Some Reactions of Benzaldehyde Acetals with Alkyl-lithium Reagents; a Stereospecific Olefin Synthesis from 1,2-Diols [1]

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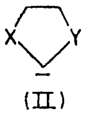
In certain cases the reaction of 2-phenyl-1,3-dioxolans with n-butyl-lithium gives olefins in a highly stereospecific fragmentation reaction. In particular, the reaction constitutes the crucial step in a convenient preparation of *trans*-cyclo-octene from *cis*-cyclo-octene.

A mechanism is proposed involving initial metallation of the dioxolan followed by concerted cycloelimination to olefin and benzoate ion. Support for this mechanism, in three instances, is provided by the isolation of products derived by *in situ* trapping of the lithium derivative of the dioxolan by benzoate ion.

THE orbital-symmetry-allowed [$_{\pi}2_s + _{\pi}4_s$]cycloaddition of an allyl anion to ethylene [2] is the prototype of a wide range of processes which can be represented in general terms by (I) $\rightleftharpoons$ (II). A recent example of the forward reaction is provided by the addition of 2-aza-allyl ions to olefins; [3] the reverse is exemplified by cycloreversion of tetrahydro-2-furyl anions.[4] Analogous cycloeliminations involving anions derived from a variety of five-membered heterocyclic compounds are now known.[5]

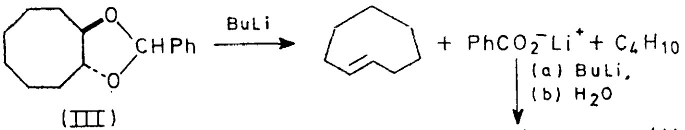
(I)



(II)

The reaction of 2-phenyl-1,3-dioxolan with phenyl-lithium,[6] in which ethylene and benzophenone are formed (see also ref. 7) appeared to be a cycloelimination of this type [(II) $\longrightarrow$ (I)], benzophenone being the product of a subsequent reaction between lithium benzoate and phenyl-lithium. As we were interested in developing a synthetic route to *trans*-cyclo-octenes we decided to investigate further the scope, the mechanism, and (particularly) the stereospecificity (with regard to the olefinic product) of the reaction in the case of substituted 2-phenyl-1,3-dioxolans.

We examined first the reaction of the benzylidene derivative (III) of *trans*-cyclo-octane-1,2-diol with alkyl-lithium derivatives. Treatment of the dioxolan (III) in light petroleum with n-butyl-lithium in hexane for 14 h (optimum conditions) gave *trans*-cyclo-octene in 75% yield. The olefin was uncontaminated with its *cis*-isomer; the other product, n-butyl phenyl ketone could conveniently be removed by adsorption chromatography. Two mol. equiv. of n-butyl-lithium were required in accordance with equation (i).



(III) (i)

The reaction of the dioxolan (III) with n-butyl-lithium was faster in tetrahydrofuran as solvent; however under these conditions some addition of alkyl-lithium to the strained double bond of *trans*-cyclo-octene occurred, giving, after quenching of the presumed intermediate 2-butylcyclo-octyl-lithium, n-butyl-cyclo-octane.

The stereospecificity of the fragmentation is underlined by the formation of *cis*-cyclo-octene from either of the diastereoisomers of the benzylidene derivative of

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[1] Preliminary communication, J. N. Hines, M. J. Peagram, G. H. Whitham, and M. Wright, *Chem. Comm.*, 1968, 1593.

[2] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 816; A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillich, D. Grashey, and E. Spindler, *Chem. Ber.*, 1967, **100**, 2192; G. Boche and D. Martens, *Angew. Chem. Internat. Edn.*, 1972, **11**, 724.

[3] T. Kaufmann and R. Eidenschink, *Angew. Chem. Internat. Edn.*, 1971, **10**, 739; T. Kaufmann and E. Köppelmann, *ibid.*, 1972, **11**, 290; R. Eidenschink and T. Kaufmann, *ibid.*, 1972, **11**, 292.

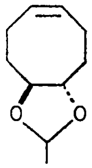
[4] R. B. Bates, L. M. Kroposki, and D. E. Potter, *J. Org. Chem.*, 1972, **37**, 560.

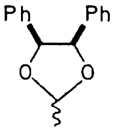
[5] *Cf.* D. M. Zimmerman and R. A. Olofson, *Tetrahedron Letters*, 1970, 3453; P. Eberhard and R. Huisgen, *J. Amer. Chem. Soc.*, 1972, **94**, 1345, 1346; R. Raap and R. G. Micetich, *Canad. J. Chem.*, 1968, **46**, 1057; U. Schöllkopf and F. Gerhart, *Angew. Chem. Internat. Edn.*, 1968, **7**, 805; J. S. Josan and F. W. Eastwood, *Austral. J. Chem.*, 1968, **21**, 2013.

[6] P. S. Wharton, G. A. Hiegel, and S. Ramaswami, *J. Org. Chem.*, 1964, **29**, 2441.

[7] K. D. Berlin, B. S. Rathore, and M. Peterson, *J. Org. Chem.*, 1965, **30**, 226.

cis-cyclo-octane-1,2-diol. It thus appears that the dioxolan olefin synthesis is applicable to the stereospecific production of 1,2-dialkylethylenes from vicinal diols, and that quite highly strained olefins may be prepared. In an attempt to obtain the still more highly strained *cis,trans*-cyclo-octa-1,5-diene[8] from the benzylidene derivative of *cis*-cyclo-oct-5-ene-*trans*-1,2-diol (IV), we only obtained products of addition of n-butyl-lithium to the diene. The latter addition is apparently faster than the original proton abstraction in this case. Further experiments with (IV) bearing on the mechanism of the reaction are described later.


(IV)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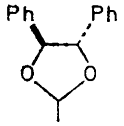
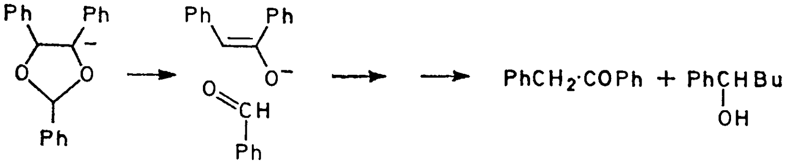
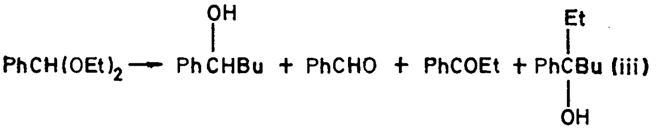

(VI)

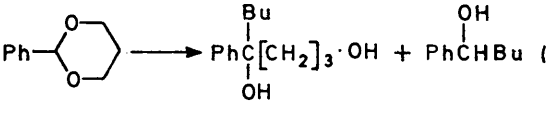
The dioxolans (V) and (VI), derived respectively from *meso*- and (±)-hydrobenzoin were subjected to reaction with n-butyl-lithium in tetrahydrofuran. In the former case (V) significant amounts of *cis*-stilbene were not formed, and with (VI) only 9% yield of *trans*-stilbene was obtained. With both substrates the main products were deoxybenzoin and 1-phenylpentan-1-ol, apparently derived by preferred proton abstraction from C-4 (or C-5) in preference to C-1, followed by cycloelimination [equation (ii)]. On the basis of these examples the dioxolan olefin synthesis is not applicable to the synthesis of conjugated aryl-substituted olefins. The presence of the aryl group at C-4 or C-5 in the dioxolan facilitates proton abstraction from one of these sites, and it may be that the greater stability of a carbanion adjacent to one rather than two oxygen atoms[9] is the additional factor which leads to the predominant mode of reaction.


(ii)

For comparison purposes the reactions of benzaldehyde diethyl acetal and of 2-phenyl-1,3-dioxan with butyl-lithium were investigated briefly. In the former case the major product was 1-phenylpentanol, formed together with smaller amounts of benzaldehyde, propiophenone, and 3-phenylheptan-3-ol [equation (iii)]. In the case of 2-phenyl-1,3-dioxan a moderate yield of 4-phenyloctane-1,4-diol, together with 1-phenylpentanol, was obtained [equation (iv)]. Apparently the lithium derivative of benzaldehyde diethyl acetal decomposes predominantly by internal *E*2 elimination as in (VII) (for a precedent see ref. 10) to give benzaldehyde, which undergoes further reaction with butyl-lithium. A minor competing process is Wittig rearrangement to (VIII) followed by collapse to propiophenone. In the case of 2-phenyl-1,3-dioxan, where an internal elimination route is sterically disfavoured, the major product can be accounted for by a Wittig rearrangement pathway involving (IX) as an intermediate. With 2-phenyl-1,3-dioxolans an analogous rearrangement would involve a four-membered ring intermediate, and does not compete with cyclo-elimination.

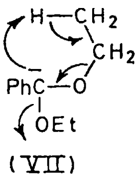


$$\mathrm{PhCH(OEt)_2} \longrightarrow \mathrm{Ph\overset{OH}{C}HBu} + \mathrm{PhCHO} + \mathrm{PhCOEt} + \mathrm{Ph\overset{Et}{\underset{OH}{C}}Bu} \quad \text{(iii)}$$


(iv)

A number of 2-phenyl-1,3-dioxolans did not undergo cycloelimination on treatment with n-butyl-lithium; these were the benzylidene derivatives of the following glycols: cyclohexane-*trans*-1,2-diol,[11] 1-methylcyclo-octane-*trans*-1,2-diol, pinacol, and catechol. In the first three cases starting material was recovered under normal reaction conditions, and complex mixtures of products were obtained on prolonged treatment. The catechol derivative gave products of an alternative reaction mode.[12]

Mechanism of the Fragmentation of 2-*Phenyl*-1,3-*dioxolans*.—In the course of experiments designed originally to allow *cis,trans*-cyclo-octa-1,5-diene to be prepared from the dioxolan (IV), the latter was treated with a range of alkyl lithium reagents under various conditions. Although we were unable to achieve a satisfactory synthesis of *cis,trans*-cyclo-octa-1,5-diene, we found that treatment of (IV) with neopentyl-lithium in ether gave the benzoyldioxolan (X) as major product. The structure of (X) was assigned on the basis of analysis and spectroscopic data. This compound is clearly derived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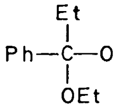
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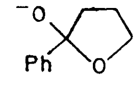
(IX)

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[8] A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1967, **89**, 4024.

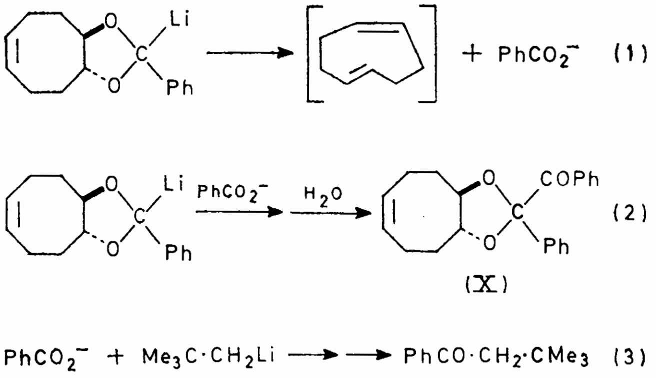
[9] J. Hine, L. G. Mahone, and C. L. Liotta, *J. Amer. Chem. Soc.*, 1967, **89**, 5911; J. Hine and P. D. Dalsin, *ibid.*, 1972, **94**, 6998.

[10] R. L. Letsinger and D. F. Pollart, *J. Amer. Chem. Soc.*, 1956, **78**, 6079.

[11] A. Rieche, E. Schmitz, W. Schade, and E. Beyer, *Chem. Ber.*, 1961, **94**, 2926.

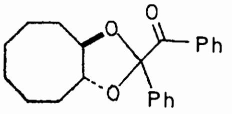
[12] E. J. Thomas, *J.C.S. Perkin I*, 1973, 2006.

by attack of the lithium derivative of (IV) on benzoate ion produced by cycloelimination, *i.e.* reaction (1) followed by reaction (2) in the Scheme. The isolation of (X) provides the first unambiguous evidence for the intervention of a discrete lithium derivative of the dioxolan in the cycloelimination process. It appears that the more sterically hindered neopentyl-lithium reacts more slowly with benzoate ion than does n-butyl-lithium, thereby allowing reaction (2) to compete efficiently.

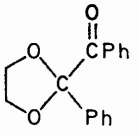


SCHEME

Analogous 'trapped' products (XI) and (XII) were isolated from the reaction of neopentyl-lithium with the benzylidene derivative of *trans*-cyclo-octane-1,2-diol (III) and 2-phenyl-1,3-dioxolan, respectively, although the yields were lower. In the case of (XI) the structure was confirmed by an independent synthesis starting from the diol and benzoin. A semiquantitative measure of the ratio of 'trapped' product to neopentyl phenyl ketone formed in these reactions was obtained by integration of the relevant peaks in the n.m.r. spectra of the crude products. Results were as follows: (X), 65 : 35; (XI), 30 : 70; (XII), 8 : 92. These ratios provide a crude estimate of the relative rate of fragmentation of the metallated dioxolans [*e.g.* reaction (1) in the Scheme], since the relative rates of reactions (2) and (3) will depend on the concentration of the metallated intermediate. The results indicate that fragmentation occurs less readily the more strained the olefin being formed. However the surprising thing is the relatively small effect observed in going from the ethylene precursor to the *trans*-cyclo-octene precursor, even though the product from the latter is highly strained. Evidently the transition state for fragmentation is reached early and has little olefin character.



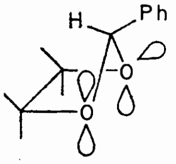
(XI)



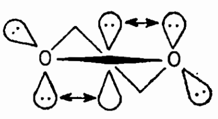
(XII)

We consider therefore that the dioxolan fragmentation involves initial formation of a lithium derivative by metal–hydrogen exchange followed by concerted cycloelimination to olefin and benzoate ion. We do not favour the stepwise mechanism proposed by Berlin *et al.*[7] since it would be difficult to explain the stereospecific formation of *trans*-cyclo-octene on this basis.

There is no completely satisfactory explanation for the behaviour of those dioxolans which do not undergo cycloelimination on treatment with alkyl-lithium reagents. With the dioxolan from *trans*-cyclohexane-1,2-diol it might have been anticipated that metallation would occur but not fragmentation; however quenching experiments with deuterium oxide indicated that metallation had not occurred. We tentatively suggest that dioxolans for which a half-chair conformation [with O–C(2)–O coplanar] is forced or favoured do not readily undergo metallation; this would apply to the *trans*-cyclohexanediol derivative, and probably also to the heavily alkylated dioxolans where an envelope conformation (XIII) is destabilised by eclipsing (torsional) interactions about C-4,C-5. It may be that the lowered acidity of the half-chair conformation is related to orbital repulsion effects which would operate in the trigonal form of the corresponding anion [see (XIV) for an exaggerated representation]. A further simple steric factor could operate in the case of the tri- and tetra-alkyldioxolans, preventing proton abstraction. This cannot be the only factor however, or else the two diastereoisomeric dioxolans from *cis*-cyclo-octane-1,2-diol would not both undergo cycloelimination.



(XIII)



(XIV)

In summary, the dioxolan olefin synthesis provides a useful stereospecific route to lightly alkylated olefins, but fails for tri- and tetra-substituted alkenes. It also fails for conjugated aryl-substituted olefins, owing to competition from an alternative mode of fragmentation. It is thus less general than some of the syntheses developed in recent years for the conversion of vicinal diols into alkenes,[13] but the availability of materials, stereospecificity, and relative mildness of reaction conditions make it, in our opinion, the best method for the synthesis of *trans*-cyclo-octene. An application of the reaction to the synthesis of diastereoisomeric *trans*-cyclo-oct-2-en-1-ols has already been described,[14] and we have also found that subjection of the optically active

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[13] *Cf.* E. J. Corey and R. A. E. Winter, *J. Amer. Chem. Soc.*, 1963, **85**, 2677; E. J. Corey, F. A. Carey, and R. A. E. Winter, *ibid.*, 1965, **87**, 934; E. J. Corey and J. I. Shulman, *Tetrahedron Letters*, 1968, 3655; G. Crank and F. W. Eastwood, *Austral. J. Chem.*, 1964, **17**, 1392; J. S. Josan and F. W. Eastwood, *ibid.*, 1968, **21**, 2013; F. W. Eastwood, K. J. Harrington, J. S. Josan, and J. L. Pura, *Tetrahedron Letters*, 1970, 5223; J. C. Carnahan and W. D. Closson, *ibid.*, 1972, 3447; K. B. Sharpless and T. C. Flood, *J.C.S. Chem. Comm.*, 1972, 370.

[14] G. H. Whitham and M. Wright, *J. Chem. Soc.* (*C*), 1971, 886.

trans-cyclo-octane-1,2-diol to the reaction sequence leads to the formation of *trans*-cyclo-octene of high optical purity.[15]

EXPERIMENTAL

Cyclo-octane-trans-1,2-*diol*.—A solution of *cis*-1,2-epoxycyclo-octane [16] (58 g) and sodium acetate trihydrate (150 g) in acetic acid (300 ml) was heated under reflux for 19 h. Acetic acid and water were then removed under reduced pressure, and water (400 ml) was added to the residue. The product, *trans*-2-acetoxycyclo-octanol, was isolated by extraction with ether and was obtained as a viscous liquid. The latter was hydrolysed by heating under reflux with a solution of potassium hydroxide (50 g) in ethanol (400 ml). Isolation with ether followed by distillation gave cyclo-octane-*trans*-1,2-diol (44 g, 70%), b.p. 78—84° at 0·1 mmHg, which partially crystallised after three days (lit.,[16] b.p. 93—94° at 0·5 mmHg). G.l.c. (polyethylene glycol adipate; 180°) indicated that the diol was 86% pure, two impurities (11 and 3%) of similar retention time being present.

10-*Phenyl*-9,11-trans-*dioxabicyclo*[6.3.0]*undecane*.— A mixture of cyclo-octane-*trans*-1,2-diol (49·9 g), benzaldehyde (73 g; freshly redistilled), and conc. sulphuric acid (0·5 ml) in toluene (200 ml) was heated under reflux (Dean and Stark apparatus; N_2) for 12 h. After addition of sufficient solid potassium carbonate to neutralise the sulphuric acid, the toluene and benzaldehyde were removed under reduced pressure. The residue was distilled to give the *dioxolan* (72 g), b.p. 148—150° at 0·5 mmHg, which slowly solidified. It was obtained as needles, (60·8 g, 76%), m.p. 44—45° [from light petroleum (100 ml)] (Found: C, 77·5; H, 8·55. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·6%), τ 7·6—9·0 (12H, complex, ring methylenes), 5·9—6·1 (2H, m, H-1 and H-8), 4·12 (1H, s, H-10), and 1·3—2·9 (5H, m, aromatic).

Reaction of 10-*Phenyl*-9,11-trans-*dioxabicyclo*[6.3.0]*undecane with n-Butyl-lithium. Preparation of* trans-*Cyclo-octene*.—n-Butyl-lithium in hexane (37 ml, 2 mol. equiv.) was added *via* a serum cap to an ice-cooled solution of the dioxolan (7·2 g) in light petroleum (30 ml) under nitrogen. After 14 h at 20° the mixture was added to water (200 ml) and the product was isolated with light petroleum. The extracts were washed with aqueous silver nitrate (3 × 50 ml; 10%) and the combined aqueous extracts were poured onto ammonia (50 ml; *d* 0·880) and ice. The hydrocarbon liberated was isolated with light petroleum (b.p. 30—40°). Removal of solvent gave *trans*-cyclo-octene (2·48 g, 73%) homogenous to g.l.c. (polyethylene glycol), $\nu_{max.}$ (film) 792, 825, 850, 935, 990, 1195, and 1645 cm^{-1}.

In a similar experiment the crude product was isolated by chromatography on silica gel. Elution with light petroleum gave *trans*-cyclo-octene uncontaminated with *cis*-cyclo-octene (g.l.c.). Further elution with ether (5%) in light petroleum gave phenyl butyl ketone identified by i.r. and by preparation of the 2,4-dinitrophenylhydrazone.

Reaction of the Dioxolan (III) *with Alkyl-lithium Reagents under Other Conditions*.—(i) The dioxolan (1 g) in dry tetrahydrofuran (6 ml) was treated with butyl-lithium (6 ml; 2·4 mol. equiv.) at 0°. The dioxolan had completely disappeared after 15 min to give *trans*-cyclo-octene and a new product (in the ratio 82 : 18; g.l.c.). The new product was identical with authentic n-butylcyclo-octane (g.l.c.). After 1 h the ratio of olefin to n-butylcyclo-octane was 62 : 38. Under the conditions of the preparative procedure (above) a negligible amount of butylcyclo-octane was formed.

(ii) Butyl-lithium (2·8 ml; 1 mol. equiv.) was added to a solution of the dioxolan (1·1 g) in tetrahydrofuran (7 ml) maintained at −80°. After 30 min, the mixture was allowed to reach 20° over 2 h. The product was isolated with light petroleum and the *trans*-cyclo-octene was removed under reduced pressure. The product remaining consisted of unchanged dioxolan and valerophenone (ratio 54 : 36; n.m.r.).

(iii) Methyl-lithium (12 ml; 2 mol. equiv.) was added to a solution of the dioxolan (2·1 g) in tetrahydrofuran (8 ml) at 0°. After 1 h, isolation with ether gave unchanged dioxolan (90%) containing a very small amount of ketone (i.r.).

A similar reaction mixture was heated under reflux for 6 h and gave a product consisting of unchanged dioxolan (76%), acetophenone, and αα-dimethylbenzyl alcohol (24% together) (g.l.c.). The latter two were identical with authentic samples (g.l.c.).

(iv) Phenyl-lithium (15 ml, 2 mol. equiv.; in ether) was added to the dioxolan (1 g) in tetrahydrofuran (5 ml) and the mixture was heated under reflux for 2 h. Isolation with light petroleum and extraction with aqueous silver nitrate gave *trans*-cyclo-octene (0·29 g, 59%). The remaining light petroleum extract contained benzophenone (g.l.c.) and unchanged dioxolan (i.r.).

(v) The dioxolan was treated in separate experiments with the following base systems: (i) potassium t-butoxide in dimethyl sulphoxide (16 h at 20°); (ii) lithium diethylamide in ether or tetrahydrofuran (40 h); (iii) potassium amide in liquid ammonia (2 h). The dioxolan was, in each case, recovered unchanged and no olefin was identified (g.l.c.).

10-*Phenyl*-9,11-cis-*dioxabicyclo*[6.3.0]*undecane* (with K. T. Burgoine).—*cis*-Cyclo-octane-1,2-diol [16] (7·0 g) was converted into the dioxolan by the procedure described for the *trans*-isomer. Distillation gave the product as an oil (7·33 g, 63%), b.p. 158° at 0·5 mmHg, shown by n.m.r. to comprise two diastereoisomers in the ratio 6 : 4. Crystallisation from light petroleum gave the major component, *isomer A* (3·54 g), m.p. 95—96° (Found: C, 77·45; H, 8·75. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·6%), τ (CCl_4) 8—9 (12H, m, ring methylenes), 5·6—6·1 (2H, m, 1-H and 8-H), 4·5 (1H, s, 10-H), and 2·5—2·8 (5H, m, aromatic). The minor component, *isomer B*, was obtained from the filtrate from the crystallisation as an oil (2·6 g), b.p. 127° at 0·1 mmHg (Found: C, 77·95; H, 8·7%).

Reaction of 10-*Phenyl*-9,11-cis-*dioxabicyclo*[6.3.0]*undecane with n-Butyl-lithium* (with K. T. Burgoine).—The dioxolan (isomer A; 1·5 g) in light petroleum (45 ml) was treated with n-butyl-lithium in hexane (2 mol. equiv.) in the usual way. After 12 h at 20° the mixture was added to water and the product was isolated with light petroleum. Evaporation followed by distillation gave an oil (0·2 g),* b.p. 70—72° at 10 mmHg, identical with *cis*-cyclo-octene (i.r. and g.l.c.).

A similar reaction with isomer B gave *cis*-cyclo-octene (0·22 g).*

10-*Phenyl*-9,11-trans-*dioxabicyclo*[6.3.0]*undec*-4-*ene*.—Cyclo-oct-5-ene-*trans*-1,2-diol (8 g) was treated with benzaldehyde (12 g) in the usual manner. Distillation of the product gave the *dioxolan* (11·7 g, 91%), b.p. 149—151°

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* No attempt was made to optimise yields in this experiment.

[15] H. Madden, Part II Thesis, Oxford, 1971; T. Aratani, Y. Nakanisi, and H. Nozaki, *Tetrahedron*, 1970, **26**, 4339.

[16] A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Amer. Chem. Soc.*, 1952, **74**, 5884.

at 0·12 mmHg, as a viscous oil (Found: C, 77·6; H, 8·0. $C_{15}H_{12}O_2$ requires C, 78·2; H, 7·8%).

Reaction of 10-*Phenyl*-9,11-trans-*dioxabicyclo*[6.3.0]*undec*-4-*ene with* n-*Butyl-lithium.*—n-Butyl-lithium in hexane (16 ml; 2 mol. equiv.) was added over 1 h to an ice-cooled solution of the dioxolan (4 g) in tetrahydrofuran (20 ml). After a further 1 h the mixture was added to water and the products were isolated with ether. Valerophenone was identified by i.r. and t.l.c. Chromatography of the product on silica and elution with light petroleum gave the hydrocarbon fraction which was distilled to give a liquid (1·4 g), b.p. 108—110° at 65 mmHg (Found: C, 86·9; H, 13·0. $C_{12}H_{22}$ requires C, 86·8; H, 13·2%). Three hydrocarbons were shown to be present by g.l.c. (Carbowax) in the ratio 15 : 29 : 56. They were separated by preparative g.l.c.

The first component had $\nu_{max.}$ (film) 3050, 1635, and 920 cm^{-1} (CH_2=CH–), τ 9·1—9·2 (6H, m, $2CH_3$), 7·7—9·0 (12H, m), 7·45 (1H, t, allylic CH), 5·0—5·15 (2H, dd, =CH_2), and 4·24 (1H, q), *m/e* 166 (M^+) and 81 (base peak). The compound is considered to be 1-butyl-2-methyl-3-vinylcyclopentane or 1-(1-methylpentyl)-2-vinylcyclobutane.

The second component showed no olefinic or allylic protons in the n.m.r. spectrum and the i.r. spectrum also indicated a saturated bicyclic compound; *m/e* 166 (M^+) and 109 (base peak). The compound is considered to be 2-n-butylbicyclo[4.2.0]octane or 2-n-butylbicyclo[3.3.0]octane.

The third, major component, τ 9·12 (3H, t, Me), 8·3—8·9 (11H, m), 7·8 (4H, m, allylic protons), and 4·4 (2H, m, olefinic protons), *m/e* 166 (M^+) and 67 (base peak), is considered to be 5-n-butylcyclo-octene. All three products could have been derived *via* initial addition of n-butyl-lithium to the strained double bond of *cis,trans*-cyclo-octa-1,5-diene.

Attempts to isolate *cis,trans*-cyclo-octa-1,5-diene by carrying out the reactions using only 1 mol. equiv. of butyl-lithium, by variation of solvent and temperature or by addition of *NNN'N'*-tetramethylethylenediamine were unsuccessful. The use of methyl-lithium or phenyl-lithium (in ether) as base was equally unfruitful.

Reaction of 10-*Phenyl*-9,11-trans-*dioxabicyclo*[6.3.0]*undec*-4-*ene with Neopentyl-lithium in Ether.*—Neopentyl-lithium in ether (40 ml of an 0·7M-solution; 0·028 mol; prepared [17] from neopentyl bromide and lithium in ether at –10°) was added, under nitrogen, to a solution of the dioxolan in ether. After 15 h at 20°, distilled water was added and the product, isolated with ether, was shown to comprise two major components by t.l.c. The compound corresponding to the less mobile component on t.l.c. was isolated as crystals (1·2 g) by cooling a solution of the crude product in the minimum amount of light petroleum to –5°. Recrystallisation from light petroleum gave 10-*benzoyl*-10-*phenyl*-9,11-trans-*dioxabicyclo*[6.3.0]*undec*-4-*ene*, m.p. 87—90° (Found: C, 78·7; H, 6·5. $C_{22}H_{22}O_3$ requires C, 79·0; H, 6·65%), τ 7·4—9·0 (8H, m, –CH_2–), 5·6—6·2 (2H, m, 1-H, 8-H), 4·1—4·7 (2H, m, 4-H, 5-H), 2·3—2·9 (8H, m, aromatic), and 1·8—2·1 (2H, m, *ortho*-protons of PhCO). Distillation of the mother liquors from the crystallisation gave neopentyl phenyl ketone (0·25 g), identical with an authentic sample (i.r. and n.m.r.), corresponding to the second product detected by t.l.c.

The molar ratio of neopentyl ketone to the benzil monodioxolan could be estimated from the n.m.r. spectrum of the crude reaction mixture to be 35 : 65.

Reaction of 2-*Phenyl*-1,3-*dioxolan with Neopentyl-lithium.*—2-Phenyl-1,3-dioxolan (2·1 g, 0·014 mol) was treated with neopentyl-lithium (0·028 mol) in ether as in the previous experiment. Separation of the product by preparative t.l.c. gave neopentyl phenyl ketone and 2-benzoyl-2-phenyl-1,3-dioxolan, identified by comparison (i.r., n.m.r., and t.l.c.) with an authentic sample.[18] The molar ratio of neopentyl phenyl ketone to the benzil monodioxolan was estimated by n.m.r. to be 92 : 8.

Reaction of 10-*Phenyl*-9,11-trans-*dioxabicyclo*[6.3.0]*undecane with Neopentyl-lithium.*—The dioxolan (3·2 g, 0·014 mol) was treated with neopentyl-lithium (0·028 mol) in ether as described above. Distillation of the crude product gave neopentyl phenyl ketone (1·3 g). Chromatography of the residue on silica gel (elution with ether–light petroleum, 1 : 4) gave 10-benzoyl-10-phenyl-9,11-*trans*-dioxabicyclo[6.3.0]undecane, identified (i.r., n.m.r., dinitrophenylhydrazone) by comparison with an authentic specimen, prepared as described below.

The molar ratio of neopentyl phenyl ketone to the benzil monodioxolan in this case was estimated by n.m.r. to be 30 : 70.

10-*Benzoyl*-10-*phenyl*-9,11-trans-*dioxabicyclo*[6.3.0]*undecane.*—Benzoin (5·3 g), cyclo-octane-*trans*-1,2-diol (3·6 g) and toluene-*p*-sulphonic acid (100 mg) were heated under reflux (N_2) in a Dean and Stark apparatus for 48 h. After cooling, addition of K_2CO_3, filtration, and evaporation the product was chromatographed on silica gel. Elution with ether–light petroleum (1 : 4) followed by crystallisation from ether–light petroleum gave the *benzoin dioxolan* of *cyclo-octane*-1,2-*diol* (4·5 g, 53%), m.p. 76—86° (Found: C, 78·4; H, 7·8. $C_{22}H_{26}O_3$ requires C, 78·1; H, 7·7%). The broad m.p. and presence of two doublets at τ 7·15 and 7·3 (exchangeable by D_2O) in the n.m.r. spectrum indicated the presence of both diastereoisomers.

The benzoin dioxolan (0·54 g) in pyridine (5 ml) was added to chromium trioxide (0·5 g) in pyridine (5 ml). After 15 h at 20° water was added and the product was isolated with ether in the usual way. Chromatography on silica gel (elution with ether–light petroleum, 1 : 9) gave the benzil monodioxolan, τ 8·0—9·2 (10H, m, –CH_2–), 7·4—8·0 (2H, m), 5·75—6·05 (2H, m, O·CH), 2·5—2·8 (8H, m, aromatic), and 1·8—2·0 (2H, m, *ortho*-aromatic). The compound was characterised as its 2,4-*dinitrophenylhydrazone*, m.p. 71—73° (Found: C, 65·4; H, 5·45; N, 10·65. $C_{28}H_{26}N_4O_6$ requires C, 65·35; H, 5·1; N, 10·9%).

Reaction of the Benzylidene Derivative of meso-*Hydrobenzoin with n-Butyl-lithium.*—The dioxolan [19] (2 g; mixture of epimers at C-2) in tetrahydrofuran (15 ml) was treated with n-butyl-lithium in hexane (9 ml, 2·1 mol. equiv.) at 20°. After stirring for 2 h the product was isolated in the usual way and chromatographed on silica gel. The following fractions were obtained: (i) 0·99 g, eluted with light petroleum–benzene (35 : 65), m.p. 55—56° (from light petroleum), identified as deoxybenzoin (m.p. 60°) by comparison with an authentic specimen; (ii) 400 mg, eluted with light petroleum–benzene (3 : 6), shown to be 1-phenylpentanol by comparison (i.r., n.m.r.) with material synthesised by addition of n-butyl-lithium to benzaldehyde; (iii) 450 mg, eluted with light petroleum–benzene (2 : 8), an impure specimen of 1-phenylpentanol containing several minor contaminants.

Reaction of the Benzylidene Derivative of (±)-*Hydro*-

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[17] H. D. Zook, J. March, and D. F. Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 1617.

[18] R. K. Summerbell and D. R. Berger, *J. Amer. Chem. Soc.*, 1959, **81**, 633.

benzoin with n-Butyl-lithium.—The (±)-dioxolan (0·5 g)[19] was treated in tetrahydrofuran (15 ml) with n-butyl-lithium (2·5 ml, 2·1 mol. equiv.) for 1·5 h at 20°, and the product (740 mg) was isolated in the usual way. A portion (400 mg) was separated into its components by preparative t.l.c. giving: (i) 11·5 mg, identified as *trans*-stilbene by i.r. and u.v.; (ii) 54 mg, unchanged starting material; (iii) 92·4 mg, identical with deoxybenzoin (i.r. and t.l.c.); and (iv) 75·2 mg, shown to be 1-phenylpentanol by comparison with authentic material.

Reaction of Benzaldehyde Diethyl Acetal with n-Butyl-Lithium.—The product from benzaldehyde diethyl acetal (1 g) and n-butyl-lithium solution (2 mol. equiv.) in tetrahydrofuran (20 ml) (1·2 g) was isolated in the usual way and chromatographed on silica gel giving: (i) 70 mg, eluted with light petroleum–benzene (2 : 3), an impure sample of propiophenone; (ii) 34 mg, eluted with light petroleum–benzene (2 : 3), identified as 1-ethyl-1-phenylpentanol by comparison with a sample prepared from propiophenone and n-butyl-lithium; (iii) 127 mg, eluted with light petroleum–benzene (2 : 3), benzaldehyde; and (iv) 566 mg, 1-phenylpentanol identified by comparison (i.r. and t.l.c.) with an authentic sample.

*Reaction of 2-Phenyl-*1,3-*dioxan with n-Butyl-lithium.*—The product (1·7 g) from 2-phenyl-1,3-dioxan (1·3 g) and n-butyl-lithium (2·2 mol. equiv.) in tetrahydrofuran (20 ml) (2 h) was chromatographed on silica gel. Besides minor fractions containing unidentified products, two main fractions were collected: (i) 145 mg, eluted with light petroleum–ether (85 : 15), 1-phenylpentanol, identical with an authentic specimen; and (ii) 568 mg, eluted with light petroleum–ether (4 : 6), 4-*phenyloctane*-1,4-*diol*, m.p. 70·5—72° (Found: C, 75·3; H, 9·9. $C_{14}H_{22}O_2$ requires C, 75·6; H, 9·95%), τ (CCl_4) 8·0—9·4 (13H, m, CH_3 and $-CH_2-$), 6·52 (2H, t, *J* 5 Hz, $CH_2{\cdot}OH$), 6·13 (2H, s, OH), and 2·75 (s, 5H, aromatic), τ [$(CD_3)_2SO$] 5·45 (1H, s, tert. OH) and 5·73 (1H, t, *J* 5 Hz, $CH_2{\cdot}OH$).

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[3/832 *Received*, 17*th April*, 1973]

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[19] J. Kovář, J. Šteffková, and J. Jarý, *Coll. Czech. Chem. Comm.*, 1965, **30**, 2793.