

Heterocyclic Polyfluoro-compounds. Part 33.¹ Competing 1,2- and 1,4-Photochemical Addition of Hexafluorobiacyetyl to 1,2-Difluoroethylene

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Photochemical addition of hexafluorobiacyetyl ($\lambda > 300$ nm) to either *cis*- or *trans*-1,2-difluoroethylene yields mainly *cis*-2,3-difluoro-5,6-bis(trifluoromethyl)-2,3-dihydro-*p*-dioxin (53–57%), and the corresponding *trans*-dioxin (12%) by 1,4-addition, together with *r*-2-trifluoromethyl-2-trifluoroacetyl-*t*-3,*t*-4-difluoro-oxetan (7–8%) and the corresponding *t*-3,*c*-4- (7–8%) and *c*-3,*t*-4-oxetans (6–7%) by 1,2-addition.

The *cis*-dioxin yields both *cis*- and *trans*-1,2-difluoroethylene upon pyrolysis, and with aluminium trichloride undergoes isomerisation to the *trans*-dioxin, and non-stereospecific exchange of one or both ring fluorines by chlorine atoms.

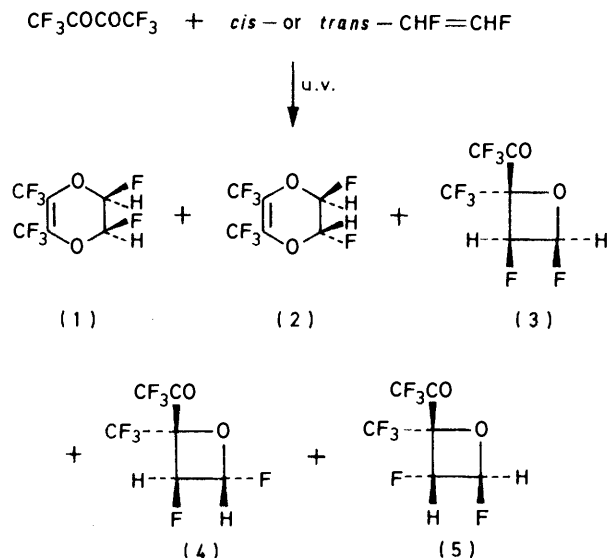
FLUOROKETONES undergo ready photochemical addition to fluoro-olefins to give oxetans,² and the reaction appears to involve the triplet state of the ketone.³ Aromatic α -diketones and *o*-quinones undergo photochemical addition to alkenes to form dihydro-1,4-dioxins or keto-oxetans,⁴ but aliphatic diketones have been little studied, although biacyetyl has been reported to form oxetans with ethyl vinyl ether, furan, and indene.⁵ We have studied the photochemical addition of hexafluorobiacyetyl to 1,2-difluoroethylene. This olefin is a particularly convenient substrate in this type of reaction, since pure *cis*- and *trans*-isomers may readily be obtained by distillation, and isomeric products are usually amenable to separation.

Ultraviolet irradiation in Pyrex of gaseous mixtures of hexafluorobiacyetyl with either *cis*- or *trans*-1,2-difluoroethylene gave essentially the same mixture of five 1 : 1-adducts, comprising the *cis*- and *trans*-dihydro-*p*-dioxins (1) and (2), the *cis*-oxetan (3), and two *trans*-oxetans (4) and (5), in the ratio 8.8 : 2.0 : 1.2 : 1.2 : 1.0, respectively, from the *cis*-olefin, in high overall yield (85% from the *cis*-olefin and 92% from the *trans*-olefin) (see Scheme 1). There is thus no memory of the stereochemistry of the original olefin, and an intermediate, or intermediates, with a life-time long compared with the time necessary for rotation about C–C single bonds is implicated. The reactions, however, were run to high conversion, and are complicated by isomerisation of the *trans*- to the *cis*-olefin. The photostability of the oxetans (3)–(5) was not checked, so their conversion into the dihydro-dioxins (1) and (2), transparent at $\lambda > 300$ nm, cannot be ruled out. The results are consistent with reaction *via* a triplet state of the ketone. The absence of the fourth possible oxetan with ring substituents CF₃, F, and F *cis* to each other is noteworthy, and steric hindrance to cyclisation may be involved. A similar absence of one possible oxetan is observed in the reactions of perfluoroaldehydes with 1,2-difluoroethylene.⁶

Dihydrodioxins can only arise from the *s-cis* form of the diketone, but oxetans can also arise from the *s-trans* form (Scheme 2), and an appreciable barrier to rotation about the C–C bond of the ketone in the excited

state is expected. Phenanthraquinone, of necessity *cis*-, gives only dihydrodioxins with olefins,⁷ and if the analogy is valid here, it suggests that the oxetans are obtained largely from the *s-trans* configuration of hexafluorobiacyetyl.

As a possible chemical test of the stereochemistry of the dihydro-*p*-dioxins, the major isomer, assigned the *cis*-configuration on spectroscopic grounds, was pyrolysed. Contrary to expectations, the *retro*-Diels-Alder cleavage gave both *cis*- and *trans*-1,2-difluoroethylene, yet on its

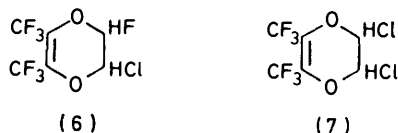


SCHEME 1

own under comparable conditions (610 °C/4–5 mmHg), the *cis*-olefin was unchanged.

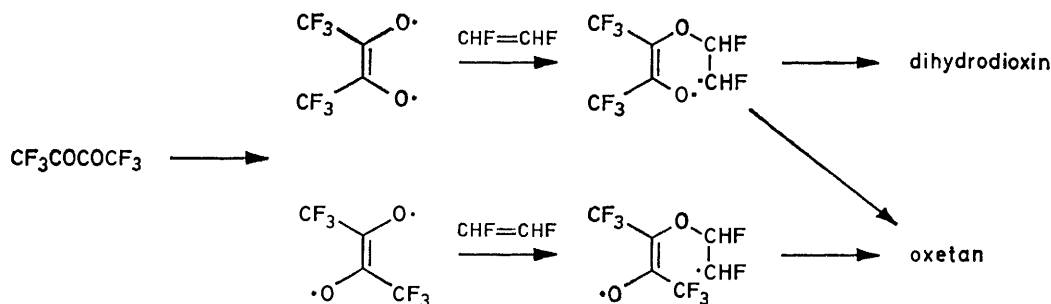
Polyfluoroethers undergo exchange of fluorine atoms next to the oxygen for chlorine with aluminium chloride.⁸ The *cis*-dihydrodioxin (1), when treated with aluminium trichloride at 35 °C for 4 days, gave recovered (1) (6%), the *trans*-dihydrodioxin (2) (47%), and products of exchange of chlorine for fluorine which were not examined in great detail, but which g.l.c.–mass spectrometry indicated to be a mixture mainly of 2-chloro-3-fluoro- (6) (18%), and 2,3-dichloro-5,6-bis(tri-

fluoromethyl)-2,3-dihydro-*p*-dioxin (7) (24%), together with unidentified material. The formation of the *trans*-dihydrodioxin (2) as the major product suggests



that this is the more stable isomer, and hence that the preferred formation of the *cis*-isomer in the photochemical reaction is a result of kinetic factors in the final cyclisation step. Similar Lewis acid-catalysed isomerisations have been observed before, and a carbenium ion mechanism suggested.^{9,10}

mmol) of hexafluoroethane (45 mg, 0.33 mmol), trifluoromethane (21 mg, 0.30 mmol) and unidentified material which condensed at -196°C , and a liquid fraction (4.042 g) which was separated by g.l.c. (2 m, 20% MS 550 silicone oil on Chromosorb at 36°C) to give *cis*-2,3-difluoro-5,6-bis(trifluoromethyl)-2,3-dihydro-*p*-dioxin (1) (2.201 g, 8.53 mmol, 53%) (Found: C, 28.1; H, 1.1; F, 59.3. $\text{C}_6\text{H}_2\text{F}_8\text{O}_2$ requires C, 27.9; H, 0.8; F, 58.9%), b.p. (Siwoloboff) 119°C at 761 mmHg; ν_{max} $1\ 697\ \text{cm}^{-1}$ (C=C str); *trans*-2,3-difluoro-5,6-bis(trifluoromethyl)-2,3-dihydro-*p*-dioxin (2) (0.498 g, 1.93 mmol, 12%) (Found: C, 28.0; H, 0.8; F, 59.1. $\text{C}_6\text{H}_2\text{F}_8\text{O}_2$ requires C, 27.9; H, 0.8; F, 58.9%); ν_{max} $1\ 695\ \text{cm}^{-1}$ (C=C str), *r*-2-trifluoromethyl-2-trifluoroacetyl-*t*-3,*t*-4-difluoro-oxetan (3) (0.291 g, 1.13 mmol, 7%) (Found: C, 27.7; H, 0.8; F, 58.6. $\text{C}_6\text{H}_2\text{F}_8\text{O}_2$ requires C, 27.9; H, 0.8; F, 58.9%); ν_{max} $1\ 781\ \text{cm}^{-1}$ (C=O str), and an inseparable 55:45 mixture (by n.m.r.) of *r*-2-trifluoro-



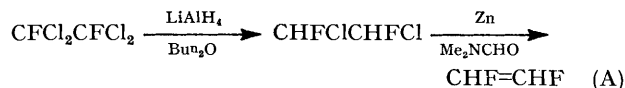
SCHEME 2

Photochemical additions of fluoro-olefins to hexafluorobiacyl thus offer a route to the rather inaccessible polyfluoro-dihydro-*p*-dioxins.

EXPERIMENTAL

Volatile materials were manipulated in a Pyrex vacuum system. Products were identified by elemental analysis, i.r. spectroscopy (Perkin-Elmer model 257), n.m.r. spectroscopy [Varian HA 100 instrument operating at 100.0 MHz for ^1H nuclei (external tetramethylsilane reference) and 94.1 Hz for ^{19}F nuclei (external trifluoroacetic acid reference)], mass spectrometry (A.E.I. MS902 spectrometer, coupled to a g.l.c. instrument), and g.l.c. (Pye 104 for analytical and Perkin-Elmer F21 for preparative separations).

Hexafluorobiacyl was prepared by the oxidation of 2,3-dichlorohexafluorobut-2-ene with chromium trioxide in fuming sulphuric acid,¹¹ and 1,2-difluoroethylene, prepared by route (A)^{12,13} was distilled using a semi-



automatic low-temperature still to give the *trans*- (>99.5% pure by g.l.c.) and *cis*-isomers (pure by g.l.c.).

Photochemical Addition of Hexafluorobiacyl to 1,2-Difluoroethylene.—(a) *With cis*-1,2-difluoroethylene. Hexafluorobiacyl (3.149 g, 16.24 mmol) and *cis*-1,2-difluoroethylene (1.030 g, 16.10 mmol), sealed in a Pyrex ampoule (300 ml) and irradiated for 45 h with light from a Hanovia UVS 500 medium-pressure mercury lamp at a distance of 25 cm, gave carbon monoxide (2.45 mmol), a mixture (1.00

methyl-2-trifluoroacetyl-*t*-3,*c*-4-difluoro-oxetan (4) and *r*-2-trifluoromethyl-2-trifluoroacetyl-*c*-3,*t*-4-difluoro-oxetan (5) (0.539 g, 2.09 mmol, 13%) (Found: C, 27.6; H, 0.8; F, 58.7. Calc. for $\text{C}_6\text{H}_2\text{F}_8\text{O}_2$: C, 27.9; H, 0.8; F, 58.9%), together with traces of minor unidentified components.

(b) *With trans*-1,2-difluoroethylene. In a similar manner, hexafluorobiacyl (2.231 g, 11.50 mmol) and *trans*-1,2-difluoroethylene (0.730 g, 11.41 mmol) were irradiated for 48 h to give carbon monoxide (0.98 mmol), a mixture of hexafluoroethane (57 mg, 0.41 mmol) and trifluoromethane (25 mg, 0.36 mmol), *cis*-1,2-difluoroethylene (22 mg, 0.34 mmol, 3%), and a liquid fraction (2.828 g), separated by g.l.c. to give dioxin (1) (1.677 g, 6.50 mmol, 57%), dioxin (2) (0.353 g, 1.37 mmol, 12%), oxetan (3) (0.235 g, 0.91 mmol, 8%), and a 55:45 mixture of oxetans (4) and (5) (0.441 g, 1.71 mmol, 15%).

Reactions of cis-2,3-Difluoro-5,6-bis(trifluoromethyl)-2,3-dihydro-*p*-dioxin.—(a) *Pyrolysis.* The title dioxin (294 mg, 1.14 mmol), passed at 4–5 mmHg pressure through a silica tube (62 cm \times 0.7 cm i.d., heated length 51 cm) heated to 610°C (contact time 0.0025 s) gave after fractionation *in vacuo*, hexafluoroethane (48 mg, 0.35 mmol, 31%), *trans*-1,2-difluoroethylene (24 mg, 0.38 mmol, 34%), *cis*-1,2-difluoroethylene (33 mg, 0.52 mmol, 46%), hexafluorobiacyl (41 mg, 0.21 mmol, 18%), a trace of recovered *cis*-dioxin, and unidentified material.

(b) *With aluminium trichloride.* The title dioxin (0.735 g, 2.85 mmol) and freshly sublimed aluminium trichloride (0.460 g, 3.46 mmol), sealed in a Pyrex tube (50 ml) and shaken at 35°C for 4 d, gave a mixture (0.757 g) which was shown by n.m.r. spectroscopy and g.l.c.-coupled (2 m MS 550 at 30°C) mass spectrometry to comprise in order of elution the *trans*-dioxin (2) (0.310 g, 1.26 mmol, 47%),

the *cis*-dioxin (1) (44 mg, 0.17 mmol, 6% recovery), *trans*-2-chloro-3-fluoro-5,6-bis(trifluoromethyl)-2,3-dihydro-*p*-dioxin (0.118 g, 0.43 mmol, 16%), *cis*-2-chloro-3-fluoro-5,6-bis(trifluoromethyl)-2,3-dihydro-*p*-dioxin (14 mg, 0.05 mmol, 2%), *trans*-2,3-dichloro-5,6-bis(trifluoromethyl)-2,3-dihydro-*p*-dioxin (0.125 g, 0.43 mmol, 16%), *cis*-2,3-dichloro-5,6-bis(trifluoromethyl)-2,3-dihydro-*p*-dioxin (61 mg, 0.21 mmol, 8%), and unidentified material (estimated 85 mg).

Structure of the Products.—The dioxin structure of two of the photo-adducts from hexafluorobiacyl and 1,2-difluoroethylene follows unequivocally from their ^1H and ^{19}F n.m.r. spectra, where the CHFCHF nuclei comprise an AA'XX'-system. Analysis yielded the following parameters:

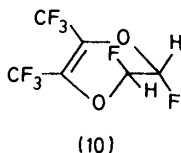
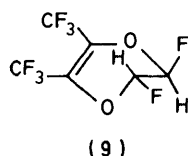
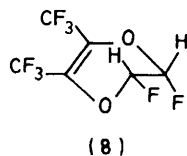
cis-dioxin (1); δ_{F} 10.8 (CF_3) and -74.8 p.p.m. (CHF), and δ_{H} 5.42 p.p.m.;

$$\left. \begin{array}{l} J_{\text{AX}} \\ J_{\text{AX}'} \end{array} \right\} + 51.8 \left({}^2J_{\text{HF}} \right), \left\{ \begin{array}{l} J_{\text{AA}'} \\ J_{\text{XX}'} \end{array} \right\} \text{ ca. } 0 \text{ Hz } \left({}^3J_{\text{HF}} \right)$$

trans-dioxin (2); δ_{F} 10.5 (CF_3) and -62.8 p.p.m. (CHF), and δ_{H} 5.62 p.p.m.;

$$\left. \begin{array}{l} J_{\text{AX}} \\ J_{\text{AX}'} \end{array} \right\} + 50.4 \left({}^2J_{\text{HF}} \right), \left\{ \begin{array}{l} J_{\text{AA}'} \\ J_{\text{XX}'} \end{array} \right\} \text{ ca. } 0 \text{ Hz } \left({}^3J_{\text{HF}} \right)$$

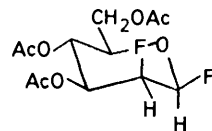
${}^2J_{\text{HF}}$ is presumed to be positive. This assignment is supported by g.l.c., where the presumably less polar *trans*-isomer is eluted first, and by the easy aluminium chloride-induced isomerisation of the *cis*- to the *trans*-isomer. The alternative *trans*- to *cis*-isomerisation is usually very difficult in related fluorinated ring systems.¹⁴ The *cis*-isomer may adopt two equivalent half-chair conformations (8), which



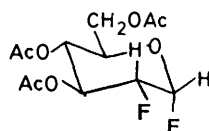
must be in rapid equilibrium for equivalent ring fluorines, and the *trans*-isomer may adopt either the conformation with equatorial fluorines (9) or with axial fluorines (10). In polyfluoro-cyclohexanes and -1,4-dioxans, axial fluorines absorb to low field of equatorial fluorines with similar neighbouring substituents.¹⁵ If the empirical substituent parameters found for 1,4-dioxans¹⁵ are applied here, they predict that the ring-fluorines of (9) and (10) should absorb 11.5 and 9.5 p.p.m. to low-field of the *cis*-isomer (8), supporting the assignment. The ${}^3J_{\text{HF}}$ values provide further support. Vicinal HF-coupling constants follow a Karplus-type relation,¹⁶ modified by other substituents on the CH·CF fragment,¹⁷ and a maximum value is expected if the nuclei are diaxial, as in (8). The carbohydrate derivatives (11) to (14) offer a relevant comparison here,¹⁸ and the ${}^3J_{\text{HF}}$ values (Hz) are shown where *e.g.*, J_{ae} refers to the coupling of an axial proton with an equatorial fluorine nucleus.

Electronegative substituents such as O or F on a CH·CF fragment cause a diminution in 3J , and this is most pro-

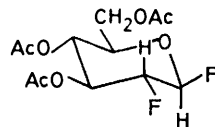
nounced when they are attached to the CH end of the fragment.¹⁷ Compared with these carbohydrate derivatives, therefore, the two dioxins should show values somewhat less than the smaller of the two values for each type of coupling.



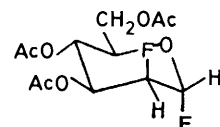
$$\begin{array}{l} (11) \ J_{ee} \ 8.0 \\ \quad \ J_{aa} \ 13.5 \end{array}$$



$$\begin{array}{l} (12) \ J_{ee} \ 0 \\ \quad \ J_{aa} \ 23.8 \end{array}$$



$$\begin{array}{l} (13) \ J_{ae} \ 11.2 \ (\text{OCFCH}) \\ \quad \ J_{ae} \ 4.0 \end{array}$$



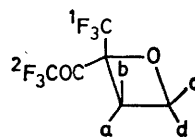
$$\begin{array}{l} (14) \ J_{ea} \ 0 \ (\text{OCHCF}) \\ \quad \ J_{ea} \ 4.0 \end{array}$$

An estimate can then be made of the maximum to be expected for (8) [$\frac{1}{2}(J_{aa} + J_{ee}) = \frac{1}{2}(13.5 + 0) = 6.8$ Hz], (9) ($J_{ae} = 4.0$ Hz) or (10) ($J_{ea} = 0$ Hz). The experimental values of 6.2 Hz for the *cis*-isomer and 2.4 Hz for the *trans*-isomer are close to these predictions, further supporting the assignment.

The structure of the three oxetans obtained from the addition of 1,2-difluoroethylene to hexafluorobiacyl

TABLE 1

Chemical shifts of 2-trifluoromethyl-2-trifluoroacetyl-3,4-difluoro-oxetans



		Chemical shifts (p.p.m.)					
		δ_{CF_3}	$\delta_{\text{CF}_3\text{CO}}$	δ_a	δ_b	δ_c	δ_d
a = d = F, b = c = H		-0.4	0.9	-127.4	5.29	5.86	-55.0
a = c = F, b = d = H		-0.5	0.0	-117.7	5.10	-41.9	5.80
a = c = H, b = d = F		3.6	1.3	5.10	-117.7	5.88	-37.9

follows largely from their n.m.r. spectra. They show C=O str in their i.r. spectra and n.m.r. absorptions characteristic of the C·CHFCHF·O grouping. Partial spectral data are shown in Tables 1 and 2.

One isomer (3), which was the first eluted on g.l.c., had ring fluorine absorptions at -127.4 and -55.0 , whereas the

TABLE 2

Magnitudes of coupling constants (Hz) of 2-trifluoromethyl-2-trifluoroacetyl-3,4-difluoro-oxetans

Compound	J_{ab}	J_{ac}	J_{ad}	J_{bc}	J_{bd}	J_{cd}	others
(3)	50.0	3.0	?	3.0	7.0	64.0	$J_{2a} = J_{2d} = 4$
(4)	50.0	?	7.5	8.0	2.0	65.0	$J_{1a} = J_{1c} = 2.4, J_{2a} = 4.5$
(5)	50.0	2.0	8.0	7.5	?	65.0	$J_{1b} = 13.5, J_{1d} = 3.0$

remaining two isomers had absorptions at -117 and *ca.* -40 p.p.m.; the low-field shifts in the latter suggest that both fluorines have a proton *cis* to them and that they are *trans*-isomers. For example, in *cis*-1,1-dichloro-2,3-difluoro-

cyclopropane, the fluorine nuclei absorb at 145 p.p.m. to high field of external trifluoroacetic acid, and at 130 p.p.m. in the *trans*-isomer.¹⁹ In the 3,4-difluoro-oxetans obtained from 1,2-difluoroethylene and the perfluoroketones $R_F R_{F'}-CO$ ($R_F = CF_3$, $R_{F'} = CF_3$ or CF_2Cl ; $R_F = CF_2Cl$, $R_{F'} = CF_2Cl$ or $CFCl_2$), the *trans*-isomers show ring fluorine absorptions in the ranges -117.3 to -122.6 and -38.3 to -38.9 p.p.m., and the *cis*-isomers, the ranges -129.8 to -133.7 and -55.0 to -61.5 p.p.m.⁶ These assignments were confirmed by the magnitudes of $^3J_{HH}$ ($J_{cis} = 3$, $J_{trans} = 2$ Hz), where coupling of *cis* protons is larger than coupling of *trans* protons in oxetans,²⁰ and of $^3J_{HF}$ ($J_{cis} = 7.5-8.0$, $J_{trans} = 7.0$ and 3.0 Hz, where the last value is associated with the presence of oxygen attached to the CH end of the CH-CF fragment). Individual assignment of the two *trans*-isomers is more difficult, and the assignment of the CF_3 and CF_3CO group absorptions is not obvious. However the long-range coupling constant of substantial magnitude (13.5 Hz) in compound (5) is characteristic of a CF_3 group *cis*- to a fluorine nucleus at C-3, in the oxetans from perfluoroketones, and this completes the assignment of this isomer. In isomer (3), neither CF_3 -absorption shows such a large long-range coupling, whence the CF_3 group and fluorine nucleus at C-3 are *trans*-, and one of the CF_3 -absorptions shows long-range coupling constants of 4 Hz, which are not found in oxetans with only fluoroalkyl group substituents, suggesting that this absorption is due to a CF_3CO group. A 4.5 Hz coupling is observed for one of the CF_3 -absorptions in isomer (4), suggesting that this too is a CF_3CO absorption, and the other CF_3 -absorption shows small long-range coupling like that in other analogous oxetans obtained from chlorofluoroacetones.

The mass spectra of the *cis*-oxetan (3) and mixture of *trans*-oxetans (4) and (5) were very similar. They showed no molecular ion, weak ions corresponding to loss of CF_3 and CF_3CO fragments, base peaks corresponding to CF_3^+ , and ions of moderate intensity (>5% of the base peak) corresponding to the fragments: $CF_3COCCHF^+$, CF_3CCHF^+ , CF_3CO^+ , $C_3HF_2O^+$, $C_3H_2FO^+$, $CHFCHF^+$, CHF_2^+ , $C_2H_2F^+$, C_2HF^+ , and CF^+ . In contrast, the dioxins (1) and (2), and particularly the *cis*-isomer, showed molecular ions, and ions corresponding to loss of F, of appreciable intensity, and base peaks for $CHFCHF^+$, corresponding to a *retro*-

Diels-Alder cleavage, although the CF_3^+ ions were prominent. Also noteworthy were ions corresponding to C_4F_6 , and fragments derived therefrom.

The structures of the chlorofluoro- and dichloro-dioxins rest largely upon their g.l.c. retention times (*trans*-isomers eluted first) and mass spectra. They all show molecular ions, base peaks corresponding to CF_3^+ , prominent ions $CHClCHX^+$ ($X = Cl$ or F), and the expected resemblances to the spectra of the difluorodioxins.

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