The Lithium Enolate of Cyclo-octa-2,4,6-trienone and its Reactions with Electrophiles

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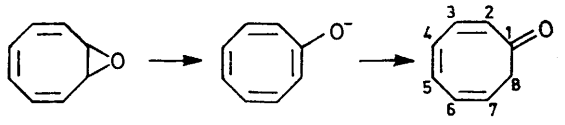
Lithium di-isopropylamide catalysed rearrangement of 7,8-epoxycyclo-octa-1,3,5-triene at low temperature gives the lithium enolate of cyclo-octa-2,4,6-trienone, which can be alkylated at C-8 with reactive electrophiles such as methyl iodide, allyl bromide, ethyl iodide, benzyl iodide, and benzeneselenenyl bromide. Bromination of the enolate also occurs at C-8, but reagents such as acetyl chloride and ethyl chloroformate yield only the products of *O*-acylation.

In 1951 Cope and Tiffany [1] reported the first preparation of cyclo-octatrienone (3) by a lithium diethylamide catalysed rearrangement of epoxycyclo-octatriene (1).



(1) (2) (3)

Further investigation [2] of the properties of cyclo-octatrienone (3) revealed that it formed normal derivatives of the carbonyl group, but that it was extremely resistant to reactions involving the enolate anion (2).

For example, although the trienone (3) was soluble in aqueous sodium hydroxide, it resisted all attempts to form alkyl derivatives by treatment with alkyl halides in the presence of alkoxides. Subsequent studies by Matsuda and his co-workers [3] revealed that, under forcing conditions, nucleophilic alkoxides attack the carbonyl group of cyclo-octatrienone and induce a ring contraction to cyclohexa-2,5-dienylacetate esters. Nevertheless, Roberts [4] has reported deuteriation experiments with cyclo-octatrienone, presumably involving the enolate (2). Five deuterium atoms were incorporated, at positions 2, 4, 6, and 8, by equilibrating cyclo-octatrienone with NaOD in D_2O under extremely forcing conditions. Using non-nucleophilic bases and various electrophiles, Gund and Carpino [5] were unable to convert cyclo-octatrienone into any substituted derivatives, and these results therefore suggest that the enolate anion (2) cannot be generated by abstracting a proton from (3).

Cope and Tiffany [1] had suggested that the formation of cyclo-octatrienone (3) from epoxycyclo-octatriene (1) involved abstraction of a proton at C-1 and rearrangement to the enolate anion (2), followed by protonation to give (3) during the subsequent work-up. We therefore concluded that the most reasonable method of generating the enolate anion (2) was by base-catalysed rearrangement of (1) at low temperatures. Capture of the enolate anion (2) by an electrophile could result in *C*- or *O*-alkylation. If *C*-alkylation were a major pathway this reaction could provide a convenient synthetic route to a wide variety of substituted cyclo-octatrienones, including a suitable precursor to cyclo-octatriene-1,2-dione. The only other method available for the preparation of cyclo-octatrienone derivatives is the rather limited and low-yielding diazoalkane-induced ring expansion of tropone.[6]

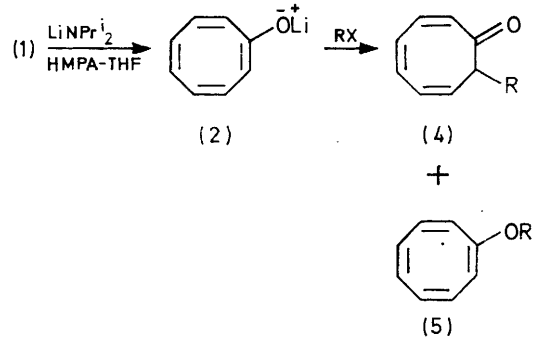
In order to test the feasibility of generating and trapping the enolate anion (2) by this method, epoxycyclo-octatriene (1) was added to a solution containing a slight excess of lithium di-isopropylamide in tetrahydrofuran at −78 °C. The mixture was allowed to warm to 0 °C, and then quenched with a large excess of acetic [^{2}H]acid. After work-up and distillation, the deuteriated cyclo-octatrienone isolated (76%) was shown by n.m.r. and mass spectrometry to have incorporated one deuterium atom at C-8 to the extent of 85%. Encouraged by this result, we investigated the reactions of carbon electrophiles. Addition of a large excess of methyl iodide to the solution of the enolate anion (2) in tetrahydrofuran, followed by stirring at room temperature (4 h) and work-up, afforded a very small amount of alkylated product (4%), the major product being cyclo-octatrienone (3) itself. The lithium enolate anion (2) generated in this way may have been too unreactive towards alkylation and had simply been protonated during the aqueous work-up. In such a situation hexamethylphosphoric triamide (HMPA) could be expected to activate the lithium enolate anion (2) to attack by carbon electrophiles. The use of a large excess of HMPA as a co-solvent in the above reaction mixture afforded a deep red solution of the enolate anion (2) which could be alkylated with an excess of methyl iodide to give 8-methylcyclo-octatrienone (4; R = Me) in 78% yield. Therefore, in all subsequent work reported here, including deuteriation experiments, HMPA was used as co-solvent.

The results of the reactions of the enolate (2) with various electrophiles are summarised in Table 1.

Table 1 shows that reactive electrophiles (methyl iodide, ethyl iodide, and allyl bromide) will alkylate the enolate anion (2) in the 8-position, whereas *O*-alkylation is not observed. However, when the only slightly less reactive ethyl bromide is used as alkylating agent, some *O*-alkylation (11%) occurs. The only reactive electrophile which gave surprisingly low amounts of *C*-alkylated product (15%) was benzyl bromide. In this case,

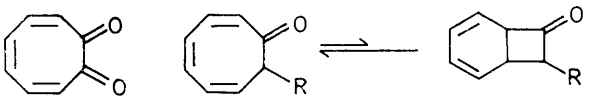
[1] A. C. Cope and B. D. Tiffany, *J. Amer. Chem. Soc.*, 1951, **73**, 4158.
[2] A. C. Cope, S. F. Schaeren, and E. R. Trumbull, *J. Amer. Chem. Soc.*, 1954, **76**, 1096.
[3] M. Ogawa, M. Takagi, and T. Matsuda, *Chem. Letters*, 1972, 527.
[4] C. Ganter, S. M. Pokras, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1966, **88**, 4235.
[5] P. H. Gund, Ph.D. Dissertation, University of Massachusetts, 1967.
[6] M. Franck-Neumann, *Tetrahedron Letters*, 1970, 2143.

however, *O*-alkylation did not seem to be a competing reaction. Rather, the enolate or an alkylation product



(2) (4) (5)

seemed to polymerise at a rate comparable to that for *C*-alkylation, and on work-up at a stage when polymerisation seemed to have been significant, the main bromination of enolates.[9] Thus, direct bromination of the enolate (2) afforded the bromo-ketone (4; R = Br) as an unstable low-melting solid. Methods for transforming this compound into the α-diketone (6) are under investigation.



(6) (4) (7)

In connection with approaches to functionalisation of the enolate (2) at C-8, its reactions with various sulphur and selenium electrophiles were studied. Addition of diphenyl disulphide or benzeneselenenyl chloride[10] to the enolate at −78 °C resulted in varying quantities of the acetophenone derivatives (9; R = SPh) and (10; R = SPh) and (9; R = SePh) and (10; R = SePh),

TABLE 1

Reactions of the enolate (2) with electrophiles

Electrophile	Time (h)	Temp. (°C)	R	Yield of (4) (%)	Yield of cyclo-octatrienone (4; R = H) (%)	Yield of (5) (%)
$MeCO_2D$	0.08	0	D	76	14	
MeI	2.0	−78 to 20	Me	78		
$CH_2{:}CH{\cdot}CH_2Br$	4.0	−78 to 20	$CH_2{:}CH{\cdot}CH_2$	74		
EtBr	12.0	−78 to −5	Et	16	22	11
EtI	12.0	−78 to −5	Et	81		
$PhCH_2Br$	3.0	−78 to −5	$PhCH_2$	15	48	
$PhCH_2I$	3.0	−78 to −5	$PhCH_2$	37	51	
MeCOCl *	2.0	−78 to −5	Ac		36	9
$ClCO_2Et$ *	2.0	−78 to −5	EtO_2C		62	28
PhSeBr †	0.5	−78 to 20	PhSe	40		
PhSCl †	0.5	−78 to 20	PhS	26		
Br_2	0.08	−78	Br	51		

* Two-fold excess of enolate used. † Inverse addition of enolate at −78 °C to electrophile at −78 °C.

characterisable by-product was cyclo-octatrienone (4; R = H) itself. The use of benzyl iodide improved the yield of (4; R = $PhCH_2$), but polymerisation was still observed to be a competing side reaction.

Attempted *C*-acylation to give a β-diketone or a β-keto-ester was completely unsuccessful. It is known that effective *C*-acylation of simple enolates depends upon adding the acylating agent to a two- or three-fold excess of the enolate.[7] Even under these conditions the reaction of the enolate (2) with acetyl chloride afforded the product of *O*-acylation (5; R = Ac) (9%), and with ethyl chloroformate (5; R = CO_2Et) (28%). With equimolar quantities of acylating agent, *O*-acylation occurred to a greater extent (26 and 63%, respectively).

Our investigation of the reactions of the enolate anion (2) was in part stimulated by our interest in the cyclo-octatrienediones.[8] Functionalisation of the enolate (2) at C-8 could be expected to provide a convenient precursor of cyclo-octatriene-1,2-dione (6). α-Functionalisation of ketones has recently been achieved by direct

respectively. The formation of these products can easily be rationalised by a reaction of the bicyclic valence tautomer (7). In the unsubstituted cyclo-octatrienone (4; R = H), the bicyclic form is known to be in equilibrium with the monocyclic form to the extent of about 5% at 20 °C.[1,11] Deprotonation of the bicyclic species (7) at the ring junction by residual base or enolate (2) could lead to a species which should form a stable enolate (8) by an aromatisation process and cleavage of the four-membered ring. Protonation of the enolate (8) would yield (9), whereas further reaction with an electrophile RX would give (10). Similar reactions have been observed by Gund.[5] This problem can be avoided by using a very reactive electrophile whose leaving group is a poor base, and by ensuring that no residual base is present to deprotonate the bicyclic valence tautomer (7). Thus, addition of a cooled (−78 °C) solution of the enolate (2) to benzeneselenenyl chloride or bromide at −78 °C gives satisfactory yields of the 8-phenylselenocyclo-octatrienone (4; R = SePh), whereas use of

[7] H. O. House, 'Modern Synthetic Reactions,' Benjamin, California, 1972, pp. 762—765.

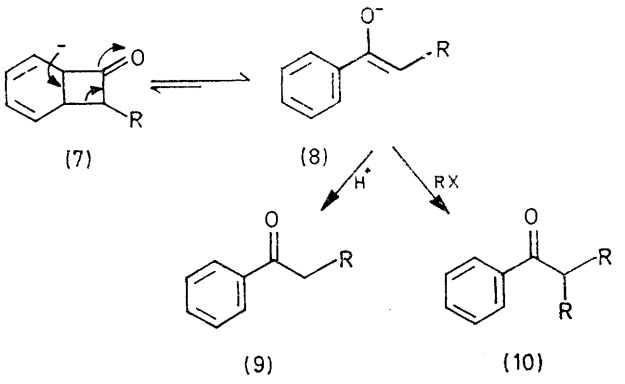
[8] P. A. Chaloner, A. B. Holmes, M. A. McKervey, and R. A. Raphael, *Tetrahedron Letters*, 1975, 265.

[9] P. L. Stotter and K. A. Hill, *J. Org. Chem.*, 1973, **38**, 2576.

[10] H. J. Reich, J. M. Renga, and I. L. Reich, *J. Amer. Chem. Soc.*, 1975, **97**, 5434.

[11] R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, Chem. Soc. Special Publ. No. 19, 1965, pp. 3—20; M. Brookhart, G. O. Nelson, G. Scholes, and R. A. Watson, *J.C.S. Chem. Comm.*, 1976, 195.

benzenesulphenyl chloride results in poorer yields of the phenylthio-compound (4; R = SPh).



The physical properties of the alkylcyclo-octatrienones (4) are similar to those of cyclo-octatrienone itself. They all possess a characteristic smell, are all yellow oils boiling at moderate temperatures, and are sensitive to air, moisture, and protic solvents. The i.r. spectra reveal that the bicyclic tautomer (7) is present to a greater extent than in cyclo-octatrienone itself (a two-fold enhancement in the intensity ratio of the band at 1 780 cm^{-1} relative to the band at 1 660 cm^{-1} is observed), and this trend is evident in the disubstituted cyclo-octatrienone studied by Franck-Neumann,[6] where the bicyclic form predominates almost completely.

The u.v. spectra of the alkyl cyclo-octatrienones (4) resemble that of cyclo-octatrienone itself (see Table 2) and a further similarity to the unsubstituted compound is their resistance to further alkylation *via* their enolate anions.

TABLE 2

U.v. and visible spectra of cyclo-octatrienones (4) in cyclohexane

R	$\lambda_{max.}$/nm (ε)			
H [a]		245 (7 000)	282 (4 300)	360 (500)
Me [b]	216 (8 800)	245 (4 900)	281 (4 000)	359 (400)
Et	216 (12 800)	247 (4 500)	281 (3 300)	360 (400)
CH_2·CH·CH_2	215 (9 800)	246 (5 900)	282 (3 600)	361 (400)
$PhCH_2$	220 (11 400)	248 (5 700)	284 (3 500)	361 (400)

[a] Ref. 1. [b] Ref. 6.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. ^{1}H N.m.r. spectra were recorded at 100 MHz with a Varian HA-100 spectrometer, and Fourier transform proton noise decoupled ^{13}C n.m.r. spectra were determined at 20 MHz with a Varian CFT-20 spectrometer, both with tetramethylsilane as standard. I.r. spectra were recorded for 2.5% (w/v) solutions with a Perkin-Elmer 257 spectrometer, and electronic spectra for solutions in cyclohexane or ethanol with a Unicam SP 1800 spectrometer. Mass spectra were recorded with an A.E.I. MS30 instrument. Microanalyses were determined by Mr. D. Flory and his staff at the University Chemical Laboratory. Preparative layer chromatography was carried out on 20 × 20 cm glass plates coated to a thickness of 1 mm with Merck Kieselgel PF_{254}.

Preparation of the Enolate Anion (2) *of Cyclo-octatrienone* (3).—A solution of lithium di-isopropylamide (3 mmol) in tetrahydrofuran (THF) (20 ml) and hexamethylphosphoric triamide (HMPA) (3 ml, 17 mmol) was prepared by adding a solution of n-butyl-lithium (Aldrich; *ca.* 17% solution in hexane; 3.3 mmol estimated by titration [12]) to di-isopropylamine (0.426 ml, 3 mmol) in the THF–HMPA solvent at −78 °C. The mixture was stirred under argon for 10 min at −78 °C, and a solution of epoxycyclo-octatriene [1] (1) (360 mg, 3 mmol) in THF (2 ml) was then added by syringe through a septum cap. A deep red colour was generated immediately, and the solution was used after having been stirred for 10 min at −78 °C. The solution was indefinitely stable at temperatures ≤ −30 °C, but above this temperature it slowly polymerised. The enolate anion (2) (3 mmol) in THF–HMPA (23 ml) was prepared as described above for all the following experiments (this description is not repeated).

[8-$^2H_1$]*Cyclo-octatrienone* (4; R = D).—A solution of the enolate (2) (3 mmol) was quenched with an excess of acetic [^{2}H]acid (prepared from Ac_2O and D_2O) at 0 °C. After being stirred for 5 min at 0 °C, the mixture was warmed to room temperature and diluted with water. The resulting solution was extracted with hexane, and the individual hexane extracts were washed sequentially with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride. The combined organic layers were dried (Na_2SO_4) and concentrated to a yellow oil which was distilled (Kugelrohr; oven temp. 85—88 °C; 12 mmHg) to give [8-$^2H_1$]cyclo-octatrienone (4; R = D) (321 mg, 89%). Comparison of the ^{1}H n.m.r. spectrum of this compound with the reported spectrum [4] of cyclo-octatrienone (4; R = H) showed that one deuterium atom had been incorporated at C-8. The ratio of the intensities of the $(M + 1)^+$ and M^+ peaks in the high resolution mass spectrum showed that the isotopic purity of the deuteriated cyclo-octatrienone (4; R = D) was *ca.* 85%.

8-*Methylcyclo-octa*-2,4,6-*trienone* (4; R = Me).[6]—Methyl iodide (2 ml, 32 mmol) (purified by filtration through basic alumina, activity 1, immediately before use) was added to a stirred solution of the enolate (2) (3 mmol) at −78 °C. The mixture was allowed to warm to room temperature over 1.5 h, during which time the colour faded to a pale yellow. After a further 0.5 h the mixture was diluted with water and extracted with hexane. The extracts were washed sequentially with water and saturated aqueous sodium chloride, then combined and dried (Na_2SO_4). Evaporation afforded a yellow oil which was distilled (Kugelrohr; oven temp. 80 °C; 15 mmHg) to give a pale yellow *oil* (4; R = Me) (290 mg, 78%); δ_H (CCl_4) 6.8—6.1 (5 H, m, H-2, -3, -4, -5, and -6), 5.34 (1 H, dd, *J* 8 and 12 Hz, H-7), 2.82 (1 H, d of q, *J* 8 and 6 H_z, H-8), and 1.24 (3 H, d, *J* 6 Hz, Me); δ_C ($CDCl_3$) 194·03 (CO), 138.42, 136.95, 135.82, 134.06, 128.00

[12] G. M. Whitesides. C. P. Casey. and J. K. Krieger, *J. Amer. Chem. Soc.*, 1971, **93**, 1379.

and 126.83 (olefinic), 45.59 (C-8), and 13.85 (Me); $\nu_{max.}$ (CCl_4) 1 780m, 1 660s, and 1 640m cm^{-1}; *m/e* 134 (M^+), 119 (40%), 105 (28), and 91 (100) (Found: C, 80.3; H, 7.7. $C_9H_{10}O$ requires C, 80.6; H, 7.5%).

8-*Allylcyclo-octa*-2,4,6-*trienone* (4; R = *allyl*).—Allyl bromide (2 ml, 23.1 mmol; purified by fractional distillation) was added to a stirred solution of the enolate (2) (3 mmol) under argon at −78 °C. The mixture was allowed to warm to room temperature over 2 h, and after 4 h the colour of the enolate had been discharged. After the work-up procedure described above the crude product was purified by preparative layer chromatography (methylene chloride). Finally, the resulting oil was distilled (Kugelrohr; oven temp. 90 °C; 15 mmHg) to give a pale yellow *oil* (4; R = allyl) (297 mg, 74%); $\delta_H(CCl_4)$ 6.8—6.1 (5 H, m, H-2, -3, -4, -5, and -6), 5.93—4.8 (4 H, m, H-7 and $CH{:}CH_2$), and 2.95—2.2 [3 H, m, H-8 and ($CH_2{\cdot}CH{:}CH_2$)]; $\delta_C(CDCl_3)$ 192.57 (CO), 138.47, 135.83, 135.73, 133.98, 128.70, 126.85, and 116.21 (olefinic), 50.92 (C-8), and 32.95 ($CH_2{\cdot}CH{:}CH_2$); $\nu_{max.}$ (CCl_4) 1 780m, 1 670s, 1 640m, and 1 620m cm^{-1}; *m/e* 160 (M^+, 53%), 145 (29), 131 (30), 119 (100), 117 (45), and 91 (92) (Found: C, 82.0; H, 7.6. $C_{11}H_{12}O$ requires C, 82.5; H, 7.6%).

8-*Ethylcyclo-octa*-2,4,6-*trienone* (4; R = Et).—Addition of ethyl iodide (2 ml, 26.8 mmol; purified immediately before use by passage through basic alumina, activity 1) to a stirred solution of the enolate (2) (3 mmol) under argon at −78 °C, followed by warming the mixture to −5 °C over 2 h, and further reaction at −5 °C for 10 h, caused complete discharge of the red colour of the enolate. The mixture was worked up as described above to give a pale yellow oil, which was purified by layer chromatography. The plate was developed in methylene chloride, and the eluate distilled (Kugelrohr; oven temp. 90 °C; 15 mmHg) to give a pale yellow *oil* (4; R = Et) (361 mg, 81%); δ_H-($CDCl_3$) 6.9—6.1 (5 H, m, H-2, -3, -4, -5, and -6), 5.36 (1 H, t, *J* 9 Hz, H-7), 2.60 (1 H, q, *J* 9 Hz, H-8), 2.30—1.50 (2 H, m, CH_2), and 0.86 (3 H, t, *J* 6 Hz, CH_3); δ_C ($CDCl_3$) 193.35 (CO), 138.75, 136.37, 135.6, 133.96, 128.64, and 126.7 (olefinic), 53.13 (C-8), 21.86 (CH_2), and 11.66 (CH_3); $\nu_{max.}$ (CCl_4) 1 780m, 1 665s, and 1 620m cm^{-1}; *m/e* 148 (M^+, 36%), 133 (50), 119 (63), 105 (54), and 91 (100) (Found: C, 80.7; H, 8.3. $C_{10}H_{12}O$ requires C, 81.0; H, 8.2%). When ethyl bromide was used as alkylating agent under identical conditions, preparative layer chromatography (methylene chloride) gave the following products in order of elution: ethoxycyclo-octatetraene (5; R = Et)[2] (52 mg, 11%); compound (4; R = Et) (71 mg, 16%), and cyclo-octatrienone (4; R = H) (80 mg, 22%).

8-*Benzylcyclo-octa*-2,4,6-*trienone* (4; R = $PhCH_2$).—Benzyl iodide [13] (0.4 ml, 3.24 mmol) was added under argon to a stirred solution of the enolate (2) (3 mmol) under argon at −78 °C, and the mixture was allowed to warm to −5 °C over 3 h, by which time it had turned deep black. The mixture was worked up as above and the crude product was purified by preparative layer chromatography (methylene chloride). The following products were obtained (in order of elution): *compound* (4; R = $PhCH_2$) (234 mg, 37%) and cyclo-octatrienone (4; R = H) (183 mg, 51%). The former was purified by Kugelrohr distillation (oven temp. 90 °C; 0.15 mmHg); δ_H (CCl_4) 7.40—6.90br (5 H, s, aromatic), 6.70—6.10 (5 H, m, H-2, -3, -4, -5, and -6), 5.80—5.20 (1 H, m, H-7), 3.50—2.60 (2 H, m, CH_2); δ_C ($CDCl_3$) 192.42 (CO), 138.42, 135.91, 135.85, 133.98, 128.94, 128.36, 126.92, and 126.12 (olefinic and aromatic), 52.78 (C-8), and 34.76 (CH_2); $\nu_{max.}$ (CCl_4) 1 780m, 1 665s, and 1 620w cm^{-1}; *m/e* 210 (M^+, 20%), 167 (13), 165 (12), 132 (57), 119 (56), 105 (58), and 91 (100) (Found: C, 85.4; H, 7.0. $C_{15}H_{15}O$ requires C, 85.7; H, 6.7%). Use of benzyl bromide in place of benzyl iodide under identical conditions, followed by preparative layer chromatography (methylene chloride) afforded, in order of elution, cyclo-octatrienone (4; R = H) (172 mg, 48%) and compound (4; R = $PhCH_2$) (94 mg, 15%).

Acetoxycyclo-octatetraene (5; R = Ac).[14]—To two separate solutions of the enolate (2) (3 mmol) under argon at −78 °C were added different quantities of acetyl chloride (250 mg, 3.2 mmol; and 115 mg, 1.5 mmol). The mixtures were allowed to warm to −5 °C over 2 h, by which time they were black and opaque. Work-up as above and extraction with ether (rather than hexane) afforded crude products which were purified by preparative layer chromatography. Development and elution with methylene chloride afforded (in order of elution) acetoxycyclo-octatetraene (5; R = Ac) (125 mg, 26%; and 46 mg, 9%, respectively), which showed physical data identical with the values reported,[14] and cyclo-octatrienone (4; R = H) (178 mg, 49%; and 130 mg, 36%, respectively).

Ethyl Cyclo-octatetraenyl Carbonate (5; R = CO_2Et).—Addition of ethyl chloroformate (328 mg, 3.2 mmol; and 162 mg, 1.5 mmol) in two separate experiments to a solution of the enolate (2) under argon at −78 °C, followed by warming to −5 °C over 2 h, and the usual work-up and chromatography as above, gave, in order of elution, the *carbonate* (5; R = CO_2Et) (364 mg, 63%; and 164 mg, 28%, respectively), and cyclo-octrienone (4; R = H) (negligible amounts; and 225 mg, 62%, respectively). The carbonate (5; R = CO_2Et) was distilled (Kugelrohr; oven temp. 100 °C, 0.2 mmHg); δ_H (CCl_4) 6.2—5.5 (7 H, m, olefinic), 4.15 (2 H, q, *J* 7 Hz, CH_2), and 1.30 (3 H, t, *J* 7 Hz, CH_3); $\nu_{max.}$ (CCl_4) 1 760s, 1 680w, and 1 640w cm^{-1}; $\lambda_{max.}$ (C_6H_{12}) 279 nm (ε 1 600); *m/e* 192 (M^+) (Found: C, 68.5; H, 6.3. $C_{11}H_{12}O_2$ requires C, 68.7; H, 6.3%).

Reaction of the Enolate (2) *with Diphenyl Disulphide*.—Diphenyl disulphide (210 mg, 1 mmol) in THF (5 ml) was added to a solution of the enolate (2) (0.8 mmol) in THF (14 ml) and HMPA (1.5 ml, 8.5 mmol) at −78 °C, and the solution was allowed to warm to room temperature over 0.5 h. After the usual work-up, the crude product was purified by preparative layer chromatography (methylene chloride–hexane, 1 : 1). In order of elution were obtained diphenyl disulphide (58 mg, 27%), 2,2-bis(phenylthio)acetophenone (10; R = PhS) (37 mg, 20%), m.p. 97—99° (lit.,[15] 98—99°), 2-phenylthioacetophenone [16] (9; R = PhS) (6.5 mg, 4%), and cyclo-octatrienone (4; R = H) (12.5 mg, 12%).

Reaction of the Enolate (2) *with Benzeneselenenyl Chloride*.—Benzeneselenenyl chloride (200 mg, 1.05 mmol) in THF (5 ml) was added to a solution of the enolate (2) (0.8 mmol) in THF (7 ml) and HMPA (1.5 ml, 8.5 mmol) at −78 °C. The mixture was allowed to warm to room temperature over 0.5 h, and was then worked up in the usual manner. Preparative layer chromatography [two developments in

[13] V. Meyer, *Ber.*, 1877, **10**, 309; G. Kumpf, *Annalen*, 1884, **224**, 126.

[14] J. Gasteiger, G. E. Gream, R. Huisgen, W. E. Konz, and U. Schnegg, *Chem. Ber.*, 1971, **104**, 2412.

[15] F. Weygand and H. J. Bestmann, *Z. Naturforsch.*, 1955, **10b**, 296.

[16] O. Behaghel and H. Seibert, *Ber.*, 1932, **65**, 812.

methylene chloride–hexane (1 : 1)] yielded, in order of elution, diphenyl diselenide (36 mg, 18%), 2,2-*bis*(*phenylseleno*)*acetophenone* (10; R = PhSe) (40 mg, 18%), and 2-*phenylselenoacetophenone* (9; R = PhSe) (21 mg, 11%) which showed similar spectral properties to the known [16] sulphide (10; R = PhS) and was not further characterised. The diseleno-compound (10; R = PhSe) had m.p. 78—79° (from hexane), δ_H ($CDCl_3$) 7.95—7.0 (11 H, m, aromatic) and 5.76 (1 H, s, methine); $\nu_{max.}$ (CCl_4) 1 675s cm^{-1}; $\lambda_{max.}$ (95% EtOH) 246 nm (ε 18 800) (Found: C, 55.6; H, 3.7. $C_{20}H_{16}OSe_2$ requires C, 55.8; H, 3.8%).

8-*Phenylselenocyclo-octa*-2,4,6-*trienone* (4; R = PhSe).—Benzeneselenenyl bromide [10,16] (3 mmol) was prepared at −78 °C *in situ* in THF (20 ml) from bromine (240 mg, 1.5 mmol) and diphenyl diselenide (5.5 mg, 1.66 mmol). A solution of the enolate (2) (3 mmol) cooled to −78 °C in a jacketed dropping funnel was added dropwise to the stirred benzeneselenenyl bromide solution at −78 °C under argon. After addition of the enolate, the deep purple colour of the benzeneselenenyl bromide was completely discharged, and the resulting solution was pale orange. After the usual work-up the crude product was purified by preparative layer chromatography (benzene); the following products were obtained in order of elution: diphenyl diselenide (127 mg, 25%), and 8-*phenylselenocyclo-octatrienone* (4; R = PhSe) (332 mg, 40%), m.p. 78—79°; (from hexane) δ_H ($CDCl_3$) 7.7—6.9 (5 H, m, aromatic), 6.8—5.4 (6 H, m, olefinic), and 4.42 (1 H, d, *J* 9 Hz, H-8), and a small signal at 4.62 (dd, *J* 6 and 3 Hz, assigned to the ring junction proton(s) of the bicyclic valence tautomer (7; R = PhSe); $\nu_{max.}$ ($CHCl_3$) 1 785m, 1 660s, and 1 615m cm^{-1}; $\lambda_{max.}$ (95% EtOH) 240sh (ε 11 200) and 280 nm (5 500); *m/e* 276 (M^+ for ^{80}Se) (Found: C, 61.0; H, 4.6. $C_{14}H_{12}OSe$ requires C, 61.2; H, 4.4%).

8-*Phenylthiocyclo-octa*-2,4,6-*trienone* (4; R = PhS).—The procedure described for (4; R = PhSe) was used. The cooled enolate (2) (2.08 mmol) in THF (20 ml) and HMPA (2.5 ml) was added dropwise to benzenesulphenyl chloride (300 mg, 2.08 mmol) (prepared by the method described for toluenesulphenyl chloride [17]) in THF (20 ml) at −78 °C under argon. After the addition, the colour of the enolate was discharged, and the mixture was stirred for 30 min while being warmed to room temperature. After the usual work-up and extraction, the crude yellow solid product was purified by preparative layer chromatography (methylene chloride) to give diphenyl disulphide (25 mg, 11%) and the *phenylthio-compound* (4; R = PhS) (126 mg, 26%). Compound (4; R = PhS) was a very unstable solid, never obtained completely pure; δ_H ($CDCl_3$) 7.18 (5 H, m, aromatic), 6.74—6.31 (5 H, m, olefinic), 5.71 (1 H, t, *J* 10 Hz, H-7), and 4.30 (1 H, d, *J* 10 Hz, H-8), and a small signal at 4.52 (dd, *J* 2 and 6.5 Hz) assigned to the ring junction proton(s) in the bicyclic valence tautomer (7; R = PhS); $\nu_{max.}$ (CCl_4) 1 790m, 1 670s, and 1 615w cm^{-1}; *m/e* 228 (M^+, 20%), 186 (8), 150 (40) 122 (56), 119 (38), and 91 (100) (Found: M^+, 228.061. $C_{14}H_{12}OS$ requires *M*, 228.061).

8-*Bromocyclo-octa*-2,4,6-*trienone* (4; R = Br).—To a solution of the enolate (2) (3 mmol) was added bromine (0.16 ml, 3 mmol) at −78 °C, and the solution was stirred for 5 min. Work-up and extraction in the usual way afforded a crude product which was purified by preparative layer chromatography at 0 °C (methylene chloride). The *bromo-compound* (4; R = Br) (306 mg, 51%) was obtained as a highly unstable pale yellow solid. It could not be purified by crystallisation, and showed δ_H ($CDCl_3$) 6.19—6.90 (5 H, m, H-2, -3, -4, -5, and -6), 5.84 (1 H, dd, *J* 9 and 10 Hz, H-7), and 4.71 (1 H, d, *J* 9 Hz, H-8); $\nu_{max.}$ (CCl_4) 1 790s, 1 677s, and 1 620s cm^{-1}; $\lambda_{max.}$ 225 nm (rel. intensity 1.0), 245sh (0.73), 280sh (0.48), and 340 nm (*ca.* 10^{-3}); *m/e* 200 and 198 (M^+, 9%) 119 (100), and 91 (97) (Found: M^+, 199.965 and 197.967. C_8H_7BrO requires *M*, 199.966 and 197.968).

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[17] F. Kurzer and J. R. Powell, *Org. Synth.*, Coll. Vol. IV, 1963, 934.