Synthesis of Bicyclo[3,3,1]nona-3,7-diene-2,6-diones and Bicyclo[3,3,1]-nona-3,6-diene-2,8-diones

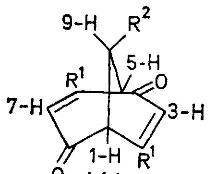
By **P. A. Knott** and **J. M. Mellor,*** Chemistry Department, The University, Southampton

Dehydration of the 2 : 1 acetylacetone–formaldehyde adduct gives both 4,8-dimethylbicyclo[3,3,1]nona-3,7-diene-2,6-dione (1b) and 4,6-dimethylbicyclo[3,3,1]nona-3,6-diene-2,8-dione (2b). The 9-methyl analogues are obtained when formaldehyde is replaced by acetaldehyde and the 9-phenyl analogues when benzaldehyde is used. Bicyclo[3,3,1]nona-3,7-diene-2,6-dione (1a) is obtained from the dienol acetate of bicyclo[3,3,1]nonane-2,6-dione by bromination with *N*-bromosuccinimide and hydrolysis of the intermediate bromo-enol acetate. Structures are assigned to the bicyclic ketones by analysis of the n.m.r. spectra. Anomalous features of their u.v. spectra are noted. Reduction of the bicyclo[3,3,1]nona-3,6-diene-2,8-diones by mercuric chloride and magnesium in pyridine gives tricyclo[3,3,1,$0^{2,8}$]nona-4,6-diones.

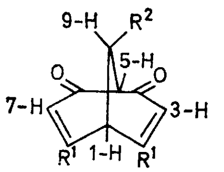
ALTHOUGH Knoevenagel[1] prepared 4,8-dimethylbicyclo[3,3,1]nona-3,7-diene-2,6-dione (1b), 4,8,9-trimethylbicyclo[3,3,1]nona-3,7-diene-2,6-dione (1c) and 4,8-dimethyl-9-phenylbicyclo[3,3,1]nona-3,7-diene-2,6-dione (1d) and the related 4,6,9-trimethylbicyclo[3,3,1]-nona-3,6-diene-2,8-dione (2c) structures have never been assigned rigorously to these unsaturated ketones.

[1] E. Knoevenagel, *Chem. Ber.*, 1903, **36**, 2136.

Since we wished to study their photochemistry we have repeated their preparation by the method of Knoevenagel and describe here their synthesis and assignment of structure.



(1)



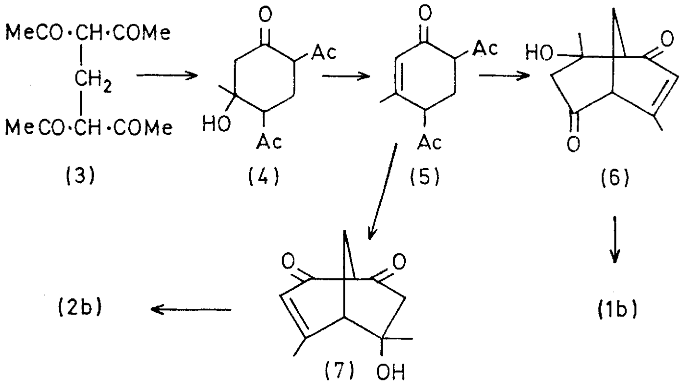
(2)

a; $R^1 = H$, $R^2 = H$
b; $R^1 = Me$, $R^2 = H$
c; $R^1 = Me$, $R^2 = Me$
d; $R^1 = Me$, $R^2 = Ph$

a; $R^1 = H$, $R^2 = H$
b; $R^1 = Me$, $R^2 = H$
c; $R^1 = Me$, $R^2 = Me$
d; $R^1 = Me$, $R^2 = Ph$

Synthesis.—Reaction of formaldehyde with acetylacetone in ethanol in the absence of an amine catalyst gives a product, m.p. 41·5—42·5°, formed from two molecules of acetylacetone and one of formaldehyde. This has been reported [2,3] to be the tetra-oxo-compound (3). In the presence of an amine catalyst other products are obtained.[4-6] An adduct, $C_{11}H_{16}O_4$, m.p. 87—89°, described as 'methylenebisacetylacetone' was isolated by Knoevenagel and the dehydration in warm concentrated sulphuric acid gave a compound $C_{11}H_{12}O_2$, m.p. 125—127° to which the structure (1b) was tentatively assigned. We find that the adduct, m.p. 41·5—42·5°, by dehydration in warm concentrated sulphuric acid, or in glacial acid containing 48% hydrobromic acid, or best in refluxing benzene containing toluene-*p*-sulphonic acid gives the dioxo-compound (1b) in 45% yield. A second minor dehydration product, $C_{11}H_{12}O_2$, m.p. 156—158°, may be obtained in 25% yield by chromatography of the reaction mixture. Structures will be assigned to the two dehydration products below but at this stage their formation may be represented as shown in the Scheme, in which no statement is implied concerning the nature of the predominant tautomeric structures of ketone (4) and ketone (5). That this sequence properly describes the formation of the dehydration products is clear from the dehydration of the tetraoxo-compound (3) in acetic acid containing hydrochloric acid. Then the major product isolated by chromatography is the monocyclic product (5), $C_{11}N_{14}O_3$, m.p. 75°. In benzene containing toluene-*p*-sulphonic acid the ketone (5) is further dehydrated to give (1b) and (2b).

Knoevenagel [1] described the reaction of acetaldehyde with acetylacetone to give 'ethylidenebisacetylacetone'



SCHEME 1

and of benzaldehyde with acetylacetone to give 'benzylidenebisacetylacetone'. By dehydration of the acetaldehyde adduct [1] [probably the trioxo-alcohol (8)], in acetic acid containing hydrobromic acid we isolated two products, $C_{12}H_{14}O_2$, m.p. 131—132° and $C_{12}H_{14}O_2$, m.p. 71—72°. By dehydration of the benzaldehyde adduct [1] in benzene containing toluene-*p*-sulphonic acid we isolated two products, $C_{17}H_{16}O_2$, m.p. 154—155° and $C_{17}H_{16}O_2$, m.p. 196—198°.

TABLE 1

N.m.r. data for bicyclo[3,3,1]nona-3,7-diene-2,6-diones and bicyclo[3,3,1]-3,6-diene-2,8-diones

	Hydrogens (τ value, multiplicity and coupling constant in Hz)							Methyls		
Compd.	1-H	2-H	3-H	5-H	6-H	7-H	9-H	C-2	C-6 (C-8)	C-9
(1a)	6·66dt, $J_{1,2}$ 7 $J_{1,9}$ 2·5	2·99q, $J_{2,3}$ 10 $J_{1,2}$ 7	4·13d, $J_{1,2}$ 10	As 1-H	As 2-H	As 3-H	7·26, $J_{1,9}$ 2·5			
(1b)	6·92, $J_{1,9}$ 3		4·37m	As 1-H		As 3-H	7·30t, $J_{1,9}$ $J_{5,9}$ 3	8·01d, J 2	As C-2	
(1c)	7·12d, $J_{1,9}$ 2·5		4·35m	As 1-H		4·35m	7·00m	8·03d, J 2	As C-2	8·80d, J 6
(1d)	6·56d, $J_{1,9}$ 3		4·42m	As 1-H		4·27m	5·88t, $J_{1,9}$ $J_{5,9}$ 3	8·06d, J 2	7·92d, J 2	
(2b)	7·04t, $J_{1,9}$ 3		4·35m	6·63t, $J_{5,9}$ 3		As 3-H	7·28t, $J_{1,9}$ $J_{5,9}$ 3	7·85d, J 2	As C-2	
(2c)	7·27		4·30m	6·85m		4·30m	7·10m	7·90d, J 3	7·85d, J 3	8·82d, J 6·5
(2d)	6·72t, $J_{1,9}$ 2·5		4·33m	6·14m		4·21m	5·79t, $J_{1,9}$ $J_{5,9}$ 2·5	7·98d, J 2	7·76d, J 2	

Structural assignment.—The dehydration products of the acetylacetone–formaldehyde adduct are also formed from the monocyclic ketone (5). Further dehydration of ketone (5) can lead to the oxo-compound (1b), which has C_{2v} symmetry or to the diketone (2b) which has a plane of symmetry. In both compounds the n.m.r. spectra (see Table 1) show a single resonance attributable to a methyl group, consistent with the structures (1b) and (2b). A distinction between the two structures may be made by consideration of the other resonances in the n.m.r. spectra. For the diketone (1b) of C_{2v} symmetry the two bridgehead hydrogens

---

[2] B. D. Wilson, *J. Org. Chem.*, 1963, **28**, 314.

[3] J. K. O'Loane, C. M. Combs, and R. L. Griffith, *J. Org. Chem.*, 1964, **29**, 1730.

[4] P. Rabe and F. Elze, *Annalen*, 1902, **323**, 83.

[5] P. Rabe, *Annalen*, 1904, **332**, 1.

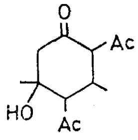
[6] W. A. Kennedy and T. B. H. McMurray, *J. Chem. Soc.* (*C*), 1969, 879.

are equivalent and this structure is assigned to the diketone, m.p. 125—127°, which has resonances at τ 6·92 and 7·30. For the oxo-compound (2b), characterised by a symmetry plane the two bridgehead hydrogens are non-equivalent and this structure is assigned to the dioxo-compound, m.p. 156—158°, which has resonances at τ 6·63 (1H), 7·04 (1H) and 7·28 (2H). The original structural assignment made by Knoevenagel[1] for the dioxo-compound (1b) is therefore correct.

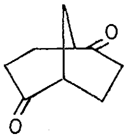
The pairs of dioxo-compounds (1c) and (2c), and (1d) and (2d) may similarly be distinguished. In each case the higher melting dioxo-compounds (2c) and (2d) show two non-equivalent bridgehead hydrogens but the lower melting dioxo-compounds (1c) and (1d) show two equivalent bridgehead hydrogens.

The analysis of the n.m.r. spectra of the dioxo-compounds is straightforward but for two points. In the dioxo-compound (1b) the signals of 1-H and 5-H which are equivalent must be distinguished from the signal of 9-H. It might be expected that 1-H and 5-H in (1b) would have a chemical shift intermediate between 1-H and 5-H in (2b). For compounds (1c) and (1d) the chemical shift of 1-H and 5-H, τ 7·12 and 6·56 respectively, confirm this expectation. For the dioxo-compound (1b), the signal at τ 6·92, intermediate between the bridgehead resonances of the dioxo-compound (2b) τ 6·63 and 7·04 is then assigned to 1-H and 5-H, the bridgehead hydrogens, and the signal at τ 7·30 is assigned to the hydrogens 9-H at the bridge.

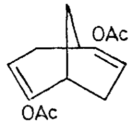
The validity of these assignments is reinforced by consideration of the n.m.r. spectrum of the diketone (1a), which was prepared from the dioxo-compound (9). Bromination of the dioxo-compound (9)[7] in acetic acid, followed by dehydrobromination of the intermediate bromo-ketones under a variety of conditions failed to give a satisfactory yield of the unsaturated dioxo-compound (1a). However conversion of the ketone (9) to the dienol acetate (10)[8] permitted allylic bromination[9] with *N*-bromosuccinimide under carefully controlled conditions to give a mixture of bromo-enol acetates (11). Without further purification the crude bromo-enol acetates (11) were hydrolysed to give the unsaturated dioxo-compound (1a) in 50% overall yield from the dioxo-compound (9).



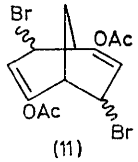
(8)



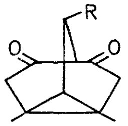
(9)



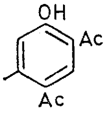
(10)



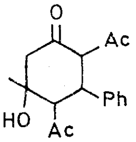
(11)



(12) a; R = H
b; R = Ph



(13)



(14)

In the n.m.r. spectrum of (1a) the bridgehead hydrogens are further split by the neighbouring vinyl hydrogen and therefore appear as a doublet of triplets with $J_{1,2}$ 7 Hz and $J_{1,9}$ 2·5 Hz. The chemical shift of the bridgehead hydrogens in (1a) at τ 6·66 and of the bridge hydrogens at τ 7·26 are in close accord with the above assignment.

The other assignment deserving comment pertains to the non-equivalent bridgehead hydrogens in the dioxo-compounds (2b), (2c), and (2d). In each case the resonance at lower field is tentatively assigned to 5-H and that at higher fields to 1-H. Synthesis of the dioxo-compound (2a) would permit confirmation of this assignment.

The yellow colour of all the bicyclo[3,3,1]nonadienediones prepared in this work indicates an interaction between the two rigidily held eneone chromophores. In Table 2 the u.v. spectra of the diene-diones are listed.

TABLE 2

U.v. spectral maxima of bicyclo[3,3,1]nonadienediones and related compounds

Compd.	Maxima (nm.)	$\varepsilon_{max.}$	Solvent
(1a)	229	8000	EtOH
	270sh	1570	
	349	560	
(1b)	236	11,950	Hexane
	330	770	
	350	770	
	366	513	
	381	206	
(1b)	237	16,850	EtOH
	268sh	1720	
	280sh	900	
	344	975	
(1c)	238	14,250	EtOH
	268sh	1432	
	348	758	
(1d)	237	15,700	EtOH
	270sh	2185	
	348	835	
(2b)	224	27,700	EtOH
	239sh	11,000	
	272	1640	
	320sh	228	
	335	200	
	362	170	
(2c)	221	30,640	EtOH
	239sh	12,780	
	271sh	2157	
	335	209	
	367	197	
(2d)	223	19,600	EtOH
	240sh	9800	
	270sh	2700	
	336	225	
	362	200	

The π–π^* transition is unexceptional both in position and intensity. The n–π^* transition of both series of diones is shifted to longer wavelength by comparison

---

[7] J. P. Schaefer and L. M. Honig, *J. Org. Chem.*, 1968, **33**, 2655.

[8] H. Meerwein, F. Kiel, G. Klosgen, and E. Schoch, *J. prakt. Chem.*, 1922, **104**, 161.

[9] C. Djerassi and C. R. Scholz, *J. Org. Chem.*, 1949, **14**, 660.

with simple cyclohexenones.[10] This shift and an enhancement have been noted in other αβ-unsaturated ketones of similar structure.[11-13] A third transition at 270 nm., due to charge transfer or a coupling of transitions is comprable to that observed in certain βγ-unsaturated ketones.[14]

The interaction of the two eneone chromophores is reflected in the photochemistry of these ketones[15] and a homoconjugative interaction is indicated in the pinacol reduction of ketone (2b) which leads to formation of the tricyclo[3,3,1,$0^{2,8}$]nonadione (12a). Reduction with magnesium and mercuric chloride in pyridine under nitrogen led smoothly to the formation of the tricyclic ketone (12a) in 70% yield. The product was characterised by the parent ion, $M^+ = 178$, $\nu_{max.}$ 1700 cm.$^{-1}$ and the n.m.r. spectrum which indicated a product with an element of symmetry. No resonance attributable to a vinyl hydrogen was observed and the cyclopropyl hydrogen was observed to resonate at τ 9·10. Similarly reduction of (2d) gave the tricyclic ketone (12b), characterised by two methyl signals at τ 8·57 and 8·66 and a cyclopropyl hydrogen at τ 8·80. Although the intermolecular pinacol reduction of αβ-unsaturated ketones[16] and the intramolecular reduction of saturated ketones[17] are known this represents a useful extension of the pinacol reduction.

EXPERIMENTAL

I.r. spectra were measured in solution in chloroform with a Unicam SP 200 spectrophotometer. N.m.r. spectra were measured in deuteriochloroform solution with a Varian A. 60 spectrometer. Bands were observed as sharp singlets except where otherwise stated. Band positions are given on the τ scale and coupling constants (*J*) in Hz. U.v. spectra were measured, unless stated otherwise, in solution in ethanol with a Unicam SP 800 spectrophotometer. Organic solutions were dried (Na_2SO_4) before evaporation. T.l.c. was carried out on Merck silica gel (Stahl) and column chromatography on Grace Kieselgel (100—200 mesh). G.l.c. was carried out on a 5% CDMS column on chromosorb W at 180° or 200°.

Bicyclo[3,3,1]*nona*-3,7-*diene*-2,6-*dione* (1a).—The enol acetate[8] (10) (225 mg.) in carbon tetrachloride (10 ml.) containing *N*-bromosuccinimide (320 mg.) was heated at 75° for 30 min. The solution was cooled and filtered, and the residue was washed with further carbon tetrachloride; the combined filtrates and washings were evaporated under reduced pressure to give a yellow oil (320 mg.), $\nu_{max.}$ 1760 cm.$^{-1}$. This was dissolved in ethanol (3 ml.) and 2N-hydrochloric acid (2 ml.) was added to it. After 15 min. at 70° the solution was evaporated under reduced pressure to give a yellow oil which slowly crystallised. Recrystallisation from ether–ethyl acetate gave *bicyclo*[3,3,1]*nona*-3,7-*diene*-2,6-*dione* as small prisms, m.p. 81—83° (Found: C, 73·0; H, 5·4%. $C_9H_8O_2$ requires C, 73·0; H, 5·4%), $\nu_{max.}$ 1678 cm.$^{-1}$; M^+, 148.

4,8,9-*Trimethylbicyclo*[3,3,1]*nona*-3,7-*diene*-2,6-*dione* (1c) *and* 4,6,9-*Trimethylbicyclo*[3,3,1]*nona*-3,6-*diene*-2,8-*dione* (2c).—Acetylacetone (20 g.) and acetaldehyde (4·4 g.) were dissolved in ethanol (45 ml.) and the solution was cooled to 0°; diethylamine (1 ml.) in ethanol (4 ml.) was then added to it. After 6 days at 0° the solvent was evaporated off under reduced pressure and the crude residue was dissolved in glacial acetic acid (100 ml.) containing hydrobromic acid (10 ml. of 45%). The solution was heated under reflux for 12 hr. concentrated under reduced pressure, and the residue partitioned between chloroform and water. The chloroform layer was washed successively with potassium hydrogen carbonate solution, and water, and then dried; the solvent was removed to afford a crude residue which was chromatographed on silica gel (400 g.). Elution with 30% ether in light petroleum (b.p. 40—60°) afforded 4,8,9-trimethylbicyclo[3,3,1]-nona-3,7-diene-2,6-dione (1c), m.p. 71—72° [from ether–light petroleum (b.p. 40—60°)] (lit.,[1] m.p. 64°); $\nu_{max.}$ 1670 and 1635 cm.$^{-1}$; M^+ 190. Elution with ether afforded 4,6,9-trimethylbicyclo[3,3,1]nona-3,6-diene-2,8-dione (2c), m.p. 131—132° (from ether) (lit.,[1] m.p. 136°); $\nu_{max.}$ 1680, 1655, and 1635 cm.$^{-1}$; M^+ 190.

2,4-*Diacetyl*-5-*methylcyclohex*-5-*en*-1-*one* (5).—Crude 3,5-diacetylheptane-2,6-dione[3] (3) (20 g.) was heated under reflux for 20 hr. with 10N-hydrochloric acid (5 ml.) in glacial acetic acid (150 ml.). The solvent was removed under reduced pressure and a portion of the residue (5 g.) was chromatographed on silica gel (150 g.). Elution with 50% ether in light petroleum (b.p. 40—60°) gave 4,8-dimethylbicyclo[3,3,1]nona-3,7-diene-2,6-dione (1b) (500 mg.) and elution with 60% ether in light petroleum (b.p. 40—60°) gave 2,4-diacetyl-5-methylcyclohex-5-enone (5) (1·85 g.). Recrystallisation from ether–light petroleum (b.p. 40—60°) gave 2,4-diacetyl-5-methylcyclohex-5-enone, m.p. 70—75° (lit.,[1] m.p. 75°), $\nu_{max.}$ 1710 and 1650—1590 cm.$^{-1}$; $\lambda_{max.}$ 225 (ε 9900) and 338 (6220); in ethanolic sodium hydroxide $\lambda_{max.}$ 312 (ε7450) and 358 nm (9750); τ 1·8 (1H, s), 3·97 (1H, m), 6·82 (1H, m), 7·20 (2H, m), 7·80 (3H, s) and 8·01 (3H, d, *J* 3 Hz); M^+ 194.

4,8-*Dimethylbicyclo*[3,3,1]*nona*-3,7-*diene*-2,6-*dione* (1b) *and* 4,6-*Dimethylbicyclo*[3,3,1]*nona*-3,6-*diene*-2,8-*dione* (2b).—(a) *Dehydration with toluene*-p-*sulphonic acid in benzene.* Crude 3,5-diacetylheptane-2,6-dione[3] (3) (177·5 g.) was heated under reflux in dry benzene (440 ml.) containing toluene-*p*-sulphonic acid (8·9 g.); water was removed with a Dean and Stark separator. After 3 days removal of water was complete (2·2 moles) and the cooled solution was washed with water, dried, and the solvent removed under reduced pressure. The orange residue was chromatographed on silica gel and the following fractions were eluted. In 2% ether in benzene: 2,4-diacetyl-5-hydroxytoluene (13) m.p. 108—109° [from ether–light petroleum (b.p. 60—80°)] (lit.,[1] m.p. 112°); $\nu_{max.}$ 1680 and 1650 cm.$^{-1}$; $\lambda_{max.}$ 244 nm (ε, 37,000) and 318 nm (3500); in ethanolic sodium hydroxide $\lambda_{max.}$ 252 nm. (ε 24,000) and 313 nm

---

[10] E. M. Kosower, G. Wu, and T. S. Sorensen, *J. Amer. Chem. Soc.*, 1961, **83**, 3147.

[11] M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, 1967, **89**, 6356.

[12] J. Ciabattoni, J. E. Crowley, and A. S. Kende, *J. Amer. Chem. Soc.*, 1967, **89**, 2778.

[13] S. Ito, H. Takeshita, Y. Shoji, Y. Toykooka, and T. Nozoe, *Tetrahedron Letters*, 1969, 443.

[14] D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc.* (*B*), 1967, 215.

[15] P. A. Knott and J. M. Mellor, *Tetrahedron Letters*, 1970, 1829.

[16] J. Wiemann, *Bull. Soc. chim. France*, 1964, 2545.

[17] T. J. Curphey, C. W. Amelotti, T. P. Layloff, R. L. McCortney, and J. H. Williams, *J. Amer. Chem. Soc.*, 1969, **91**, 2817.

(24,800); τ −2·45 (1H, s), 2·8 (1H, s), 3·2 (1H, s) 7·33 (3H, s) and 7·42 (6H, s); M^+ 192.

In 15% ether in benzene: 4,8-dimethylbicyclo[3,3,1]-nona-3,7-diene-2,6-dione (1b), m.p. 125—127° [from ether–light petroleum (b.p. 60—80°)] (lit.,[1] m.p. 125—127°) (Found: C, 74·9; H, 6·9%. Calc. for $C_{11}H_{12}O_2$: C, 75·0; H, 6·9%); $\nu_{max.}$ 1670 and 1635 cm.$^{-1}$; M^+ 176.

In 20% ether in benzene: a substance, m.p. 135—137° which is the subject of a separate investigation.

In 75% ether in benzene 4,6-*dimethylbicyclo*[3,3,1]*nona*-3,6-*diene*-2,8-*dione* (2b), m.p. 156—158° (from chloroform–ether) (Found: C, 75·0; H, 6·9%. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·9%); $\nu_{max.}$ 1680, 1655, and 1630 cm.$^{-1}$; M^+ 176.

(b) *Dehydration in acetic acid.* Crude 3,5-diacetylheptane-2,6-dione (3) (2 g.) was heated under reflux in glacial acetic acid (50 ml.) containing toluene-*p*-sulphonic acid (25 mg.) for 24 hr. The solution was concentrated under reduced pressure, cooled, and the residue partitioned between ether and water. The dried ethereal layer was analysed by g.l.c. 3,5-Diacetylheptane-2,6-dione (1·6 g.) was treated under the same conditions for 24 hr. with 10N-hydrochloric acid [0·5 ml. in acetic acid (25 ml.)] as catalyst and with 45% hydrobromic acid [0·5 ml. in acetic acid (25 ml.)].

(c) *Dehydration in sulphuric acid.* 3,5-Diacetylheptane-2,6-dione (2 g.) dissolved in 10N-sulphuric acid (5 ml.) was left for 24 hr. at 20°. The solution was poured into water and ether extraction afforded a yellow oil which was analysed by g.l.c.

(d) *Dehydration of* 2,4-*diacetyl*-5-*methylcyclohex*-5-*ene*-1-*one* (5). 2,4-Diacetyl-5-methylcyclohex-5-ene-1-one (5) (379 mg.) was heated under reflux in benzene (150 ml.) for 2 days with toluene-*p*-sulphonic acid (32 mg.). The cooled solution was washed with water, dried, and the solvent removed to give a crude residue which was chromatographed on silica gel. The following fractions were eluted: in 20% ether in light petroleum (b.p. 40—60°) 2,4-diacetyl-5-hydroxytoluene (13) (32 mg.); in 50% ether in light petroleum (b.p. 40—60°) 4,8-dimethylbicyclo[3,3,1]nona-3,7-diene-2,6-dione (1b) (174 mg.); and in 75% ether in light petroleum 4,6-dimethylbicyclo[3,3,1]nona-3,6-diene-2,8-dione (2b) (75 mg.).

The analysis by g.l.c. of the products of dehydration shows that in all experiments formation of the monocyclic ketone (5) was rapid. Subsequent dehydration was most easily achieved with hydrobromic acid in glacial acetic acid or toluene-*p*-sulphonic acid in benzene. Little (<5%) 4,6-dimethylbicyclo[3,3,1]nona-3,6-diene-2,8-dione (2b) was formed in acetic acid; in benzene the ratio of (1b) to (2b) was 2 : 1.

4,8-*Dimethyl*-9-*phenylbicyclo*[3,3,1]*nona*-3,7-*diene*-2,6-*dione* (1d) *and* 4,6-*Dimethyl*-9-*phenylbicyclo*[3,3,1]*nona*-3,6-*diene*-2,8-*dione* (2d).—(a) *Dehydration with toluene*-p-*sulphonic acid in benzene.* The ketone [1] (14), m.p. 166° (77 g.) was heated under reflux in dry benzene (500 ml.) containing toluene-*p*-sulphonic acid (5 g.); water was removed with a Dean and Stark separator. After 3 days the solution was cooled to give a crystalline product. Recrystallisation from benzene–ethanol afforded pale yellow crystals of 4,8-dimethyl-9-phenylbicyclo[3,3,1]nona-3,7-diene-2,6-dione (1d), m.p. 153—154° (lit.,[1] m.p. 154°) (Found: C, 81·1; H, 6·4%. Calc. for $C_{17}H_{16}O_2$: C, 80·9; H, 6·4%), $\nu_{max.}$ 1660 and 1630 cm.$^{-1}$; M^+ 252.

The mother liquors on crystallisation from chloroform–light petroleum (b.p. 60—80°) afforded a second dione. Recrystallisation from benzene–chloroform gave as pale yellow crystals 4,6-*dimethyl*-9-*phenylbicyclo*[3,3,1]*nona*-3,6-*diene*-2,8-*dione* (2d), m.p. 196—198° (Found: C, 81·1; H, 6·5%. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%), $\nu_{max.}$ 1685, 1655, and 1635 cm.$^{-1}$; M^+ 252.

(b) *Dehydration in acetic acid.* The ketone (14), m.p. 166°, was heated in acetic acid with toluene-*p*-sulphonic acid, or hydrochloric acid or hydrobromic acid as dehydration catalyst in a similar manner to that used for the dehydration of 3,5-diacetylheptane-2,6-dione. The products were analysed by g.l.c.

Analysis by g.l.c. showed that in acetic acid with hydrobromic acid as catalyst ketone (2d) was a minor product (<5%). In benzene the ratio of (1d) to (2d) was 2 : 1.

2,8-*Dimethyltricyclo*[3,3,1,0^{2,8}]*nonane*-4,6-*dione* (12a).—4,6-Dimethylbicyclo[3,3,1]nona-3,6-diene-2,8-dione (2b) (1·32 g.), mercuric chloride (1·02 g.), and magnesium (0·18 g.) were stirred at 0° in pyridine (20 ml.) under nitrogen for 18 hr. After filtration, the residue was washed with a little pyridine, the washings and filtrate were combined and concentrated under reduced pressure. The concentrate was diluted with water, and the products were extracted into chloroform. The chloroform solution was washed successively with 0·5N-hydrochloric acid, sodium carbonate solution, and water and was then dried; evaporation gave a yellow oil (1 g.). Chromatography on silica gel (30 g.) afforded in ether–light petroleum (b.p. 40—60°) the reduction product (510 mg.) and in ether unchanged starting material. Recrystallisation of the first fraction gave 2,8-*dimethyltricyclo*[3,3,1,0^{2,8}]*nonane*-4,6-*dione* (12a), m.p. 54—56° [from ether–light petroleum (b.p. 60—80°)] (Found: C, 74·0; H, 7·9%. $C_{11}H_{14}O_2$ requires C, 74·1; H, 7·9%); $\nu_{max.}$ 1700 cm.$^{-1}$; $\lambda_{max.}$ 315 nm (ε 375); τ 6·82 (1H, t, J 3 Hz), 7·32 (4H, s) 7·54 (2H, t, J 3 Hz), 8·78 (6H, s), 9·10 (1H, t, J 3 Hz). Irradiation of 4,6-dimethylbicyclo[3,3,1]nona-3,6-diene-2,8-dione (2b) as a 1% solution in benzene-isopropyl alcohol (1 : 1) with a 125-W mercury lamp through Pyrex led to a number of photoproducts, one of which on t.l.c. showed an identical retention time to that of 2,8-dimethyltricyclo[3,3,1,0^{2,8}]-nonane-4,6-dione (12a).

2,8-*Dimethyl*-9-*phenyltricyclo*[3,3,1,0^{2,8}]*nonane*-4,6-*dione* (12b).—4,6-Dimethyl-9-phenylbicyclo(3,3,1)nona-3,6-diene-2,8-dione (2d) (12 g.), mercuric chloride (4·5 g.), and magnesium (1·4 g.) were stirred at 0° in pyridine (150 ml.) under nitrogen for 36 hr. After filtration and concentration of the filtrate under reduced pressure, water was added. The products were extracted with ether and the ether layer was washed successively with 0·5N-hydrochloric acid, sodium carbonate solution, and water. Removal of the solvent gave a crude residue which on recrystallisation from chloroform–light petroleum (b.p. 60—80°) gave powdery crystals (9·7 g.) of 2,8-dimethyl-9-phenyltricyclo-[3,3,1,0^{2,8}]nonane-4,6-dione (12b), m.p. 162—163° (Found: C, 79·9; H, 7·1%. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%); $\nu_{max.}$ 1720, 1695, and 1600 cm.$^{-1}$; $\lambda_{max.}$ 252 (ε 620), 258 (520), 265 (420), 287 (250), 297 (250), and 315 nm. (226); τ 2·5—2·9 (5H, m), 6·09 (1H, t, J 3 Hz), 6·62 (1H, d, J 3 Hz), 7·25 (2H, s), 7·32 (2 H, s), 8·57 (3H, s), 8·66 (3H, s) and 8·80 (1H, m); M^+, 254.

[0/745 *Received, May 7th*, 1970]