Bromo-derivatives of Dimethyl 4-Oxo-*trans*-2,6-diphenylcyclohexane-1,1-dicarboxylate and Their Dehydrobromination

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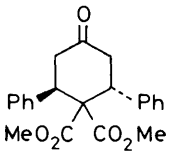
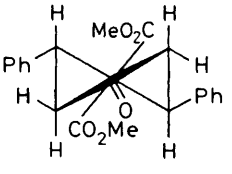
The structures and stereochemistry of various bromo-derivatives of dimethyl 4-oxo-*trans*-2,6-diphenylcyclohexane-1,1,-dicarboxylate are reported. The dehydrobromination of these derivatives is described and, in some cases a phenol is produced by demethoxycarbonylation.

THE Michael reaction of dimethyl malonate with 1,5-diphenylpenta-1,4-dien-3-one in the presence of sodium methoxide to give high yields of crystalline dimethyl 4-oxo-2,6-diphenylcyclohexane-1,1-carboxylate (1) was described by Kohler and Dewey in 1924.[1] The spectral properties (n.m.r., u.v., and i.r.) are entirely in accord with the structure (1). It was not possible to decide the stereochemistry of the phenyl groups in (1) from the proton spectrum of the system O=C·CH_2·CHPh, but the fact that the signals from the two methoxycarbonyl groups were coincident can be accommodated easily if the two phenyl groups are *trans* in the conformation (2). [The same coincidence of signals is also observed in the spectra of the thioacetal (3) and some other compounds to be described.] The conformation (2) allows both phenyl groups a stable orientation and is consistent with the usual reversible mechanism of the Michael reaction which gives thermodynamically stable products. Moreover, the results of the bromination of (1), to be described, can be interpreted very satisfactorily on the basis of the conformation (2). The stereochemistry of the phenyl groups was not considered by Kohler and Dewey.[1] It



(1)



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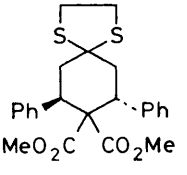
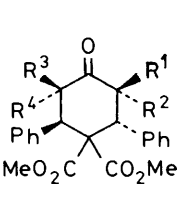


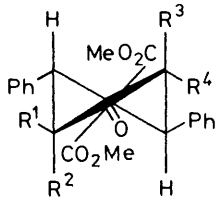
(3)

should be pointed out that the twist-boat conformations assigned to (1) and its bromination products are tentative since, without further study, averaging over other ground-state conformations cannot be excluded.

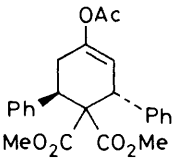
The ketone (1), on bromination with bromine (1 mol) in anhydrous acetic acid containing hydrogen bromide gave, as the major product, the monobromide (4), m.p. 182—183 °C, together with the monobromide (5), m.p. 201—203 °C, as the minor product (*ca.* 10%). The major product (4) shows an i.r. ketonic carbonyl signal at $\nu_{max.}$ 1 715 cm^{-1}, and two doublets in the ^1H n.m.r. spectrum at δ 4.53 (*J* 13 Hz, C*H*Ph·CHBr) and δ 5.35 (*J* 13 Hz, CHPh·C*H*Br). These results suggest that in compound (4) the carbon–bromine bond is coplanar with the carbonyl group (hence the augmented carbonyl frequency) and that between the hydrogen atoms in the system CHPh·CHBr there is a dihedral angle of *ca.* 180°. The *J* value observed is close to that reported for coupling between 2β- and 1α-H in 2α-bromo-3-keto-steroids.[2] The bromo-compound (4), therefore, probably has the conformation (4A), where all the groups have a stable orientation.

The minor product (5) was not separated completely





(A)



(6)

(4) R^1 = Br, R^2 = R^3 = R^4 = H
(5) R^2 = Br, R^1 = R^3 = R^4 = H
(7) R^1 = R^4 = Br, R^2 = R^3 = H
(8) R^1 = R^3 = Br, R^2 = R^4 = H
(9) R^1 = R^2 = R^3 = Br, R^4 = H
(10) R^1 = R^2 = R^4 = Br, R^3 = H
(11) R^1 = R^2 = R^3 = R^4 = Br
(12) R^1 = R^2 = Br, R^3 = R^4 = H

from its isomer (4) from the product of direct bromination of compound (1), but was obtained by the bromination of the enol-acetate (6). The bromo-compound (5) shows an i.r. ketonic carbonyl signal at $\nu_{max.}$ 1 704 cm^{-1}, suggesting that the carbon–bromine bond is not coplanar with the carbonyl group, and two doublets in the ^1H n.m.r. spectrum at δ 4.35 (*J* 8 Hz, CHBr·C*H*Ph) and δ 6.54 (*J* 8 Hz, C*H*Br·CHPh), suggesting from the steroid analogy,[2] that between the hydrogen atoms of the CHBr·CHPh group there is a dihedral angle of *ca.* 60°. Compound (5) is thus assigned the conformation (5A). The proton signal of the CHBr group appears at low field, presumably because the R^1-hydrogen lies within the deshielding influence of the neighbouring phenyl- and carbonyl-groups. The preponderance of compound (4) over (5) in the product of bromination of the ketone (1) reflects the more stable orientation of the bromine atom in structure (4A) compared with (5A).

Similar dibromination of the ketone (1) gave two isomeric dibromides. The major product (*ca.* 75%) (7),

m.p. 210—212 °C, shows an i.r. ketonic carbonyl signal at $\nu_{max.}$ 1 712 cm^{-1}, and two doublets in the ^1H n.m.r. spectrum at δ 4.32 (*J* 12 Hz, CHBr·C*H*Ph) and δ 5.14 (*J* 12 Hz, C*H*Br·CHPh). Given these *J* values and the carbonyl frequency, the two bromine atoms are likely to be *trans* in the conformation (7A). In this conformation, the two methoxycarbonyl groups are in an identical environment and this is reflected in the coincident proton signals of these groups. The structure of the minor product (8), m.p. 260 °C, obtained from this dibromination is given as (8A) on the grounds of its i.r. ketonic carbonyl signal at $\nu_{max.}$ 1 709 cm^{-1}, and two pairs of doublets in the ^1H n.m.r. spectrum at δ 4.30 (*J* 8 Hz, C*H*Ph·CHBr) and 6.74 (*J* 8 Hz, CHPh·C*H*Br), and δ 4.63 (*J* 13 Hz, C*H*Ph·CHBr) and 5.44 (*J* 13 Hz, CHPh·C*H*Br). The low-field signal of the R^4-proton in structure (8A) [*c.f.* the R^1-proton in (5A)] is explained if this proton is under the deshielding influence of the neighbouring phenyl- and carbonyl-groups, together with a slightly more distant coplanar and dipolar C–Br bond. The preponderance of compound (7) over (8) in the dibromination product reflects the greater stability of the orientation of the bromine atoms in (7A) compared with (8A).

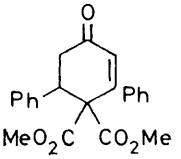
It is relevant to note here that, on treatment with acetic acid containing hydrogen bromide and acetic anhydride, compound (5) yields a mixture of (4) and (5), and compound (8) a mixture of (7) and (8). The mixtures have approximately the same composition as those obtained in the direct mono- and di-bromination of compound (1).

Further bromination of the ketone (1) gave the tribromide (9), m.p. 250—252 °C, in small quantities, and the tetrabromide (11), m.p. 201—202 °C. The tribromide shows, in its i.r. spectrum, a ketonic carbonyl signal at $\nu_{max.}$ 1 727 cm^{-1}, and two doublets in the ^1H n.m.r. spectrum at δ 4.45 (*J* 7 Hz, CHBr·C*H*Ph) and 7.10 (*J* 7 Hz, C*H*Br·CHPh), together with a singlet at δ 4.80 (C*H*Ph·CBr_2). Following previous argument these observations can be accommodated by the conformation (9A). From its low-field signal, it appears that the R^4-proton is deshielded by both the neighbouring carbonyl- and phenyl-groups and the more distant, coplanar dipolar C–Br bond, as is the R^4-proton in the dibromide (8A) previously mentioned. No tribromide (10) was detected in the product, even though this might be expected to be formed in addition to compound (9), since the dibromide (7) is formed in addition to compound (8) in the dibromination of the ketone (1) and (10) differs stereochemically from (9) in the same way that (7) differs from (8). A similar result has been reported in the base-catalysed bromination of cholestan-3-one to give 2,2,4β-tribromocholestan-3-one only [4a] and in the acid-catalysed bromination of 2,2-dichlorocholestan-3-one to give only the 4β-bromo-derivative.[4b]

The tetrabromide (11) shows a ketonic carbonyl signal at $\nu_{max.}$ 1 721 cm^{-1}, and a singlet in its ^1H n.m.r. spectrum δ 5.75 (C*H*Ph·CBr_2). The proton signals of the two methoxycarbonyl groups were coincident, suggesting the conformation (11A), where the environment of these groups is the same [*cf.* the same coincidence in the proton spectra of compounds (1), (3), and (7)].

Bromination of the ketone (1) in the presence of potassium acetate gave a mixture of the bromides (11) and (12). The geminal dibromide (12), m.p. 164 °C, gives a ketonic carbonyl signal, $\nu_{max.}$ 1 715 cm^{-1}, a singlet in the ^1H n.m.r. spectrum at δ 4.98 (C*H*Ph·CBr_2), but no signals attributable to a system CHPh·CHBr. The dibromide is given the conformation (12A). Attempts to rearrange this dibromide with hydrogen bromide in acetic acid to give compounds (7) or (8), following the analogy of the rearrangement of 2,2-dibromocholestan-3-one with its 2α,4α-isomer,[4a,5] resulted in the recovery of starting material.

The dehydrobromination of these bromides was achieved in pyridine. The monobromide (4) was smoothly dehydrobrominated to give the enone (13), m.p. 126—128 °C, the structure of which follows from its u.v. and i.r. spectra, $\lambda_{max.}$ 279 nm; $\nu_{max.}$ 1 681 and 1 618 cm^{-1} (enone) and a singlet proton signal in its ^1H n.m.r. spectra at δ 6.40. However, no conditions were found



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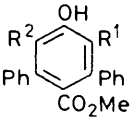
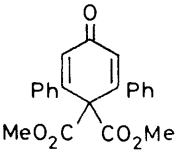
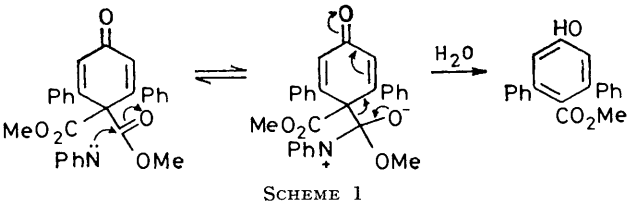


(14) $R^1 = R^2 = H$
(16) $R^1 = R^2 = Br$
(17) $R^1 = H, R^2 = Br$



(15)

whereby significant yields of dienones could be obtained from the dibromide (7), the tribromide (9), or the tetrabromide (11). In the first case the major product, and in the other two cases the only product, was a phenol resulting from demethoxycarbonylation. Thus, dehydrobromination of the dibromide (7) gave the phenol (14), m.p. 170 °C, together with small quantities of the dienone (15), m.p. 135 °C. The phenol (14) has a very simple ^1H n.m.r. spectrum of singlets at δ 3.32 (Me·OCO) and 6.74 (OH), while the dienone (15) has the following spectral characteristics $\nu_{max.}$ 1 667 and 1 626 cm^{-1} (enone), $\lambda_{max.}$ 284 nm, and singlets in its ^1H n.m.r. spectrum at δ 3.55 (*Me*OCO) and 6.65 (OC·C*H*=CPh). Presumably, in the dehydrobromination the dienone (15) is formed initially, but is vulnerable to aromatisation, as shown in Scheme 1.

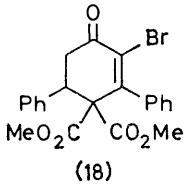


SCHEME 1

The tetrabromide (11) was similarly aromatised on dehydrobromination to give only the phenol (16) [δ 3.10

(*Me*OCO), 6.40 (O*H*)], and the tribromide (9) in the same way gave only the phenol (17) [δ 3.30 (*Me*OCO) and 6.78 (O*H*)]. The i.r. carbonyl frequencies of the phenols (14), (17), and (16) are 1 689, 1 681, and 1 709 cm^{-1}, respectively. These figures probably reflect the fact that in the dibromophenol(16), but not in the other two, the bromine atoms cause the deconjugation of the OH group from the CO_2Me group, thereby raising its carbonyl frequency.

Dehydrobromination of the geminal dibromide (12) gave the phenol(14) and only small quantities of the enone (18), which as a result, was not completely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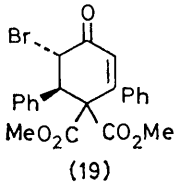
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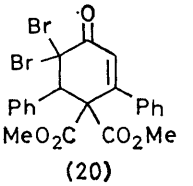
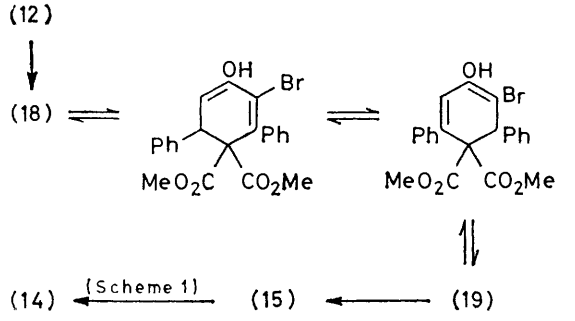

(20)

characterised. The formation of the phenol (14) probably occurs as shown in Scheme 2, although neither compounds (15) nor (19) were detected in the reaction product.



SCHEME 2

The reaction of bromine and hydrogen bromide with the enone (13) was also investigated. Neither bromine in chloroform nor in acetic acid containing collidine added to the double bond. Whether this failure to react stems from the extensive conjugation of the system O=C·CH=CH·CHPh, or from the stereochemical difficulties, in this case, of the usual *trans*-diaxial addition mechanism is not certain. However, the reaction of the ketone (13) with bromine in acetic acid in the presence of hydrogen bromide gave the monobromide (19), m.p. 140—143 °C, the ^1H n.m.r. spectrum of which showed two doublets at δ 4.42 (*J* 13 Hz, CHBr·C*H*Ph) and 5.52 (*J* 13 Hz, C*H*Br·CHPh); the coupling constants of these indicate that the two hydrogen atoms in the system CHBr·CHPh have a *trans*-diaxial orientation. The bromide (19) on dehydrobromination gave, as expected, the phenol (14).

Base-catalysed bromination of the enone (13) gave an amorphous dibromide (20), δ 4.95 (PhC*H*·CBr_2) which, as expected, gave the phenol (17) on dehydrobromination in pyridine.

EXPERIMENTAL

Melting-points were determined in capillary tubes. U.v. spectra are for solutions in ethanol on a Cary-118X spectrophotometer. I.r. spectra were recorded in Nujol and chloroform solutions on P-E257 and Infracord 137 spectrophotometers. ^1H N.m.r. spectra were obtained on P-E R32 and R34, and Bruker WP80 instruments, using deuteriochloroform as solvent and tetramethylsilane as internal standard. Alumina used for chromatography was Peter Spence Grade H, deactivated with 5% of 10% acetic acid. All solvents used were AnalaR grade.

Dimethyl 4-*Oxo*-trans-2,6-*diphenylcyclohexane*-1,1-*dicarboxylate* (1).—Compound (1) was prepared by the method of Kohler and Dewey [1] as prisms, m.p. 138—139 °C (from methanol); $\nu_{max.}$ 1 698 cm^{-1} (C=O); δ 2.95 (4 H, m), 3.30 (6 H, s), 4.32 (2 H, m), and 7.20 (10 H, m); $\lambda_{max.}$ 283 (ε 46), 267 (223), 263 (348), 257 (427), and 251 nm (330) (Found: C, 72.0; H, 6.0. $C_{22}H_{22}O_5$ requires C, 72.1; H, 6.0%).

Dimethyl 4-*Acetyl*-trans-2,6-*diphenylcyclohex*-3-*ene*-1,1-*dicarboxylate* (6).—A solution of the ketone (1) (1.5 g) and toluene-*p*-sulphonic acid (100 mg) in acetic anhydride (40 ml) was refluxed for 12 h. A low rate of distillation was maintained throughout to remove acetic acid. The solid product was recovered after the addition of sodium hydrogencarbonate and was purified by elution from alumina (50 g) in pentane–diethyl ether (5 : 1). The *enol-acetate* (6) was crystallised from methanol as prisms (1.1 g), m.p. 145—146 °C; δ 2.15 (3 H, s), 2.52 (2 H, m), 3.25 (3 H, s), 3.60 (3 H, s), 3.80 (1 H, m), 4.50 (1 H, m), 5.55 (1 H, m), and 7.27 (10 H, m); $\lambda_{max.}$ 263 (ε 331), 257 (425), and 251 nm (347) (Found: C, 71.0; H, 6.1. $C_{24}H_{24}O_6$ requires C, 70.6; H, 5.9%).

Bromination of the Enol-acetate (6).—A solution of the enol-acetate (6) (300 mg), potassium acetate (1.0 g), and bromine (120 mg) was kept in the dark for 18 h at room temperature. The solid product was recovered after the addition of sodium hydrogencarbonate and was recrystallised from ethanol to give *dimethyl* c-3-*bromo*-4-*oxo*-r-2,t-6-*diphenylcyclohexane*-1,1-*dicarboxylate* (5) as prisms, m.p. 201—203 °C (100 mg); $\nu_{max.}$ 1 704 cm^{-1} (C=O); δ 3.10 (2 H, m), 3.32 (3 H, s), 3.60 (3 H, s), 4.35 (1 H, d, *J* 8 Hz), 4.45 (1 H, m), 6.54 (1 H, d, *J* 8 Jz) and 7.25 (10 H, m) (Found: C, 59.5; H, 4.8; Br, 17.7. $C_{22}H_{21}BrO_5$ requires C, 59.3; H, 4.7; Br, 18.0%).

Acid-catalysed Bromination of the Ketone (1).—A solution of the ketone (1) (732 mg) and bromine (340 mg) in acetic acid (18 ml), containing acetic anhydride (3 ml) and a saturated solution of hydrogen bromide in acetic acid (0.3 ml), was kept at room temperature in the dark for 20 h. Neutralisation with sodium hydrogencarbonate gave a solid product which crystallised from methanol to give *dimethyl* t-3-*bromo*-4-*oxo*-r-2,t-6-*diphenylcyclohexane*-1,1-*dicarboxylate* (4) as prisms (450 mg), m.p. 182—183 °C; $\nu_{max.}$ 1 715 cm^{-1} (C=O); δ 3.40 (2 H, m), 3.23 (3 H, s), 3.46 (3 H, s), 4.15 (1 H, m), 4.53 (1 H, d, *J* 13 Hz), 5.35 (1 H, d, *J* 13 Hz), and 7.25 (10 H, m) (Found: C, 59.5; H, 4.6; Br, 17.6. $C_{22}H_{21}BrO_5$ requires C, 59.3; H, 4.7; Br, 18.0%).

The mother liquors obtained from the crystallisation deposited a solid on slow evaporation. This was purified by elution from alumina (15 g) in diethyl ether–pentane (1 : 5), and recrystallisation from ethanol to give prisms (70 mg), m.p. 160—170 °C. The n.m.r. spectrum revealed that this was a mixture of the monobromides (4) and (5) in the ratio 1 : 2.

Acid-catalysed Dibromination of the Ketone (1).—A solution of the ketone (1) (732 mg) and bromine (680 mg) in acetic acid (20 ml), containing acetic anhydride (3 ml) and a saturated solution of hydrogen bromide in acetic acid (0.3 ml), was kept in the dark for 24 h at room temperature. The product was recovered after the addition of sodium hydrogencarbonate and crystallised from ethanol to give *dimethyl* t-3,c-5-*dibromo*-4-*oxo*-r-2,t-6-*diphenylcyclohexane*-1,1-*dicarboxylate* (7) as needles (250 mg), m.p. 210—212 °C; $\nu_{max.}$ 1 712 cm^{-1} (C=O); δ 3.30 (6 H, s), 4.32 (2 H, d, *J* 12 Hz), 5.14 (2 H, d, *J* 12 Hz), and 7.27 (10 H, s) (Found: C, 49.9; H, 4.1; Br, 30.7. $C_{22}H_{20}Br_2O_5$ requires C, 50.3; H, 3.8; Br, 30.5%).

On slow evaporation the mother liquors deposited a solid which crystallised from acetone to give *dimethyl* t-3,t-5-*dibromo*-4-*oxo*-r-2,t-6-*diphenylcyclohexane*-1,1-*dicarboxylate* (8) (70 mg) as needles, m.p. 260 °C; $\nu_{max.}$ 1 709 cm^{-1} (C=O); δ 3.30 (3 H, s), 3.58 (3 H, s), 4.30 (1 H, d, *J* 8 Hz), 4.63 (1 H, d, *J* 13 Hz), 5.44 (1 H, d, *J* 13 Hz), 6.74 (1 H, d, *J* 8 Hz), and 7.30br (10 H, s) (Found: C, 50.4; H, 3.6; Br, 30.4. $C_{22}H_{20}Br_2O_5$ requires C, 50.3; H, 3.8; Br, 30.5%).

Further Acid-catalysed Bromination of the Ketone (1).—Similar bromination of the ketone (1) (732 mg) with bromine (1 020 mg) in acetic acid (20 ml), containing acetic anhydride (3 ml) and a saturated solution of hydrogen bromide in acetic acid (0.3 ml), gave a solid product which was washed with hot ethanol (50 ml). The washings, on being cooled, deposited the dibromide (7) (200 mg). The residue was crystallised several times from acetone to give *dimethyl* 3,3,t-5-*tribromo*-4-*oxo*-r-2,t-6-*diphenylcyclohexane*-1,1-*dicarboxylate* (9) as small prisms (50 mg), m.p. 250—252 °C; $\nu_{max.}$ 1 727 cm^{-1} (C=O); δ 3.28 (3 H, s), 3.87 (3 H, s), 4.45 (1 H, d, *J* 7 Hz), 4.80 (1 H, s), 7.10 (1 H, d, *J* 7 Hz), and 7.37 (10 H, m) (Found: C, 44.4; H, 3.1; Br, 39.2. $C_{22}H_{19}Br_3O_5$ requires C, 43.8; H, 3.2; Br, 39.8%).

Bromination of the ketone (1) in the same way with bromine (1 360 mg) gave a solid product which was recrystallised from methanol to give *dimethyl* 3,3,5,5-*tetrabromo*-4-*oxo*-trans-2,6-*diphenylcyclohexane*-1,1-*dicarboxylate* (11) as prisms (220 mg), m.p. 201—202 °C; $\nu_{max.}$ 1 721 cm^{-1} (C=O); δ 3.35 (6 H, s), 5.75 (2 H, s), and 7.38 (10 H, m) (Found: C, 38.8; H, 2.6; Br, 46.4. $C_{22}H_{18}Br_4O_5$ requires C, 38.7; H, 2.6; Br, 46.9%).

Base-catalysed Bromination of the Ketone (1).—A solution of the ketone (1) (732 mg), bromine (680 mg), and potassium acetate (2.0 g anhydrous) in acetic acid (40 ml) was kept at 90 °C for 30 min. The mixture was neutralised with sodium hydrogencarbonate, and the solid product was washed with warm methanol (20 ml). The washings, on being cooled to 0 °C deposited *dimethyl* 3,3-*dibromo*-4-*oxo*-r-2,t-6-*diphenylcyclohexane*-1,1-*dicarboxylate* (12) as prisms (100 mg), m.p. 164 °C; $\nu_{max.}$ 1 715 cm^{-1} (C=O); δ 3.20 (3 H, s), 3.35 (2 H, m), 3.45 (3 H, s), 4.80 (1 H, m), 4.97 (1 H, s), and 7.30 (10 H, m) (Found: C, 50.0; H, 3.7; Br, 30.8. $C_{22}H_{20}Br_2O_5$ requires C, 50.3; H, 3.8; Br, 30.5%).

The solid residue was recrystallised from methanol to give the tetrabromide (11) (250 mg), m.p. 201—202 °C.

Preparation of the Ethylene Thioacetal (3).—A solution of the ketone (1) (1.83 g), ethanedithiol (1 ml), and boron trifluoride–diethyl ether (1 ml) in acetate acid (30 ml) was kept at room temperature for 36 h. The deposited solid was recrystallised from acetone to give *dimethyl* 3,5-trans-*diphenylcyclohexanespiro*-2′-*thidane*-4,4-*dicarboxylate* (3) as prisms (1.6 g), m.p. 208—210 °C; δ 2.87 (2 H, m), 3.08 (6 H, s), 3.23 (4 H, m), 4.30 (2 H, m), and 7.20 (10 H, m) (Found: C, 64.8; H, 5.8; S, 14.4. $C_{24}H_{26}O_4S_2$ requires C, 65.2; H, 5.9; S, 14.5%).

Dehydrobromination of the Monobromide (4).—The bromide (4) (100 mg) was refluxed in pyridine (8 ml) under nitrogen for 2 h. The cooled mixture was acidified with 2M hydrochloric acid at 0 °C; the product was isolated in diethyl ether. It was purified by elution from alumina (10 g) in diethyl ether–pentane (2 : 5) to give *dimethyl* 4-*oxo*-2,6-*diphenylcyclohex*-2-*ene*-1,1-*dicarboxylate* (13) which crystallised from methanol as prisms (65 mg), m.p. 126—128 °C; $\nu_{max.}$ 1 681 and 1 618 cm^{-1} (=CH·C=O); $\lambda_{max.}$ 279 nm (ε 12 250); δ 3.05 (2 H, m), 3.35 (3 H, s), 3.63 (3 H, s), 4.35 (1 H, m), 6.40 (1 H, s), and 7.33 (10 H, m) (Found: C, 72.0; H, 6.1. $C_{22}H_{20}O_5$ requires C, 72.5; H, 5.5%).

Dehydrobromination of the Dibromide (7).—The dibromide (7) (150 mg) was kept in pyridine (10 ml) at 100 °C under nitrogen for 2 h. The product, obtained by evaporation of the solvent was purified on alumina (15 g). Pentane–diethyl ether (10 : 3) eluted *dimethyl* 4-*oxo*-2,6-*diphenylcyclohexa*-2,5-*dieno*-1,1-*dicarboxylate* (15) which crystallised from diethyl ether–pentane as prisms (10 mg), m.p. 135 °C; $\nu_{max.}$ 1 667 and 1 636 cm^{-1} (=CH.C=O); $\lambda_{max.}$ 284 nm (ε 17 850); δ 3.55 (6 H, s), 6.55 (2 H, s), and 7.37 (10 H, m) (Found: C, 72.5; H, 5.3. $C_{22}H_{18}O_5$ requires C, 72.9; H, 5.0%). Pentane–diethyl ether (1 : 2) eluted *methyl* 4-*hydroxy*-2,6-*diphenylbenzoate* (14) which crystallised from diethyl ether–pentane as needles (60 mg), m.p. 170 °C; $\nu_{max.}$ 3 333, 1 689, 1 603, and 1 590 cm^{-1}; δ 3.32 (3 H, s), 6.74 (1 H, s), and 7.32br (12 H, s) (Found: C, 78.7; H, 5.0. $C_{20}H_{16}O_3$ requires C, 78.9; H, 5.3%).

Dehydrobromination of the Tetrabromide (11).—Dehydrobromination of the tetrabromide (11) (200 mg) in the way described above gave *methyl* 3,5-*dibromo*-4-*hydroxy*-2,6-*diphenylbenzoate* (16) as prisms (80 mg) from light petroleum (b.p. 60—80 °C)–diethyl ether, m.p. 162—163 °C; $\nu_{max.}$ 3 390, 1 709, and 1 538 cm^{-1}; δ 3.10 (3 H, s), 6.40br (1 H), and 7.38 (10 H, m) (Found: C, 51.8; H, 3.0; Br, 34.5. $C_{20}H_{14}Br_2O_3$ requires C, 51.9; H, 3.0; Br, 34.6%).

Dehydrobromination of the Tribromide (9).—Similar dehydrobromination of the tribromide (9) (100 mg) gave methyl 3-bromo-4-hydroxy-2,6-diphenylbenzoate (17) (30 mg) as a glass; $\nu_{max.}$ 3 330, 1 671, 1 577, and 1 558 cm^{-1}; δ 3.30 (3 H, s), 6.78 (1 H, s), and 7.34 (11 H, m). This compound was not obtained crystalline and analytically pure.

Dehydrobromination of the Dibromide (12).—Dehydrobromination of the dibromide (12) (100 mg) in the way described above gave small quantities (<5 mg) of dimethyl 3-bromo-4-oxo-2,6-diphenylcyclohex-2-ene-1,1-dicarboxylate (18), m.p. 125—130 °C; $\nu_{max.}$ 1 689 and 1 630 cm^{-1} (=CH·C=O); δ 3.10 (2 H, m), 3.30 (3 H, s), 3.75 (3 H, s), 4.55 (1 H, m), and 7.33 (10 H, m). This compound was not obtained pure and the major product (35 mg) was the phenol (14).

Bromination of the Enone (13).—(*a*) A solution of the enone (13) (120 mg) and bromine (59 mg) in acetic acid (7 ml) which contained a saturated solution of hydrogen bromide in acetic acid (0.05 ml), was kept at room temperature in the dark for 24 h. The solid product recovered after neutralisation with sodium hydrogencarbonate was crystallised from methanol to give *dimethyl* 5-*bromo*-4-*oxo*-2,6-*diphenylcyclohex*-2-*ene*-1,1-*dicarboxylate* (19) as prisms (70 mg) m.p. 140—143 °C; $\nu_{max.}$ 1 678 and 1 616 cm^{-1} (=CH·C=O); $\lambda_{max.}$ 290 nm (ε 13 350); δ 3.30 (3 H, s), 3.75 (3 H, s), 4.42 (1 H, d, *J* 13 Hz), 5.52 (1 H, d, *J* 13 Hz), 6.50 (1 H, s), and 7.30 (10 H, m) (Found: C, 59.6; H, 4.4;

Br, 18.4. $C_{22}H_{19}BrO_5$ requires: C, 59.6; H, 4.3; Br, 18.1%).

(*b*) A solution of the enone (13) (120 mg), bromine (120 mg), and potassium acetate (400 mg, anhydrous) in acetic acid was kept at 90 °C for 1 h. The mixture was neutralised with sodium hydrogencarbonate. The product was recovered in diethyl ether and purified by elution from alumina (10 g) in diethyl ether–pentane (3 : 5). Dimethyl 5,5-dibromo-4-oxo-2,6-diphenylcyclohex-2-ene-1,1-dicarboxylate (20) was recovered as an amorphous solid (70 mg); $\nu_{max.}$ 1 689 and 1 613 cm^{-1} (=CH·C=O); $\lambda_{max.}$ 299 nm (ε 11 350); δ 3.45 (3 H, s), 3.48 (3 H, s), 4.95 (1 H, s), 6.65 (1 H, s), and 7.39 (10 H, m). This substance was not obtained analytically pure.

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REFERENCES

[1] E. P. Kohler and C. S. Dewey, *J. Am. Chem. Soc.*, 1924, **46**, 1267.

[2] A. K. Bose, M. S. Manhas, and E. R. Malinowski, *J. Am. Chem. Soc.*, 1963, **85**, 2795; C. W. Shoppee, T. E. Bellas, Ruth E. Lack, and S. Sternhell, *J. Chem. Soc.*, 1965, 2483; R. J. Abraham and J. S. E. Holker, *J. Chem. Soc.*, 1963, 806.

[3] E. R. H. Jones and D. J. Wluka, *J. Chem. Soc.*, 1959, 907.

[4] (*a*) C. W. P. Crowne, R. M. Evans, G. F. H. Green, and A. G. Long, *J. Chem. Soc.*, 1956, 4351; (*b*) B. Ellis and V. Petrow, *J. Chem. Soc.*, 1953, 3869.

[5] E. Warnhoff, M. Rampersad, P. Sundara Raman, and F. W. Yerhoff, *Tetrahedron Lett.*, 1978, 1659.