

Reactions of Diastereomeric 2,4,5-Triphenyl-1,3-dioxolans with *N*-Bromosuccinimide and *t*-Butyl Perbenzoate

By Hiok-Huang Lee* and Seong-Fong Chen, Department of Chemistry, University of Singapore, Bukit Timah Road, Singapore 10

Two diastereomeric 2,4,5-triphenyl-1,3-dioxolans isolated from the acetalization of *meso*-hydrobenzoin with benzaldehyde have been assigned their respective configurations based on spectroscopic evidence. The reactions of *r*-2,*c*-4,*t*-5-triphenyl-1,3-dioxolan (4) with *N*-bromosuccinimide and with *t*-butyl perbenzoate catalysed by cuprous chloride have been shown to give *erythro*-1-benzoyloxy-2-bromo-1,2-diphenylethane and *meso*-hydrobenzoin dibenzoate respectively. The corresponding reactions of *r*-2,*c*-4,*c*-5-triphenyl-1,3-dioxolan (5) and *r*-2,*t*-4,*t*-5-triphenyl-1,3-dioxolan (6), on the other hand, gave *threo*-1-benzoyloxy-2-bromo-1,2-diphenylethane and (\pm)-hydrobenzoin dibenzoate respectively. These stereospecific results are consistent with S_N2 ring opening involving a dioxolenyl cation.

BROMINATION of 2-phenyl-1,3-dioxolans with *N*-bromosuccinimide has been reported to yield bromohydrin benzoates¹ which are useful intermediates in organic syntheses. The reaction has been found to be stereospecific, from indirect evidence,² and is envisaged as proceeding *via* the bromo-ether (1) which ionizes to the dioxolenyl cation (2), followed by bromide attack at carbon-4 or -5 and ring opening.³ A consequence of this is a product (3; X = Br) with inversion of configuration at the carbon centre undergoing displacement. In this work we describe direct evidence obtained from the bromination of diastereoisomeric 2,4,5-triphenyl-1,3-dioxolans † which corroborate the proposed mechanism.

Reaction of (\pm)-hydrobenzoin with an excess of benzaldehyde in the presence of catalytic amount of toluene-*p*-sulphonic acid gave the known *r*-2,*c*-4,*t*-5-triphenyl-1,3-dioxolan^{5a,b} (4) [(\pm)-hydrobenzoin *OO*-benzylidene acetal]. Similar reaction of *meso*-hydrobenzoin, however, gave a mixture consisting of the known *meso*-hydrobenzoin *OO*-benzylidene acetal^{5b,c} (5) and a minor product (6), separated by fractional recrystallizations. That the latter compound is a diastereoisomer of the former is established by spectroscopic as well as experimental evidence (*vide infra*). The mass spectra of the two compounds are very similar and not different from that of (4). All three show a barely detectable M^+ peak, a weak $M^+ - 1$ peak and a base peak at m/e 196 corresponding to ($M - 1 - C_6H_5CO$). Other common significant peaks are m/e 195 ($M^+ - 1 - C_6H_5CHO$) and 167 (195 - CO). Comparison of the n.m.r. spectra of (4), (5), (6) and that of 2-phenyl-1,3-dioxolan (7) provides important clues to the stereochemistry of (5) and (6). Whereas the benzylidene proton of (7) absorbs at δ 5.73 and that of (4) at 6.30, those of (5) and (6) were found to absorb at δ 6.05 and 6.68 respectively. Baggett and his co-workers⁶ have

shown that the signal of the benzylidene proton of *trans*-2,4-diphenyl-1,3-dioxolan is displaced to lower field than that of the *cis*-isomer. Inch and Williams⁷ also observed the same chemical-shift difference in a series of *trans*- and *cis*-4-substituted 2-phenyl-1,3-dioxolans. Thus, assuming no conformational difference exists between the 2,4-diphenyl- and 2,4,5-triphenyl-1,3-dioxolans, the fact that the benzylidene proton of (6) is at a lower field and that of (5) is at a higher field relative to the same proton of (4) allows the assignment of (6) to the *r*-2,*t*-4,*t*-5-configuration and (5) as *r*-2,*c*-4,*c*-5-triphenyl-1,3-dioxolan. Examination of models also shows that because of restricted rotation the 4- and 5-phenyl groups in (6) are oriented perpendicular to the plane of the 1,3-dioxolan ring thereby placing the benzylidene proton in the planes of the two benzene rings, consistent with the observed deshielding effect exerted on that proton. That the all-*cis*-isomer (5) is the major product may be rationalized by suggestions made in related studies⁸ that in (5) the ring puckers to allow the phenyl substituents to assume pseudo-equatorial orientation, whereas in the *trans*-isomer (6), unfavourable 1,3-phenyl-hydrogen interaction would lead to destabilization.

The reaction of (4) with *N*-bromosuccinimide proceeded smoothly to give *erythro*-1-benzoyloxy-2-bromo-1,2-diphenylethane⁹ (8) in quantitative yield. Similar reaction of (5) and (6) yielded, on the other hand, the diastereoisomeric *threo*-1-benzoyloxy-2-bromo-1,2-diphenylethane (9), albeit in yields of 51 and 34% respectively. The productions of *erythro*-bromo-ester (8) from (4) and *threo*-bromo-ester (9) from (5) and (6) are consistent with the involvement of (2) as intermediate and ring opening by S_N2 displacement of bromide ion at

⁴ I.U.P.A.C. Tentative Rules for the Nomenclature of Organic Chemistry, Section E: Fundamental Stereochemistry', I.U.P.A.C. Information Bulletin no. 35, 1969.

⁵ (a) J. Read, I. G. MacNaughton Campbell, and T. V. Baker, *J. Chem. Soc.*, 1929, 2305; (b) J. Kovar, J. Steffkova, and J. Jary, *Coll. Czech. Chem. Comm.*, 1975, **30**, 2793; (c) R. L. Huang and S. E. Loke, *J. Chem. Soc.*, 1965, 6737.

⁶ N. Baggett, K. W. Buck, A. B. Foster, M. H. Randall, and J. M. Webber, *J. Chem. Soc.*, 1965, 3394.

⁷ T. D. Inch and N. Williams, *J. Chem. Soc. (C)*, 1970, 263.

⁸ S. A. Barker, E. J. Bourne, R. M. Pinkard, M. Stacey, and D. H. Whiffen, *J. Chem. Soc.*, 1968, 3232.

⁹ K. B. Wiberg and K. A. Saegebarth, *J. Amer. Chem. Soc.*, 1957, **79**, 6256.

† Designation of *cis*- and *trans*-stereochemistry is in accord with I.U.P.A.C. recommendations.⁴

¹ A. Reiche, E. Schmitz, W. Schade, and E. Beyer, *Chem. Ber.*, 1961, **94**, 2926; J. D. Prugh and W. C. McCarthy, *Tetrahedron Letters*, 1966, 1351; T. L. Hullar and S. B. Siskin, *J. Org. Chem.*, 1970, **35**, 225; D. H. R. Barton, L. Bould, D. L. C. Clive, P. D. Magnus, and T. Hase, *J. Chem. Soc. (C)*, 1971, 2204; M. M. Ponpipom and S. Hanessian, *Canad. J. Chem.*, 1972, **50**, 253.

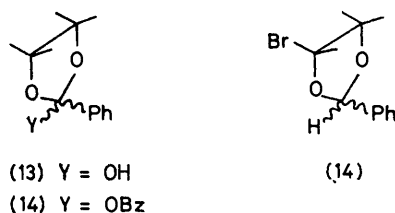
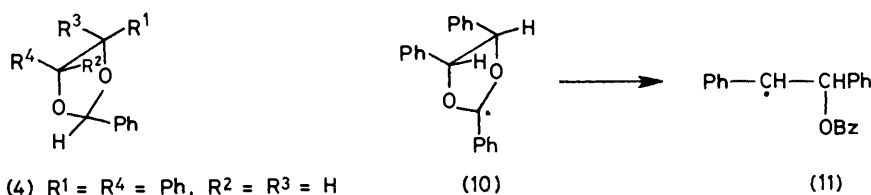
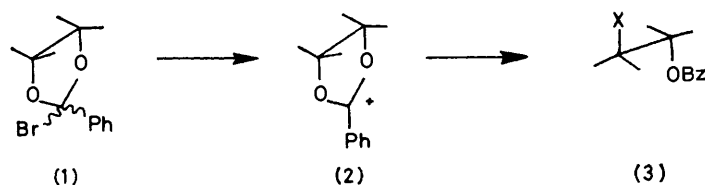
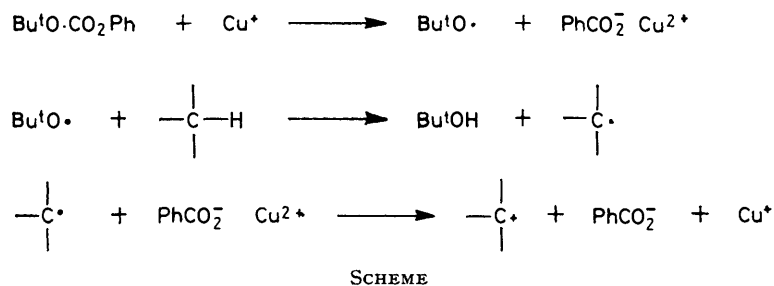
² D. A. Seeley and J. McElwee, *J. Org. Chem.*, 1973, **38**, 1691.

³ H. Perst, 'Oxonium Ions', Academic Press, New York, 1971, p. 82.

carbon-4 or carbon-3 of (2) with inversion of configuration. The possibility of the reaction proceeding by a radical path can be ruled out since intermediate (10) generated from (5) has been shown^{5c} to undergo ready rearrangement to (11) and in such a case would not be expected to yield stereospecific bromo-ester.

From the reactions of (5) and (6) were also isolated, by column chromatography, *erythro*-2-benzoyloxy-1,2-diphenylethanol^{5c} (12), benzoic benzoate, benzil, and

two reactions. Mechanistic studies¹⁰ of the perester reaction point to the operation of a chain reaction as indicated in the Scheme. It might be expected that reaction of perbenzoate with (4), (5), and (6) would result in the generation of their respective dioxolenium ions (2) which would then undergo S_N2 displacement by benzoate ion with ring opening to give stereospecific glycol diester (3; X = PhCO₂). Preliminary studies with (7) were found indeed to give an 81% yield of



meso-hydrobenzoin. The formation of (12) is likely caused by adventitious presence of moisture which attacked the cationic centre of (2) to yield *via* (13) the glycol monoester with retention of configuration. That benzoic benzoate is an oxidation product of (12) and benzil is derived from the reaction of benzoic benzoate with *N*-bromosuccinimide were confirmed experimentally, although the possibility that these products may have arisen from bromo-ester (14) cannot be entirely eliminated.

The copper(I) ion-catalysed reaction of *t*-butyl perbenzoate is of interest in relation to the bromination of (4)—(6) because of certain common features in the

ethylene glycol dibenzoate and a small amount of ethylene glycol monobenzoate. Under the same conditions, (4) was found to give besides unchanged starting material, *meso*-hydrobenzoin dibenzoate, *threo*-2-benzoyloxy-1,2-diphenylethanol⁹ (15) and trace amount of benzil. The reactions of (5) and (6), on the other hand, yielded the expected (±)-hydrobenzoin dibenzoate and *erythro*-2-benzoyloxy-1,2-diphenylethanol (12). The presence of (12) and (15) may again be attributed to the formation of (13) during the reaction, or hydrolysis of (16) during the chromatographic

¹⁰ G. Sosnovsky and S. O. Lawesson, *Angew. Chem. Internat. Edn.*, 1964, **3**, 269.

processes used in the separation of products. In either case, it lends support to the argument for the existence of (2) as an intermediate.

EXPERIMENTAL

M.p.s and b.p.s are uncorrected. I.r. spectra were measured with a Pye–Uvicam SP 1000 spectrophotometer. N.m.r. spectra were determined in the solvent stated at 60 MHz with a Hitachi–Perkin–Elmer R208 spectrometer and with SiMe₄ as an internal reference. Mass spectra were recorded at 70 eV on a MS 30 mass spectrometer. G.l.c. analysis was conducted on an Aerograph A-90-P gas chromatograph, employing a 3 m × 2 mm column packed with 20% SE-30 on 60/80 mesh HMDS Chromosorb W and using hydrogen as carrier gas. Analytical t.l.c. and p.l.c. were performed respectively on Merck pre-coated 0.25 mm and 2 m Kieselgel 60 F₂₅₄ glass-backed plates and visualized by u.v. illumination. Alumina used was Merck active, neutral alumina for column chromatography deactivated to Grade III. Light petroleum refers to the fraction b.p. 60–80 °C. Elemental analyses were carried out by the Microanalytical Laboratory, University of Singapore.

r-2,c-4,t-5-Triphenyl-1,3-dioxolan (4).—A solution of (±)-hydrobenzoin (6.7 g, 31 mmol), freshly distilled benzaldehyde (46 g, 434 mmol) and toluene-*p*-sulphonic acid (50 mg) in benzene (100 ml) was refluxed under nitrogen in a Dean-and-Stark apparatus for 10 h, cooled, washed with dilute sodium hydroxide (5%), and dried (K₂CO₃). Solvent and excess of benzaldehyde were removed under reduced pressure and the solid residue after three recrystallizations from absolute ethanol afforded pure compound (4) (6.9 g, 73%), m.p. 85.5–87 °C (lit.^{5a,b} 84 °C, 82–84 °C). T.l.c. gave *R*_F 0.38 (n-hexane:C₆H₆, 1:1). ν_{\max} (KBr) cm⁻¹: 1 095, 1 065, 1 015; δ (CCl₄) 4.78 (2 H, s), 6.30 (1 H, s), and 7.23–7.76 (18 H, m); *m/e* (rel. int.) 302 (*M*⁺, 0.1), 301 (*M*⁺ – 1, 0.45), 197 (17), 196 (100), 195 (29), 178 (17), 167 (45), 152 (8), 105 (21), 90 (23), 89 (20), and 77 (17).

r-2,c-4,c-5-Triphenyl-1,3-dioxolan (5) and *r-2,t-4,t-5-Triphenyl-1,3-dioxolan* (6).—The crude product from the reaction of *meso*-hydrobenzoin (5 g, 23 mmol) and benzaldehyde (25 g, 240 mmol) prepared similarly as described above was triturated with light petroleum and filtered, m.p. 85–100 °C. T.l.c. analysis (n-hexane:C₆H₆, 1:1) showed the presence of a strong spot at *R*_F 0.31 and a faint spot at *R*_F 0.40 respectively. The mixture was recrystallized repeatedly from light petroleum until t.l.c. showed a single spot corresponding to the major product. Two further recrystallizations from absolute ethanol gave pure compound (5) as needles (3.8 g, 41%), m.p. and mixed m.p.* 106–107 °C (lit.^{5b,c} 104–105, 109–110 °C); ν_{\max} (KBr) cm⁻¹ 1 090, 1 060, 1 030sh, and 1 005; δ (CCl₄) 5.35 (2 H, s), 6.05 (1 H, s), 6.92 (10 H, s), and 7.30–7.82 (5 H, m); *m/e* (rel. int.) 302 (*M*⁺, 0.1), 301 (*M*⁺ – 1, 0.6), 197 (17), 196 (100), 195 (29), 178 (17), 167 (45), 152 (8), 118 (4), 105 (21), 90 (19), 89 (16), and 77 (14).

The light petroleum mother liquor was concentrated to dryness and the residue recrystallized from absolute ethanol until (6) was pure by t.l.c. (850 mg, 9%), m.p. 113–115 °C. Mixed m.p. with (5) was 92–100 °C (Found:

C, 83.4; H, 6.3. C₂₁H₁₈O₂ requires C, 83.4; H, 6.0%); ν_{\max} (KBr) cm⁻¹ 1 100, 1 070, 1 020, and 1 000; δ (CCl₄) 5.27 (2 H, s), 6.68 (1 H, s), 6.97 (10 H, s), and 7.23–7.65 (5 H, m); *m/e* (rel. int.) 302 (*M* – <0.1) (*M*⁺ – 1, 0.3), 197 (17), 196 (100), 195 (32), 179 (9), 178 (13), 168 (17), 167 (63), 152 (6), 118 (4), 105 (23), 90 (33), 89 (20), and 77 (20).

Reaction of r-2,c-4,t-5-Triphenyl-1,3-dioxolan (4) with *N*-Bromosuccinimide (NBS).—A solution of compound (4) (2 g, 6.61 mmol), NBS (1.18 g, 6.63 mmol), and azobisisobutyronitrile (9 mg) in dry benzene (40 ml) under nitrogen was cautiously warmed on a steam-bath. After the initial vigorous reaction had subsided, the mixture was refluxed for a further 4 h and then cooled. Succinimide (538 mg, 82%) was filtered off, m.p. and mixed m.p. 123–125 °C (lit.¹¹ 126 °C). The filtrate was concentrated to dryness, the residue triturated with cyclohexane, and filtered. The solid product (2.33 g), m.p. 169–170 °C after recrystallization from benzene–light petroleum, was identified as *erythro*-1-benzoyloxy-2-bromo-1,2-diphenylethane (8) (lit.⁹ 167.5–168.5 °C) by comparison of i.r., t.l.c. (C₆H₆; *R*_F 0.47), and mixed m.p. with an authentic sample, δ (CDCl₃) 5.30 (1 H, d, *J* 7 Hz), 6.45 (1 H, d, *J* 7 Hz), and 7.10–8.00 (15 H, m). The combined filtrate and mother liquor from recrystallization were evaporated and the residue chromatographed over alumina. Elution with light petroleum gave (i) a mixture which on trituration with hot cyclohexane yielded a further crop of *erythro*-bromobenzoate (8) (25 mg, total yielded 94%) and a yellow residue from which benzil (45 mg, 0.21 mmol), m.p. 94–95 °C (lit.¹¹ 95 °C), was isolated by sublimation at 50–80 °C/0.5 mmHg and identified by i.r., mixed m.p., and t.l.c. (C₆H₆; *R*_F 0.41). Further elution with light petroleum–benzene (3:1) gave benzoin benzoate (8 mg, 0.025 mmol), m.p. 123–125 °C (lit.¹¹ 125 °C), identified by i.r. and mixed m.p.

Reaction of r-2,c-4,c-5-Triphenyl-1,3-dioxolan (5) with *N*-Bromosuccinimide.—The reaction of (5) (2.0 g, 6.61 mmol) with NBS (1.18 g, 6.63 mmol) in dry benzene (40 ml) initiated with azobisisobutyronitrile (8 mg) was carried out as described in the preceding experiment. After removal of succinimide (579 mg, 88%), the filtrate was concentrated to dryness to leave a yellow oil which solidified on cooling in ice. The solid was triturated with light petroleum, filtered, and recrystallized twice from methanol to give pure *threo*-1-benzoyloxy-2-bromo-1,2-diphenylethane (9) (971 mg), m.p. 101–102 °C, identified by comparison of i.r., t.l.c. (C₆H₆; *R*_F 0.47), and mixed m.p. with an authentic sample prepared by benzoylation of *threo*-2-bromo-1,2-diphenylethanol¹² (Found: C, 66.0; H, 4.8; Br, 20.7. C₂₁H₁₇BrO₂ requires C, 66.15; H, 4.5; Br, 21.0%); δ (CDCl₃) 5.30 (1 H, d, *J* 9 Hz), 6.38 (1 H, d, *J* 9 Hz), 7.18 (10 H, s), and 7.25–8.25 (5 H, m). The combined filtrate and mother liquor from recrystallizations were evaporated and the residue chromatographed over alumina. Elution with light petroleum gave a mixture from which was obtained a further amount of *threo*-bromobenzoate (9) (3.08 mg, total yield 51%) by recrystallizations from methanol and benzil (49 mg, 0.23 mmol) from the filtrate. Elution with light petroleum containing increasing quantities of benzene (5–50%) gave (i) benzoin benzoate (69 mg, 0.22 mmol), and (ii) *erythro*-2-benzoyloxy-1,2-diphenylethanol (12) (47 mg, 0.15 mmol),

¹¹ A. I. Vogel, 'Practical Organic Chemistry', 3rd ed., Longman, Green and Co. Ltd., London, 1967.

¹² H. O. House, *J. Amer. Chem. Soc.*, 1955, **77**, 3074.

* We thank Dr. S. E. Loke for a gift of the compound.

m.p. and mixed m.p.* 163—165 °C from light petroleum-benzene (lit.,^{5c} 164—165 °C). Elution with ether gave *meso*-hydrobenzoin (76 mg, 0.36 mmol) followed by succinimide (18 mg).

Reaction of r-2,t-4,t-5-Triphenyl-1,3-dioxolan (6) with N-Bromosuccinimide.—The reaction of (6) (2.0 g, 6.61 mmol) with NBS (1.18 g, 6.63 mmol) initiated by azobisisobutyronitrile (9 mg) was carried out and worked up as described in the reaction of (4) to give first succinimide (633 mg, 97%) and then *threo*-1-benzoyloxy-2-bromo-1,2-diphenylethane (9) (410 mg) from the mother liquor. The residue from evaporation of the filtrate was chromatographed over alumina. Elution with light petroleum containing benzene (10—20%) gave a mixture (887 mg) shown by t.l.c. to consist of unchanged (6) and *threo*-bromobenzoate (9). Two recrystallizations from light petroleum gave the pure *threo*-bromobenzoate (9) (454 mg, total yield 34%). From the mother liquor was isolated compound (6) (55 mg, 0.18 mmol) after recrystallization from absolute ethanol. Continued elution with light petroleum-benzene (1:1) gave benzil (98 mg, 0.47 mmol). Further elution with benzene containing ether (20—50%) gave *erythro*-2-benzoyloxy-1,2-diphenylethanol (12) (66 mg, 0.21 mmol). Elution with ether gave *meso*-hydrobenzoin (30 mg, 0.14 mmol).

Reaction of 2-Phenyl-1,3-dioxolan (7) with t-Butyl Perbenzoate.—The dioxolan (7) was prepared according to published procedure, b.p. 128 °C/35 mmHg (lit.,¹³ 115—116 °C/16 mmHg); ν_{\max} (liq. film) 1 095, 1 070, and 1 030 cm^{-1} ; δ (CCl_4) 3.73—4.02 (4 H, m), 5.73 (1 H, s), and 7.16—7.60 (5 H, m). To a stirred mixture of (7) (6.02 g, 40 mmol) and cuprous chloride (42 mg, 0.4 mmol) in dry benzene (40 ml) under nitrogen at reflux was added a solution of redistilled *t*-butyl perbenzoate (5.05 g, 26 mmol) in benzene (15 ml) dropwise over a period of 1.5 h. After being heated for a total of 22 h, g.l.c. analysis of an aliquot of the reaction mixture indicated the presence of unchanged compound (7) (16 mmol, 40%). The cooled reaction mixture was washed with saturated aqueous sodium hydrogen carbonate and dried (MgSO_4). Removal of solvent under reduced pressure left a solid residue which was washed with cold light petroleum followed by methanol and filtered to give ethylene glycol dibenzoate (3.61 g), m.p. and mixed m.p. 70—72 °C (lit.,¹¹ 73 °C). The filtrate was distilled to give unchanged compound (7) (1.12 g), b.p. 126—128 °C/35 mmHg, and the residue chromatographed over alumina. Elution with light petroleum gave a further amount of unchanged compound (7) (724 mg). Continued elution with light petroleum containing benzene (20—50%) gave ethylene glycol dibenzoate (1.65 g, total yield 81%). Further elution with benzene and benzene-ether (4:1) gave ethylene glycol monobenzoate (156 mg, 0.94 mmol), b.p. 90—95 °C/0.1 mmHg (lit.,¹⁴ 154—155 °C/13 mmHg) (Found: C, 65.4; H, 6.1. Calc. for $\text{C}_9\text{H}_{10}\text{O}_3$: C, 65.05; H, 6.1%). Benzoylation of this gave ethylene glycol dibenzoate.

Reaction of r-2,c-4,t-5-Triphenyl-1,3-dioxolan (4) with t-Butyl Perbenzoate.—A mixture of compound (4) (3.02 g, 10 mmol) and cuprous chloride (12 mg, 0.12 mmol) in dry benzene (25 ml) was treated with *t*-butyl perbenzoate (1.39 g, 7.2 mmol) as described in the preceding experiment. The reaction mixture was refluxed for a total of 40 h, cooled, and the white precipitate filtered off and washed with benzene. The solid (439 mg) was identified as *meso*-

hydrobenzoin dibenzoate by i.r., m.p., and mixed m.p. 250—252 °C (lit.,⁹ 247—248 °C). The benzene filtrate was washed with saturated aqueous sodium hydrogen carbonate and dried (MgSO_4). Solvent was removed under reduced pressure and the residue warmed with hot absolute ethanol and filtered. This yielded a further crop of *meso*-hydrobenzoin dibenzoate (200 mg). The alcoholic solution when cooled in ice deposited unchanged compound (4) (1.0 g). The residue after evaporation of ethanol was chromatographed over alumina. Elution with petroleum afforded (i) unchanged (4) (430 mg, total recovery 47%) and (ii) benzil (33 mg, 0.16 mmol). Elution with light petroleum containing benzene (10—50%) gave a resinous material (450 mg) from which *meso*-hydrobenzoin dibenzoate (38 mg, total yield 30%) was obtained by trituration with benzene. Further elution with benzene gave *threo*-2-benzoyloxy-1,2-diphenylethanol (15) (69 mg, 0.22 mmol), m.p. and mixed m.p. 155—157 °C from benzene-light petroleum (lit.,⁹ 152.5—154 °C).

Reaction of r-2,c-4,c-5-Triphenyl-1,3-dioxolan (5) with t-Butyl Perbenzoate.—A mixture of compound (5) (1.51 g, 5 mmol) and cuprous chloride (8 mg, 0.08 mmol) in dry benzene (20 ml) was treated with *t*-butyl perbenzoate (700 mg, 3.6 mmol) and worked up as described in the reaction of (4). Chromatography (alumina, 120 g) of the residue after removal of solvent gave unchanged (5) (729 mg, 48% recovery) eluted with light petroleum. Elution with light petroleum containing benzene (10—50%) gave (\pm)-hydrobenzoin dibenzoate (200 mg, 18%), identified by i.r., m.p. and mixed m.p. 131—133 °C from ethanol (lit.,⁹ 132—133 °C). Elution with benzene and benzene containing ether (5%) gave *erythro*-2-benzoyloxy-1,2-diphenylethanol (12) (191 mg, 0.6 mmol).

Reaction of r-2,t-4,t-5-Triphenyl-1,3-dioxolan (6) with t-Butyl Perbenzoate.—A mixture of (6) (1.51 g, 5 mmol) and cuprous chloride (5 mg, 0.05 mmol) in dry benzene (20 ml) was treated with *t*-butyl perbenzoate (680 mg, 3.5 mmol) and worked up as described in the reaction of compound (4). The residue after evaporation of solvent was triturated with light petroleum, filtered, and washed with cold absolute ethanol to give unchanged compound (6) (642 mg). The filtrate was concentrated to dryness and the residue chromatographed over alumina. Elution with light petroleum gave further unchanged (6) (148 mg, total recovery 52%). Elution with light petroleum containing benzene (20—50%) and benzene gave (\pm)-hydrobenzoin dibenzoate (245 mg, 24%). Further elution with benzene containing ether (20%) gave *erythro*-2-benzoyloxy-1,2-diphenylethanol (12) (69 mg, 0.22 mmol), followed by *meso*-hydrobenzoin (22 mg, 0.1 mmol) eluted with ether.

Reaction of erythro-2-Benzoyloxy-1,2-diphenylethanol (12) with N-Bromosuccinimide.—A solution of compound (12) (158 mg, 0.49 mmol), NBS (90 mg, 0.51 mmol), and a few crystals of azobisisobutyronitrile in dry benzene (5 ml) was refluxed under nitrogen for 4 h. After removal of solvent, the residue was separated by p.l.c. developed with benzene to give the following products: (i) α -bromobenzyl phenyl ketone, R_F 0.48 (10 mg, 7%) identified by comparison of i.r. t.l.c., and mixed m.p. 53—54 °C (lit.,¹⁵ 54.5—56 °C) with an authentic sample, (ii) benzoin benzoate, R_F 0.36 (92 mg, 60%), and (iii) succinimide (39 mg, 57%).

¹⁴ H. Marwein, K. Bodenbenner, P. Borner, F. Kunert, and K. Wunderlich, *Annalen*, 1960, **632**, 38.

¹⁵ I. J. Borowitz, P. E. Rusek, and R. Wirkhaus, *J. Org. Chem.*, 1969, **34**, 1595.

* We thank Dr. S. E. Loke for a gift of the compound.

¹³ E. S. Huyser and Z. Garcia, *J. Org. Chem.*, 1962, **27**, 2716.

Reaction of Benzoin Benzoate with N-Bromosuccinimide.— A solution of benzoin benzoate (1.27 g, 4 mmol), azobisisobutyronitrile (7 mg, 0.4 mmol), and NBS (356 mg, 2 mmol) in dry benzene (20 ml) was refluxed for 4 h under nitrogen. The cooled solution was washed successively with saturated aqueous sodium bisulphite and then sodium hydrogen carbonate and then dried (MgSO_4). After removal of solvent, the residue was chromatographed over alumina.

Elution with light petroleum containing benzene (30%) gave benzil (216 mg, 34%) followed by unchanged benzoin benzoate (310 mg, 24% recovery).

We thank Professor K. C. Chan, University of Malaya, for the n.m.r. and mass spectra.

[7/1450 Received, 9th August, 1977]
