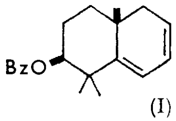
447. *Oxidation of* 3β-*Benzoyloxy*-1,2,3,4,8,9-*hexahydro*-4,4,9-*trimethylnaphthalene by t-Butyl Chromate.

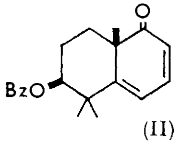
By N. B. Haynes, D. Redmore, and C. J. Timmons.

t-Butyl chromate oxidises the conjugated diene (I) to the mono-unsaturated α-diketone (III).

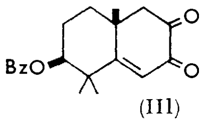
During synthetic work on bicyclic triterpene intermediates the dienone (II) had been obtained in low yield by oxidation of the diene (I) with selenium dioxide;[1] t-butyl chromate which normally oxidises allylic methylene groups to carbonyl groups[2] was therefore tried as an alternative oxidising reagent. A yellow crystalline product was obtained which was different from the required dienone (II). The molecular formula was found to be $C_{20}H_{22}O_4$ and evidence cited below showed the compound to be the α-diketone (III).



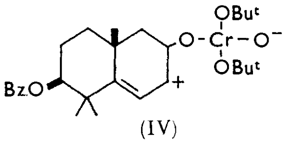
(I)



(II)



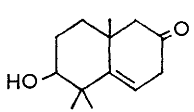
(III)



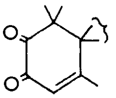
(IV)

The ultraviolet absorption spectrum in neutral ethanol was characterised by a low-intensity band at 485 mμ (ε 64). This indicated an α-diketone chromophore in which the carbonyl groups were approximately coplanar, as it is known[3] that the position of this band is sensitive to the dihedral angle (θ) between the carbonyl groups, varying from 466 to 340 mμ as the groups are rotated from the planar (θ = 0°) to the orthogonal conformation (θ = 90°). The bathochromic shift to 485 mμ is consistent with the additional conjugation with the double bond. On addition of alkali the spectrum changed considerably.

The infrared spectrum showed two strong bands in the carbonyl region, at 1770 and 1723 cm.$^{-1}$, the intensity of the latter indicating that it was due only in part to the benzoate group. Whilst non-planar and planar *trans*-α-diketones show only one carbonyl band, planar *cis*-α-diketones usually show two bands,[3,4] and the positions of the bands for (III) are similar (see Table 1) to those reported for the unsaturated *cis*-α-diketone system (VI).[5]



(V)



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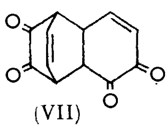
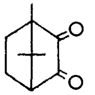
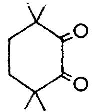


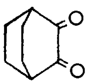
(VII)



(VIII)



(IX)



(X)

The α-diketone structure was confirmed by preparation of the following derivatives. A mono-2,4-dinitrophenylhydrazone was obtained by use of Brady's reagent. Its light-absorption properties (Table 2), when compared with those of a mono-derivative of a saturated diketone,[6] indicated that the 2-carbonyl group had reacted. Treatment of the diketone with 2,4-dinitrophenylhydrazine in dioxan afforded the bis-derivative. A quinoxaline derivative was also obtained.

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[1] King, Ritchie, and Timmons, *Chem. and Ind.*, 1956, 1230; Haynes and Timmons, *Proc. Chem. Soc.*, 1958, 345.

[2] See, *e.g.*, Mukherjee and Dutta, *J.*, 1960, 67.

[3] (*a*) Leonard and Mader, *J. Amer. Chem. Soc.*, 1950, **72**, 5388; (*b*) Alder, Schäfer, Esser, Krieger, and Reubke, *Annalen*, 1955, **593**, 23; (*c*) Cookson and Trevett, *J.*, 1956, 3864; (*d*) Ford and Parry, *Spectrochim. Acta*, 1958, **12**, 78.

[4] Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 2nd edn., 1958, p. 141.

[5] Barton, McGhie, and Rosenberger, *J.*, 1961, 1215.

[6] Timmons, *J.*, 1957, 2613.

TABLE 1.

Light-absorption properties of some six-membered ring *cis*-α-diketones and related compounds.

		α-Diketone band			C=O bands		
Compound	$\theta°$	$\lambda_{max.}$	$\varepsilon_{max.}$	Solvent	$\nu_{max.}$	$\varepsilon^{a}_{max.}$	Solvent
(III)	0—10 [b]	485	64	EtOH	1770	300	CCl_4
					1723 [c]	1400	
(I)	—	—	—	—	1721	650	CCl_4
(V)	—	—	—	—	1715 [d]		
(VI)	0—10 [b]				1761 [e]		Nujol mull
					1723		
(VII)	0—10 [b,f]	430—435 [g]	130	Dioxan			
(VIII)	0—10	466 [h]	31	EtOH	1776 [i,j]		CCl_4
					1760		
(IX)	0—60	380 [h]	11	EtOH	1709		Nujol mull
(X)	0—5 [b]	478 [i]	40	C_6H_{12}	1760		CCl_4
					1731		
Steroidal 11,12-diketones	25—30 [b]				1726 [k]		CS_2
Biacetyl	*ca.* 160 [l]				1718 [m]		CCl_4

[b] Measured from Dreiding models. [c] Superimposed α-diketone and benzoate bands. [d] Halsall, Rodewall, and Willis, *J.*, 1959, 2798; solvent not stated. [e] Ref. 5. [f] θ quoted for the conjugated α-diketone group. [g] Birnbaum, Cookson, and Lewin, *J.*, 1961, 1224. [h] Ref. 3*a*. [i] Ref. 3*b*. [j] Ref. 3*a* quotes only one band at 1753 cm.$^{-1}$ for a Nujol mull. [k] Jones, Humphries, and Dobriner, *J. Amer. Chem. Soc.*, 1950, **72**, 956. [l] Cureton, Le Fèvre, and Le Fèvre, *J.*, 1961, 4447. [m] Rasmussen, Tunnicliffe, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068.

TABLE 2.

Light-absorption properties of 2,4-dinitrophenylhydrazones of (III) and of reference compounds, in 1 : 9 v/v $CHCl_3$–EtOH.

	Neutral		0·01N in NaOH	
Compound	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
(III), mono-derivative	391	25,300	555	33,000
Pr^n·CO·COEt, mono-derivative *	351	23,500	512	34,000
Cholest-4-en-3-one derivative *	384	31,000	462	25,500
(III), bis-derivative †	371	42,800	590	30,000
	467	27,000		
Pr^n·CO·COEt, bis-derivative *	392	38,000	558	44,500
	451 ‡	28,000		

* Ref. 6. † 3 : 7 v/v $CHCl_3$–EtOH. ‡ Inflexion.

The proton magnetic resonance spectrum confirmed structure (III). The spectrum showed peaks corresponding to three methyl groups, a singlet olefinic proton (τ 3·19) due to the 1-proton, and a peak at τ 7·84 due to the 4-protons.

The mechanism of this oxidation presumably involves initially the donation of electrons from the 6,7-double bond to the chromate;[7] the resulting 6-carbonium ion (IV) may react with a chromate anion. Final hydrolysis would give the α-diketone (III). This oxidation bears some similarities to the oxidation of butyrospermol by t-butyl chromate.[8]

EXPERIMENTAL

7β-*Benzoyloxy*-8,8,10-*trimethyl*-$\Delta^{1(9)}$-*octalin*-2,3-*dione* (III).—A solution of t-butyl chromate [from t-butyl alcohol (30 g.) and chromium trioxide (14 g.) in carbon tetrachloride (120 ml.), acetic acid (50 ml.), and acetic anhydride (20 ml.)] was added at 50° to a solution of 3β-benzoyloxy-4,4,9-trimethyl-1,2,3,4,8,9-hexahydronaphthalene (5 g.) in carbon tetrachloride (120 ml.), acetic acid (20 ml.), and acetic anhydride (5 ml.) during 2 hr. with stirring. The solution was cooled, treated with an excess of saturated aqueous oxalic acid, and made alkaline with aqueous sodium carbonate. The organic layer was separated. The aqueous layer was extracted with

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[7] Waters, *Quart. Rev.*, 1958, **12**, 277.

[8] Lawrie, Hamilton, Spring, and Watson, *J.*, 1956, 3272; de Mayo, "The Higher Terpenoids," Interscience Publ., Inc., New York, 1959, p. 111.

ether (2 × 100 ml.) and the combined ether extracts were washed with water and dried ($MgSO_4$). The gum obtained on evaporation was chromatographed on alumina from light petroleum (b. p. 60—80°) and eluted with chloroform. Concentration and crystallisation from methanol gave the *diketone* (III) as yellow needles (400 mg.), m. p. 186—188° [Found: C, 73·3; H, 6·55%; *M* (Rast), 336. $C_{20}H_{22}O_4$ requires C, 73·6; H, 6·75%; *M*, 326], $\lambda_{max.}$ in EtOH, 231, 273, and 485 mμ (ε 15,000, 7600, and 64, respectively), $\nu_{max.}$ (in CCl_4) 2960, 2882, and 1769 (ε^a 340, α-diketone C=O), 1722 (ε^a 1500, superimposed α-diketone and benzoate C=O), 1604 (C=C), and 1282 (ε^a 590, benzoate) cm.$^{-1}$, τ (in $CHCl_3$) 3·19 (singlet, 1-H), 5·06 (incompletely resolved quartet, 7-H), 7·84 (84-H_2), and 8·0—9·0 (CH_2 and CH_3, unresolved).

Treatment of the diketone with Brady's reagent, chromatography of the product on alumina, and crystallisation from ethyl acetate–light petroleum (b. p. 60—80°) gave the *mono-2,4-dinitrophenylhydrazone* as an orange-red powder, m. p. 207—210° (Found: C, 61·5; H, 5·1; N, 11·5. $C_{26}H_{26}N_4O_7$ requires C, 61·6; H, 5·2; N, 11·1%), $\lambda_{max.}$ (in 10% v/v $CHCl_3$–EtOH) 230, 259, and 391 mμ (ε 27,000, 15,400, and 25,300, respectively), $\lambda_{max.}$ (in 10% v/v $CHCl_3$–EtOH, 0·01N-NaOH) 230 and 555 mμ (ε 28,000 and 33,000, respectively).

Reaction of the diketone with 2,4-dinitrophenylhydrazine in 10% v/v dioxan–methanol containing sulphuric acid gave after several days the *bis-2,4-dinitrophenylhydrazone*; chromatography on alumina and crystallisation from chloroform–methanol gave an orange powder, m. p. 301—303° (Found: C, 55·5; H, 4·3; N, 16·5. $C_{32}H_{30}N_8O_{10}$ requires C, 56·0; H, 4·4; N, 16·3%), $\lambda_{max.}$ (in 3 : 7 $CHCl_3$–EtOH) 233, 269, 371, and 467 mμ (ε 37,000, 25,600, 42,800, and 27,000, respectively), $\lambda_{max.}$ (in 3 : 7 $CHCl_3$–EtOH, 0·01N-NaOH) 238, 398, and 590 mμ (ε 45,000, 28,400, and 30,000, respectively).

The *quinoxaline derivative* sublimed at 180°/0·1 mm. as prisms, m. p. 195—197° (Found: C, 78·2; H, 6·1; N, 7·3. $C_{26}H_{26}N_2O_2$ requires C, 78·4; H, 6·54; N, 7·0%), $\lambda_{max.}$ (in EtOH) 218, 224, 338, and 356 mμ (ε 32,400, 32,300, 15,400, and 14,800, respectively), $\nu_{max.}$ (KBr) 3589, 3433, 3075, 3063, 2948, 2921, 2877, 2851, 1721, 1620, 1601, 1587, and 1274 cm.$^{-1}$.

General.—M. p.s were determined on a Kofler hot stage and are corrected. The alumina used was Peter Spence's grade H. Infrared spectra were determined on a Unicam S.P. 100 spectrophotometer with a prism-grating double monochromator. The intensities quoted (ε^a) are the apparent values, as observed with a spectral slit width of about 2 cm.$^{-1}$. Ultraviolet spectra were determined on a Unicam S.P. 700 spectrophotometer. Nuclear magnetic resonance spectra were determined with an A.E.I. RS 2 spectrometer at 60 Mc./sec., with tetramethylsilane as internal standard.

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