakt. Chem.*, [2] **74**, 131 (1906).

[11] J. Algar, *Proc. Roy. Irish Acad.*, **33B**, 86 (1916); *C. A.*, **10**, 2577 (1916).

Table I

Synthesis of Bis-(β-diketones) of the Type $RCOCH_2CO{-}Y{-}COCH_2COR$[a,b]

Bis-(β-diketones)	R	-Y-	M.p., °C.	Yield, %	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Adipyldiacetophenone	C_6H_5	$(CH_2)_4$	117–118	33	$C_{22}H_{22}O_4$	75.41	75.35	6.33	6.50
Pimelyldiacetophenone	C_6H_5	$(CH_2)_5$	64.5–65.5	25	$C_{23}H_{24}O_4$	75.80	76.04	6.64	6.86
Suberyldiacetophenone	C_6H_5	$(CH_2)_6$	107.5–108	5	$C_{24}H_{26}O_4$	76.16	75.98	6.93	7.12
Azelyldiacetophenone	C_6H_5	$(CH_2)_7$	62.5–63.5	15	$C_{25}H_{28}O_4$	76.50	76.54	7.19	7.37
Terephthaloyldiacetophenone	C_6H_5	1,4-C_6H_4	176–177	31	$C_{24}H_{18}O_4$	77.82	77.72	4.90	4.76
Isophthaloyldiacetophenone	C_6H_5	1,3-C_6H_4	153–154	32	$C_{24}H_{18}O_4$	77.82	77.99	4.90	5.04
Terephthaloylbis-(*p*-methoxyacetophenone)	4-$CH_3OC_6H_4$	1,4-C_6H_4	233–234	18	$C_{26}H_{22}O_6$	72.55	72.31	5.15	5.12
4,4′-Bis-(benzoylacetyl)-biphenyl	C_6H_5	4,4′-$C_6H_4C_6H_4$	194–196	31	$C_{30}H_{22}O_4$	80.70	80.53	4.97	5.08
1,3-Bis-(4-pentenoylacetyl)-benzene	$CH_2{=\!=}CH(CH_2)_2$	1,3-C_6H_4	122.2–122.5	18	$C_{20}H_{22}O_4$	73.59	73.44	6.80	6.85
1,21-Docosadiene-5,7,16,18-tetraone	$CH_2{=\!=}CH(CH_2)_2$	$(CH_2)_8$	47.7–48	14	$C_{22}H_{34}O_4$	72.89	72.79	9.43	9.53

[a] All compounds gave a red color with methanolic $FeCl_3$. [b] All analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

here the synthesis and properties of the bis-(β-diketones) where $R = C_6H_5$, $Y = (CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$, $(CH_2)_7$, 1,3-C_6H_5, 1,4-C_6H_4 and 4,4′-C_6H_4-C_6H_4, R = 4-$CH_3OC_6H_4$, Y = 1,4-C_6H_4; and $R = CH_2{=\!=}CH(CH_2)_2$, $Y = (CH_2)_8$ and 1,3-C_6H_4.

Experimental

Analyses of compounds prepared together with melting points and yields are given in Table I.

Pimelyldiacetophenone, $[C_6H_5COCH_2CO(CH_2)_2]_2CH_2$.—Pimelic acid (5.3 g., 0.033 mole) and thionyl chloride (14.2 g., 0.12 mole) were warmed on a steam-bath for 48 hr. Excess thionyl chloride was removed *in vacuo*. A suspension of the sodium salt of acetophenone in 300 ml. of dry ether was prepared by the procedure of Hauser[12] from acetophenone (24 g., 0.2 mole) and $NaNH_2$ (7.8 g., 0.2 mole). The suspension was cooled in an ice–water-bath and the crude pimelyl chloride added rapidly with vigorous stirring. The mixture was stirred 5 min. in an ice–water-bath and then 20 min. with the bath removed. Finally, it was poured over crushed ice and concd. hydrochloric acid (27 ml., 0.32 mole). The ether layer was separated, washed with saturated $NaHCO_3$ solution and dried over anhydrous Na_2SO_4. Ether and excess acetophenone were distilled. The residual oil solidified on standing and was recrystallized from methanol several times to give white crystals, m.p. 64.5–65.5° The yield after one recrystallization was 3.0 g.

Adipyldiacetophenone, $(C_6H_5COCH_2COCH_2CH_2)_2$, was similarly prepared from acetophenone (36.0 g., 0.30 mole), $NaNH_2$ (11.7 g., 0.30 mole) and adipyl chloride (9.2 g., 0.05 mole): yield was 5.8 g. Upon several recrystallizations from methanol, white platelets were obtained, m.p. 117–118°.

Terephthaloyldiacetophenone, 1,4-$(C_6H_5COCH_2CO)_2$-C_6H_4.—Sodium amide (15.6 g., 0.40 mole) was added portionwise to a mixture of acetophenone (24.0 g., 0.2 mole) and dimethyl terephthalate (19.4 g., 0.1 mole) in 300 ml. of dry ether at 5–10°. The mixture was stirred 1 hr., decomposed with ice-water and the insoluble material filtered. The aqueous layer when saturated with CO_2 yielded 11.4 g. of the desired product. Several recrystallizations from methanol gave yellow crystals, m.p. 176–177°.

Isophthaloyldiacetophenone, 1,3-$(C_6H_5COCH_2CO)_2C_6H_4$, was prepared in a similar manner from dimethyl isophthalate (19.4 g., 0.1 mole), acetophenone (30.0 g., 0.25 mole) and $NaNH_2$ (19.5 g., 0.5 mole). The reaction mixture was stirred 2 hr. at 0–5°, 2 hr. at room temperature and decomposed with ice-water. Saturation of the aqueous layer with CO_2 yielded 12.0 g. of product. Several recrystallizations from methanol gave yellow needles, m.p. 153–154°.

Terephthaloylbis-(*p*-methoxyacetophenone), 1,4-(*p*-CH_3-$OC_6H_4COCH_2CO)_2C_6H_4$, was similarly prepared from dimethyl terephthalate (19.4 g., 0.1 mole), *p*-methoxyacetophenone (37.5 g., 0.25 mole) and $NaNH_2$ (19.5 g., 0.5 mole). The reaction mixture was stirred 5.5 hr. at 0–5°, stored in the refrigerator overnight and decomposed with ice-water. Treatment of the aqueous layer with Dry Ice yielded 7.5 g. of product. Upon recrystallization from chlorobenzene, brilliant yellow crystals were obtained, m.p. 233–234°.

Suberyldiacetophenone, $[C_6H_5COCH_2CO(CH_2)_3]_2$.—**Diethyl suberate** was prepared in 76% yield by the azeotropic mixture method as described in Vogel,[13] b.p. 120–126° (4–5 mm.), $n^{25}D$ 1.4313; reported[14] b.p. 164° (22 mm.), $n^{25}D$ 1.4326.

Condensation of Diethyl Suberate and Acetophenone.—Acetophenone (12.2 g., 0.10 mole) in 50 ml. of dry ether was added during a 5-min. period to a stirred suspension of $NaNH_2$ (8.6 g., 0.22 mole) in 200 ml. of dry ether. After 5 min., diethyl suberate (11.5 g., 0.05 mole) in 50 ml. of dry ether was added in a similar manner. The reaction mixture was stirred 1.5 hr. and poured over crushed ice. The aqueous layer was separated, acidified with glacial acetic acid and the resulting oil extracted with ether. The combined extracts were washed with 5% $NaHCO_3$ solution, dried over anhydrous Na_2SO_4 and distilled. About 1 g. of residual solid was obtained. An analytical sample was recrystallized from methanol four times; white needles, m.p. 107.5–108°.

Azelyldiacetophenone, $[C_6H_5COCH_2CO(CH_2)_3]_2CH_2$.—**Diethyl azelate** was prepared in 65% yield by the procedure of Vogel[12]; b.p. 165–168° (17–18 mm.), $n^{25}D$ 1.4350; reported[15] b.p. 142–143° (5 mm.), $n^{16}D$ 1.4380.

Condensation of Diethyl Azelate and Acetophenone.—The condensation of diethyl azelate (14.5 g., 0.06 mole) and acetophenone (15.6 g., 0.13 mole) in the presence of $NaNH_2$ (10.2 g., 0.26 mole) was carried out at 0–5°. The reaction mixture was stirred overnight at room temperature and the product (3.5 g.) isolated in the same way as suberyldiacetophenone. An analytical sample was recrystallized from methanol–water yielding white crystals, m.p. 62.5–63.5°.

1,3-Bis-(4-pentenoylacetyl)-benzene, 1,3-$(CH_2{=\!=}CHCH_2$-$CH_2COCH_2CO)_2C_6H_4$, was prepared in a similar manner by condensation of 5-hexene-2-one (10.8 g., 0.11 mole) and dimethyl isophthalate (9.7 g., 0.05 mole) in the presence of $NaNH_2$ (8.6 g., 0.22 mole). The reaction mixture was stirred 0.5 hr. at 0–5° and about 3 hr. at room temperature. The reaction mixture was poured over crushed ice, the aqueous layer separated and treated with Dry Ice. The resulting precipitate was extracted with ether, the extracts dried over anhydrous Na_2SO_4 and distilled. The residual solid (3.0 g.) was recrystallized from methanol and white platelets were obtained, m.p. 122.2–122.5°.

1,21-Decosadiene-5,7,16,18-tetraone, $[CH_2{=\!=}CH(CH_2)_2$-$COCH_2CO(CH_2)_4]_2$.—The condensation of 5-hexene-2-one

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[12] C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. VIII Chapter 3, John Wiley and Sons, Inc., New York, N. Y., 1954.

[13] A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1956, p. 429.

[14] A. I. Vogel, *J. Chem. Soc.*, 333 (1934).

[15] F. Fourneau and S. Sabetay, *Bull. soc. chim.*, **45**, 834 (1929).

TABLE II

TENTATIVE ASSIGNMENTS: INFRARED ABSORPTION SPECTRA[a] OF BIS-(β-DIKETONES), $RCOCH_2CO\text{-}Y\text{-}COCH_2COR$

		Hydroxyl		Carbonyl		Enol-chelate	
R	Y	μ	Cm.$^{-1}$	μ	Cm.$^{-1}$		Cm.$^{-1}$
			A. Solid phase				
CH_3	....	2.95	3390	5.83	1715	6.25	1600sh
						6.33	1580B
C_6H_5	....	2.95	3390			6.25	1600
						6.40	1563B
C_6H_5	$(CH_2)_2$	2.95	3390			6.21	1610
						6.36	1572
C_6H_5	$(CH_2)_4$			6.00	1667sh	6.28	1592B
						6.43	1555B
C_6H_5	$(CH_2)_5$					6.20	1613
						6.33	1580
C_6H_5	$(CH_2)_6$					6.18	1618
						6.32	1582
C_6H_5	$(CH_2)_7$					6.21	1610
						6.33	1580
CH_3	$(CH_2)_8$	2.95	3390B			6.08	1644
						6.24	1603
$CH_2{=}CH(CH_2)_2$	$(CH_2)_8$					6.08	1644
C_6H_5	$(CH_2)_8$					6.21	1610
						6.36	1572
$CH_2{=}CH(CH_2)_2$	1,3-C_6H_4					6.18	1618B
C_6H_5	1,3-C_6H_4					6.22	1608
						6.40	1563B
CH_3	1,4-C_6H_4	2.94	3401			6.20	1613
C_6H_5	1,4-C_6H_4	2.90	3448B			6.23B	1605B
						6.33–6.49	1580–1541
4-$CH_3OC_6H_4$	1,4-C_6H_4					6.21	1610
C_6H_5	4,4′-$C_6H_4C_6H_4$					6.21	1610
			B. $Cl_2C{=}CCl_2$ solution				
C_6H_5	....			5.62	1779	6.23	1605
				5.68	1761	6.44	1553B
C_6H_5	$(CH_2)_5$			5.62	1779	6.23	1605
				5.68	1761		
CH_3	$(CH_2)_8$			5.62	1779	6.22	1608B
				5.68	1761		
C_6H_5	$(CH_2)_8$			5.62	1779	6.23	1605B
				5.69	1757		
			C. $CHBr_3$ solution				
CH_3	1,4-C_6H_4	2.78	3597			6.22	1608
		2.92	3424			6.32	1582
C_6H_5	1,4-C_6H_4	2.78	3697			6.22	1608B
		2.90	3448B			6.38–6.45	1567–1550

[a] B, broad; sh, shoulder.

(11.8 g., 0.12 mole) and dimethyl sebacate (11.5 g., 0.05 mole) in the presence of $NaNH_2$ (9.4 g., 0.24 mole) was carried out similarly. The product was isolated in a similar manner except that glacial acetic acid was used to acidify the aqueous layer. The product (2.5 g.) was recrystallized from methanol several times yielding white crystals which softened at 46° and melted at 47.5–48°.

4,4′-Bis-(benzoylacetyl)-biphenyl, 4,4′-$(C_6H_5COCH_2CO)_2$-$C_6H_4C_6H_4$.—**4,4′-Diacetylbiphenyl** was prepared in 44% yield according to the directions of Long and Henze[16]; white platelets (95% ethanol), m.p. 187–188°; reported 190°.

Condensation of 4,4′-Diacetylbiphenyl and Ethyl Benzoate.—A solution of 4,4′-diacetylbiphenyl (3.88 g., 0.016 mole) in 50 ml. of ethyl benzoate was added dropwise to a stirred suspension of $NaNH_2$ (2.54 g., 0.065 mole) in 50 ml. of ethyl benzoate at 55–60°. The reaction mixture was stirred at 55–60° for 5 hr., overnight at room temperature and filtered. The dried solid was washed thoroughly with hot benzene and dried *in vacuo*. The powdered solid was suspended in 30 ml. of glacial acetic acid and stirred vigorously for 4 hr. The product was collected, washed thoroughly with water and air-dried; yield 2.2 g. Upon several recrystallizations from methanol–chloroform, a light brown solid was obtained, m.p. 194–196°.

Infrared Absorption Spectra.—All spectra were obtained by Perkin–Elmer model 21 recording infrared spectrophotometer using a sodium chloride prism. The spectra in the solid phase were made by incorporating the materials in potassium bromide pellets.[17] The spectra in the dissolved state were taken in tetrachloroethylene or bromoform (Eastman Kodak Co. spectro-grade) at a concentration of 20 mg. per 5 ml. using a 0.517-mm. cell with a 0.52 mm. cell in the reference beam. Tentative assignments are summarized in Table II.

The spectra of oxalyl-, sebacoyl- and terephthaloyldiacetone, and oxalyl-, succinyl- and terephthaloyldiacetophenone have absorption bands near 2.95 μ which are attributable to hydroxyl stretching frequency.

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[16] L. M. Long and H. R. Henze, THIS JOURNAL, **63**, 1939 (1941).

[17] M. M. Stimson and J. J. O'Donnell, *ibid.*, **74**, 1805 (1952); U. Scheidt and H. Reinwein, *Z. Naturforsch.*, **7B**, 270 (1952).

Only the spectrum of oxalyldiacetone has a prominent absorption band (at 5.83 μ) which might be attributed to normal carbonyl absorption. The spectrum of adipyldiacetophenone has a well-defined shoulder at 6.00 μ which is attributed to conjugated carbonyl absorption.

With the exception of the compound $[CH_2{=}CH(CH_2)_2\text{-}COCH_2CO(CH_2)_4\text{-}]_2$, whose spectrum has an absorption band at 6.08 μ, the spectra of all bis-(β-diketones) have a strong absorption band in the region 6.18–6.28 μ. In addition, a second band, generally in the region 6.32–6.36 μ, appears in the spectra of six bis-(β-diketones) (oxalyldiacetone, succinyl-, pimelyl-, suberyl-, azelyl- and sebacoyldiacetophenone).

In tetrachloroethylene solution, the spectra of oxalyl-, pimelyl-, sebacoyl-diacetophenone and sebacoyldiacetone lack bands at 2.9 μ but have bands at 5.62 and 5.69 μ which are due to carbonyl absorption; all have an absorption band centered at 6.23 μ associated with the enol-chelate structure. The spectra of bromoform solutions of terephthaloyldiacetone and terephthaloyldiacetophenone have prominent bands at 2.78 and 2.90–2.92 μ; both lack absorption bands attributable to undisturbed carbonyl group absorption, but again have prominent bands at 6.22 μ.

Ultraviolet Absorption Spectra.—All spectra were obtained with a Warren Spectracord with a hydrogen lamp light source using a 2-cm. quartz cell. Samples were obtained by dilution of stock solutions containing 10 mg. of bis-(β-diketone) per 100 ml. of 95% ethanol. Samples of enolate anions were prepared similarly except that an amount of 0.1867 *N* $(CH_3)_4NOH$ ten times that required to neutralize the bis-(β-diketone) was added. The ultraviolet absorption maxima and extinction coefficients of bis-(β-diketones) of the type $RCOCH_2CO\text{-}Y\text{-}COCH_2COR$ in 95% ethanol are listed in Table III.

TABLE III

ULTRAVIOLET ABSORPTION SPECTRA OF BIS-(β-DIKETONES) OF THE TYPE $RCOCH_2CO\text{-}Y\text{-}COCH_2COR$ IN 95% ETHANOL

R	Y	Molarity × 10^5	λ, mμ	I	ϵ_{max} × 10^{-4}	log ϵ_{max}
C_6H_5	....	1.70	248	0.496	1.46	4.61
			333	.343	1.01	4.00
C_6H_5	$(CH_2)_2$	1.55	230	.382	1.23	4.09
			247	.395	1.27	4.10
			320	.89	2.87	4.46
C_6H_5	$(CH_2)_4$	1.43	248	.330	1.15	4.06
			312	.84	2.94	4.47
C_6H_5	$(CH_2)_5$	1.37	247.5	.264	0.96	3.98
			313	.830	3.03	4.48
		2.75	247	.565	1.03	4.02
			312	1.6	2.9	4.5
C_6H_5	$(CH_2)_6$	1.32	248	0.128	0.48	3.68
			313	.63	2.38	4.38
C_6H_5	$(CH_2)_7$	1.28	247	.135	0.53	3.72
			310	.66	2.58	4.41
C_6H_5	$(CH_2)_8$	1.23	231.5	.206	0.84	3.92
			249	.296	1 20	4.08
			312	.840	3.41	4.53
CH_3	$(CH_2)_8$	1.77	273	.778	2.20	4.34
$CH_2{=}CH(CH_2)_2$	$(CH_2)_8$	1.38	276.5	.602	2.18	4.45
C_6H_5	1,3-C_6H_4	1.35	257	.328	1.22	4.09
			357	1.1	4.07	4.61
$CH_2{=}CH(CH_2)_2$	1,3-C_6H_4	1.53	231.5	0.288	0.94	3.94
			254	.212	0.69	3.84
			343	.94	3.07	4.49
C_6H_5	1,4-C_6H_4	1.35	258	.332	1.19	4.08
CH_3	1,4-C_6H_4	2.03	253	.380	0.935	3.97
			340	1.15	2.83	4.45
Enolate anions						
C_6H_5	$(CH_2)_6$	1.32	241	0.412	1.56	4.19
			325	.808	3.06	4.56
C_6H_5	$(CH_2)_7$	1.28	241	.410	1.60	4.20
			325	.800	3.12	4.49
C_6H_5	$(CH_2)_8$	1.23	240	.55	2.24	4 35
			325	.95	3.86	4.59

Discussion

Synthesis of Bis-(β-diketones).—The properties of ten bis-(β-diketones) of the type $RCOCH_2CO\text{-}Y\text{-}COCH_2COR$ prepared in this investigation are summarized in Table I. Eight of the bis-(β-diketones) were prepared by the Claisen condensation. The use of this condensation in the synthesis of β-diketones has been discussed by Hauser.[12]

The Claisen condensation, as applied to the synthesis of a bis-(β-diketone) $RCOCH_2CO\text{-}Y\text{-}COCH_2COR$, consists in treating one mole of a dicarboxylic ester, $R''OOC\text{-}Y\text{-}COOR'$, with two moles of a ketone, $RCOCH_3$, in the presence of 4 moles of sodium amide. The product is isolated and purified by conventional procedures.[12] Alternatively, it may be desirable to prepare a bis-(β-diketone) from the reaction of two moles of a monocarboxylic ester, $RCOOR'$, and one mole of a diketone, $CH_3\text{-}CO\text{-}Y\text{-}COCH_3$ [*cf.*, synthesis of 4,4′-bis-(benzoylacetyl)-biphenyl].

The Claisen condensation cannot be used to prepare adipyldiacetophenone and pimelyldiacetophenone [$R = C_6H_5$, $Y = (CH_2)_4, (CH_2)_5$] because of the competing Dieckmann cyclization reaction. In an attempt to prepare adipyldiacetophenone from diethyl adipate and acetophenone in the presence of sodium amide, the Dieckmann cyclization product, 2-carbethoxycyclopentanone, was obtained in 77% yield.[3] Diethyl pimelate also would be expected to undergo Dieckmann cyclization rather than ketone acylation. To circumvent this difficulty, the method used to prepare adipyldiacetophenone and pimelyldiacetophenone consists in treating an ether suspension of six moles of the sodium salt of a ketone (prepared by the procedure of Hauser)[12] with one mole of the diacyl chloride. The product was isolated in a conventional manner,[12] and purified by recrystallization. This method is an extension of one used by Linn and Hauser[18] to prepare certain β-diketones. These workers found that the use of a ratio of three equivalents of the sodium salt of a ketone to one of acid chloride avoided any possibility of further acylation of the β-diketone.

There are further limitations to the use of the Claisen condensation. Malonic and succinic esters usually undergo aldol and Stobbe[19] condensations, respectively. The reaction of acetophenone, diethyl succinate and sodium hydride (molar ratio 1:3:3) gave a 92% yield of the unsaturated ester acid.[3] It is interesting to note that from the condensation of di-*t*-butyl succinate (0.019 mole) and acetophenone (0.015 mole) in the presence of sodium hydride (0.041 mole), there was obtained, in addition to a 58% yield of the half-ester, a 34% yield of succinyldiacetophenone.[8]

Diethyl malonate undergoes an aldol-type condensation with cyclohexanone. The reaction of diethyl malonate and cyclohexanone in the presence of sodium ethoxide and a trace of sodium iodide gave a 25–30% yield of the β,γ-unsaturated ester, diethyl 1-cyclohexenylmalonate.[20] Presumably diethyl malonate would undergo a similar reaction with other ketones.

Certain bis-(β-diketones) cannot be isolated as

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[18] B. O. Linn and C. R. Hauser, THIS JOURNAL, **78**, 6066 (1956).

[19] W. S. Johnson and G. H. Daub, "Organic Reactions," Vol. VI, Chapter 1, John Wiley and Sons, Inc., New York, N. Y., 1951.

[20] F. Giral and A. F. Guzman, *Ciencia e invest.* (*Buenos Aires*), **2**, 39 (1946).

such because of the occurrence of intramolecular cyclization. For example, from the reaction of diethyl phthalate and acetophenone in the presence of sodium ethoxide, Schwerim obtained 2-benzoyl-1,3-diketohydrindene.[21] Cyclization also occurred when acetone or methyl ethyl ketone was used instead of acetophenone.

Infrared Absorption Spectra.—Bis-(β-diketones) of the type $RCOCH_2CO$–Y–$COCH_2COR$ exist predominantly in the enolic form in the solid state. This is evidenced by the lack of normal carbonyl absorption in the spectra of all compounds except oxalyldiacetone and adipyldiacetophenone. Furthermore, the sixteen bis-(β-diketones) studied have either one or two enol-chelate absorption bands of high intensity. The absence of hydroxyl absorption bands in the spectra of ten of the sixteen bis-(β-diketones) is due to the fact that the bands have been shifted to, and obscured by, the C–H stretching vibration bands. A similar effect has been observed in the spectra of acetylacetone and other enolic β-diketones and is taken as evidence of strong intramolecular hydrogen-bonding.[22,23]

The position of the enol-chelate band(s) is influenced by structural variations. The enol-chelate bands in sebacoyldiacetone are at 6.08 and 6.24 μ but in oxalyldiacetone are at 6.25 and 6.33 μ. This shift is a reflection of the greater degree of conjugation possible in oxalyldiacetone. The substitution of a phenyl for an alkyl terminal group increases the degree of conjugation; consequently, oxalyldiacetophenone has enol-chelate bands at 6.25 and 6.40 μ as opposed to 6.25 and 6.33 μ for oxalyldiacetone. Less conjugation is possible when the two β-diketone groups are joined by a methylene chain. Thus, succinyl-, pimelyl-, suberyl-, azelyl- and sebacoyldiacetophenone have enol-chelate bands centered at 6.20 and 6.34 μ. The bands for adipyldiacetophenone (6.28 and 6.43 μ) are inconsistent; the reason for this is not immediately evident. The position of the enol-chelate band(s) for bis-(β-diketones) with an aromatic link (*ca.* 6.21 μ) does not represent a marked shift from that observed for those compounds having a non-aromatic linkage.

The spectra of the four bis-(β-diketones) in tetrachloroethylene lack absorption bands at 2.90 μ attributable to hydroxyl stretching, although such bands appear in the solid phase spectra of two of the four bis-(β-diketones), *viz.*, oxalyldiacetophenone and sebacoyldiacetone. The bromoform solution spectra of terephthaloyldiacetone and terephthaloyldiacetophenone have prominent hydroxyl absorption near 2.90 μ as do the solid phase spectra. The tetrachloroethylene solution spectra exhibit carbonyl group absorption at 5.62 and 5.68 μ; but the bromoform spectra do not show an absorption in that region. The enol-chelate band near 6.22 μ is observed in the solid phase and in solution. In solid phase and bromoform solution spectra, two enol-chelate bands are observed in approximately the same position; in tetrachloroethylene solution only the band near 6.22 μ appears. In tetrachloroethylene the tendency for the bis-(β-diketones) to exist in the keto form appears to be greater than in solid state.

Ultraviolet Absorption Spectra.—On the basis of what is known about the ultraviolet absorption of the tautomeric forms of β-diketones, it appears that bis-(β-diketones) of the type $RCOCH_2CO$–Y–$COCH_2COR$ exist predominantly in the enolic form in 95% ethanol.[24] The spectra of sebacoyldiacetone and its analog $[CH_2{=\!=}CH(CH_2)_2COCH_2$-$CO(CH^6)_4$-$]_2$ exhibit a single maximum (*ca.* 275 mμ) of high intensity (log ϵ_{max} is 4.34 and 4.45, respectively) which would be expected for the enolic form.

The high intensity maximum occurring at 310 mμ or greater in the spectra of bis-(β-diketones) having terminal phenyl groups and/or a phenylene linkage is attributed to enol form absorption with negligible keto form absorption; the band near 250 mμ for the same compounds is probably a composite one. The position of the "enol band" near 310 mμ can be qualitatively related to the amount of conjugation which is possible. Thus, when R is phenyl and Y a methylene chain the "enol band" appears near 312 mμ (succinyldiacetophenone, 320 mμ) and progressively shifts for oxalyldiacetophenone (333 mμ), terephthaloyldiacetone (340 mμ), isophthaloyldiacetophenone (357 mμ) and terephthaloyldiacetophenone (>360 mμ).

It was of interest to determine qualitatively the enol content. Since the absorption of the keto form near 310 mμ would be negligible, the percentage of the enol form present should be 100 (ϵ_m/ϵ_e), where ϵ_m is the observed extinction at about 310 mμ and ϵ_e is that of the pure enol. It is assumed that the extinction of the enolate anion is approximately equal to the pure enol. Thus the calculated enol percentages in 95% ethanol are: suberyldiacetophenone (77.8), azelyldiacetophenone (82.8) and sebacoyldiacetophenone (88.4). The enolic contents of the other bis-(β-diketones) were not determined, but are probably comparable since the extinction coefficients are of the same magnitude for all bis-(β-diketones) studied.

Acknowledgments.—The authors gratefully acknowledge the help of Mr. Richard E. Dagle who made the infrared absorption spectral measurements and of Mrs. Barbara B. Martin who made the ultraviolet absorption spectral measurements.

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(21) E. Schwerim, *Ber.*, **27**, 104 (1894).

(22) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

(23) R. Mecke and E. Funck, *Z. Elektrochem.*, **60**, 1124 (1956).

(24) The application of ultraviolet absorption studies to the problem of keto-enol tautomerism is discussed by Gillam and Stern (A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold (Publishers) Ltd., London, 1954, pp. 223–229).