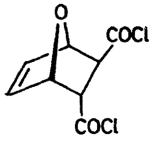
Diels–Alder Reaction of Furan and Fumaryl Chloride: *X*-Ray Crystal and Molecular Structure of an Oxabicyclo[2.2.1]heptane Derivative. Synthesis of Reduction Products of *cis*-Maneonene-A

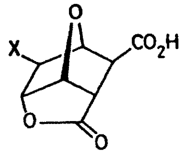
By CLIVE L. D. JENNINGS-WHITE, ANDREW B. HOLMES,* and PAUL R. RAITHBY*
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary The addition of fumaryl chloride to furan, followed by hydrolysis and bromolactonisation of the adduct, leads to the bromo-lactone acid (**2a**) which serves as a precursor for the synthesis of the reduction products (**5a**), (**5b**), and (**6a**) of *cis*-maneonene-A and of the tosylate (**6b**) whose *X*-ray crystal structure has been determined.

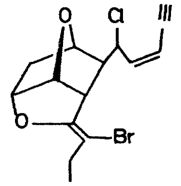
THE cycloaddition[1] of fumaric acid or diethyl fumarate to furan at room temperature is preparatively unsatisfactory since yields are modest unless ultrahigh pressures are used.[2] We now report that the more reactive fumaryl chloride[3] reacts quantitatively with furan at room temperature over 24 h (as shown by ^{1}H n.m.r. spectroscopy of the reaction mixture) to give the adduct (**1**) which was without isolation rapidly hydrolysed to the disodium salt and then converted in 75% yield into the known[4] bromo-lactone acid (**2a**) by sequential treatment with base and then bromine at 0 °C.



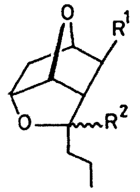
(1)



(2)
a; X = Br
b; X = H

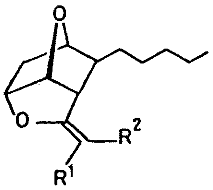


(3)



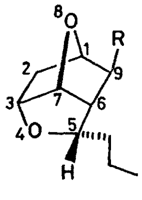
(4)

a; $R^1 = CO_2H, R^2 = OH$
b; $R^1 = CO_2Me, R^2 = OMe$
c; $R^1 = CH_2OH, R^2 = OMe$
d; $R^1 = CH_2OTs, R^2 = OMe$
e; $R^1 = C_5H_{11}, R^2 = OMe$



(5)

a; $R^1 = Et, R^2 = H$
b; $R^1 = H, R^2 = Et$



(6)

a; $R = C_5H_{11}$
b; $R = CH_2OTs$
c; $R = CH_2OH$

$Ts = MeC_6H_4SO_2$-*p*

The utility of the bromo-lactone acid (**2a**) in synthesis is illustrated in the preparation of the reduction products (**5a**), (**5b**), and (**6a**) derived from the naturally occurring *cis*-maneonene-A (**3**).[5] Reduction of the bromo-compound (**2a**) with $Bu^n{}_3SnH$ gave (86%) the lactone acid (**2b**),† m.p. 176—177 °C, δ [$(CD_3)_2SO$–$CDCl_3$] 5·36 (H-7, t, *J* 5 and 5 Hz) and 4·98 (H-1, d, *J* 4 Hz), which with propyl magnesium bromide in the presence of tetramethylethylenediamine (TMEDA) gave (76%) the hemiacetal acid (**4a**),† m.p. 126—128 °C. Simultaneous esterification and acetalisation gave (85%) the ester acetal (**4b**), which was reduced (57%) with lithium borohydride to the alcohol (**4c**)†. Tosylation of the alcohol gave (40%) the tosylate (**4d**)† which was coupled[6] with Bu_2CuLi to give (64%) the acetal (**4e**),† which gave (71%) a 5 : 2 mixture of the enol ethers (**5a**) and (**5b**) upon pyrolysis in refluxing *NN*-dimethylacetamide. These were separated and shown to exhibit identical spectroscopic data with those of authentic samples.[5]

Borane–tetrahydrofuran complex reduced both the carboxy and hemiacetal groups of compound (**4a**) to give (57%) the hydroxyether (**6c**)† whose structure was confirmed by an *X*-ray structure determination of the tosylate (**6b**)† which formed transparent platelets, m.p. 71–73 °C, upon recrystallisation from cyclohexane. This tosylate was coupled (64%) with Bu_2CuLi to give the ether (**6a**) which was also obtained by catalytic reduction of both (**5a**) and (**5b**).[5] The structures of these compounds have therefore been fully confirmed by synthesis.

Crystal data: (**6b**): $C_{18}H_{24}O_5S$, $M = 352{\cdot}134$, triclinic, $a = 5{\cdot}859(2)$, $b = 12{\cdot}761(4)$, $c = 13{\cdot}269(4)$ Å, $\alpha = 107{\cdot}01(2)$, $\beta = 108{\cdot}11(2)$, $\gamma = 91{\cdot}95(2)°$, $U = 893{\cdot}1$ Å, $Z = 2$, $D_c = 1{\cdot}318$ g cm^{-3}, μ(Cu-K_α) = 17·09 cm^{-1}, $F(000) = 380{\cdot}00$, space group $P\bar{1}$. 3532 intensities ($2\theta_{max} = 125{\cdot}0°$) were recorded on a Syntex $P2_1$ four-circle diffractometer, with graphite-monochromated Cu-K_α radiation. The data were corrected for L_p factors and averaged to give 2641 observed intensities [$F > 4\sigma(F)$]. The structure was solved by multisolution Σ_2 sign expansion and refined by blocked-cascade least-squares. The C, O, and S atoms were refined with anisotropic thermal parameters, while the aromatic and remaining hydrogen atoms were refined with common isotropic temperature factors, respectively. The hydrogen atoms were constrained to lie in geometrically idealised positions 1·08 Å from their respective carbon atoms. The methyl groups were refined as rigid bodies. The final

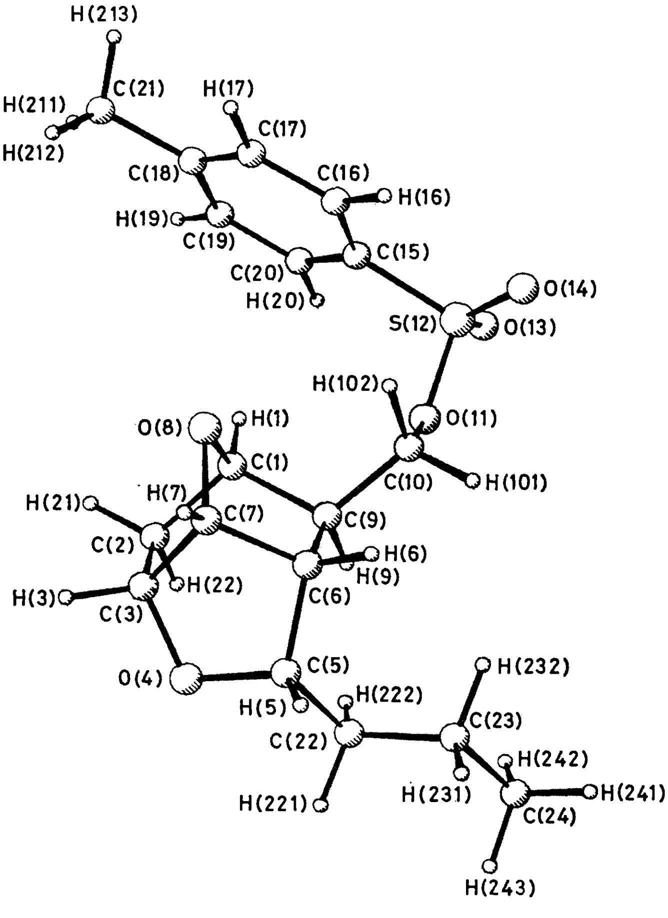


FIGURE. The molecular structure of the tosylate (**6b**). Some bond lengths are: C(1)–C(2), 1·526(3); C(2)–C(3), 1·536(3); C(3)–C(7), 1·534(4); C(7)–C(6), 1·542(2); C(6)–C(9), 1·555(3); C(1)–C(9), 1·546(2); C(1)–O(8), 1·442(3); C(7)–O(8), 1·425(3); C(3)–O(4), 1·428(2); O(4)–C(5), 1·452(3); and C(5)–C(6), 1·532(3) Å; and ∠C(7)–C(3)–O(4), 107·3(2); ∠C(3)–O(4)–C(5), 109·5(2); ∠O(4)–C(5)–C(6), 105·0(1); ∠C(5)–C(6)–C(7), 102·8(2); and ∠C(6)–C(7)–C(3), 99·3(2)°.

---

† All new compounds exhibited spectroscopic and analytical data consistent with the proposed structure.

residuals were $R = 0{\cdot}040$ and $R_W = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_0|] = 0{\cdot}047$.‡

The molecular geometry of the tosylate (**6b**) is shown in the Figure which includes some bond parameters. The propyl group is in the *endo*-configuration which suggests that the borane reagent delivers H^- to an oxonium ion species from the less hindered face.

We thank the S.R.C. for financial support, Dr. K. Erickson for supplying reference spectra of compounds (**5a**), (**5b**), and (**6a**), and Dr. J. P. Michael for helpful discussions.

(*Received*, 19*th March* 1979; *Com.* 285.)

---

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] T. A. Eggelte, H. de Koning, and H. O. Huisman, *Tetrahedron*, 1973, **29**, 2491, 2445.
[2] W. G. Dauben and H. O. Krabbenhoft, *J. Amer. Chem. Soc.*, 1976, **98**, 1992.
[3] J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, 1964, **97**, 3183; J. Sauer, D. Lang, and H. Wiest, *ibid.*, p. 3208.
[4] J. A. Berson and R. Swidler, *J. Amer. Chem. Soc.*, 1953, **75**, 1721.
[5] S. M. Waraszkiewicz, H. H. Sun, K. L. Erickson, J. Finer, and J. Clardy, *J. Org. Chem.*, 1978, **43**, 3194.
[6] C. R. Johnson and G. A. Dutra, *J. Amer. Chem. Soc.*, 1973, **95**, 7777.