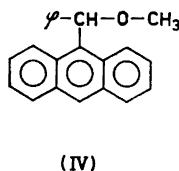
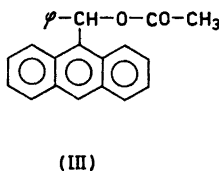
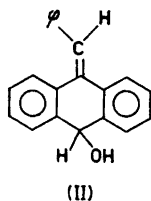
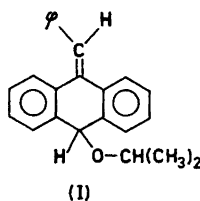


Synthesis and Transannular Rearrangement of 9-Benzylidene- 10-isopropoxy-9, 10-dihydroanthracene

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In connection with our investigations of transannular rearrangements of dihydroanthracenes, we have successfully prepared 9-benzylidene-10-isopropoxy-9,10-dihydroanthracene (I). Treatment of (I) with hot, glacial acetic acid gives 9- ω -acetoxybenzyl anthracene (III), presumably through a transannular 1,5-anionotropic rearrangement.



In earlier work, Julian *et al.*¹ prepared the alcohol analogue (II) of the ether (I) by a Meerwein-Ponndorf reduction of 9-benzylidene anthrone. However, they were not able to prepare any ether derivatives of the alcohol, although several attempts appear to have been made. We have found that using the same conditions as Julian *et al.*, gives not only the "normal" Meerwein-Ponndorf reduction product — the alcohol, (II) but also the ether

(I). If the reaction mixture is allowed to stand for an extended period none of the alcohol can be detected in the reaction mixture and the only isolable material is the ether, in over 65 % yield.

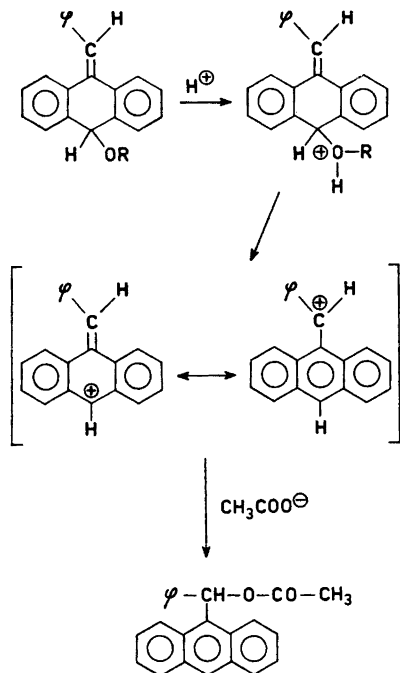
It is of interest to note that this is one of only a few well-defined examples in which an ether rather than an alcohol is formed by a Meerwein-Ponndorf reduction. A similar reaction on 10,10-dimethylanthrone has been mentioned in the review by Wilds.² The reference cited in this review, however, is to unpublished work.

Unambiguous identification of (I) was made spectrally. Thus, its infrared spectrum had a sharp medium absorption at 1590 cm^{-1} (double-bond stretching) and strong absorption at 1120 cm^{-1} (C-O stretching, ether).³ Its ultraviolet spectrum in ethanol was nearly identical to that obtained by Julian *et al.* for the alcohol (II).¹ The NMR spectrum of (I) in benzene showed a doublet centered at 1.26 ppm ($J = 6$ cps) and a multiplet centered at 4.07 ppm, consistent with an isopropyl group⁴ (all values relative to TMS). The C-10 proton appeared as a singlet at 5.70 ppm (δ). The vinylic proton was masked by a complex absorption of the rest of the molecule and could not be seen.

The ether (I) was found to undergo an unusually facile rearrangement to the acetate (III) as a result of short boiling with glacial acetic acid. Identity of (III) was proven through spectral analysis, micro-analysis and by methanolysis to the known ether (IV). The ether could have been formed by etherification of the expected alcohol or, by alkyl-oxygen cleavage of the ester. Julian *et al.* have observed the former and the latter is not unexpected if the structure of the acetate is considered.

The conversion of the dihydroanthracene derivative (I) to the anthracene (III) can be viewed as a displacement accompanied by a 5-carbon anionotropic rearrangement of the same type studied by Julian and co-workers^{1,5} and earlier by Cook.⁶ Thus, the reaction most probably proceeds through protonation of the ether oxygen and elimination as the alcohol generating a positive charge on the external benzylic carbon. Attack by the acetate ion then gives the observed product. The reaction could, of course, be stepwise or concerted.

Further studies on transannular rearrangements are in progress.



Experimental. Infrared spectra were obtained using a Perkin-Elmer Model 137 spectrometer. Ultraviolet spectra were obtained using a Beckmann Model DU and NMR spectra using a Varian A-60 spectrometer.

The aluminium isopropoxide was used as received from Hopkins and Williams Ltd. The aluminium oxide used for chromatography was Woelm, neutral, activity No. 1.

9-Benzylidene-10-isopropoxy-9,10-dihydroanthracene (I). The 9-benzylidene anthrone (10.0 g, 0.0351 mole) and the aluminium isopropoxide (44.0 g, 0.22 mole) were combined with 350 ml of isopropanol. The resultant mixture was brought to reflux and distilled slowly through a Widmer column until the test for acetone was negative (about 8 h). The reaction mixture was allowed to stand for 8 days in the dark. It was then added to 600 ml of 3% NaOH and extracted with 450 ml of diethyl ether. The ether layer was separated, washed with 300 ml of 3% NaOH, followed by 3 washes with 300 ml portions of distilled water. The ether extracts were dried for 3 days over CaCl_2 and were then concentrated by distillation giving an oily residue. The oil was further concentrated using a vacuum evap-

orator. The oil was taken up in 30 ml of anhydrous benzene. About 10 ml of the benzene solution was chromatographed on 60 g of aluminium oxide which had been heated at 120° for one hour. The column was eluted with 160 ml of pentane in four fractions followed by 150 ml of pentane: benzene (4:1) in 7 fractions. A total of 2.5 g of an oil was collected from fractions 3–11. The infrared spectrum of each fraction was taken and showed all the fractions to be composed of essentially the same material. Fractions 5–11 were re-chromatographed using only petroleum ether ($30\text{--}45^\circ$) as an eluant. A center fraction was taken from this chromatogram and used for obtaining the ultraviolet, infrared and NMR spectra and for the reaction described below. The yield, based on the results of the first chromatography, was about 70%.

9- ω -Acetoxybenzyl anthracene (III). About 0.6 g of the isopropyl ether derived from the second chromatograph was boiled for one minute with a few milliliters of glacial acetic acid. The solution was cooled ambiently depositing 0.5 g of a yellow solid, m.p. $135\text{--}8^\circ$. Three recrystallizations from methanol gave an analytical sample as bright-yellow cubes, m.p. $141.5\text{--}3^\circ$. Its infrared spectrum had a strong carbonyl absorption at 1720 cm^{-1} as expected for an ester group. A strong absorption between 880 and 900 cm^{-1} was consistent with a monosubstituted anthracene moiety.⁸ The ultraviolet spectrum exhibited a maximum at $255.5\text{ m}\mu$ with $\epsilon = 1.35 \times 10^5$ as anticipated for an anthracene derivative.¹ (Found: C 84.62; H 5.67. Calc. for $\text{C}_{23}\text{H}_{18}\text{O}_2$ (326.37): C 84.64; H 5.56).

Methanolysis of 9- ω -acetoxybenzyl anthracene (III) to 9- ω -methoxybenzyl anthracene (IV). One gram (0.003) of the ester (III) was boiled gently for 30 min with 8 drops of concentrated HCl in 25 ml of methanol. The solution was allowed to cool ambiently, followed by filtration 10 h later to remove a trace of long, silky needles (probably anthraquinone). The filtrate deposited a white solid spontaneously, m.p. $123\text{--}5^\circ$. The yield was 0.7 g, 80% of theory. Julian has reported a m.p. of $129\text{--}30^\circ$ for 9- ω -methoxybenzyl anthracene. The infrared spectrum was consistent with the expected product.

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The microanalyses were carried out at the Analytical Department of the Chemical Institute.

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An Integrated Set of Programmes for Crystallographic Calculations

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In connection with the installation at this institute of a digital computer for which no crystallographic programmes were available we have written a set of routines for X-ray structure analyses. The programmes are intended to be completely general and easy to use for the crystallographer. The input data are presented in the form of directives (e.g. Table 1) and are as free from punching conventions as possible. All parameters that do not change during a structure analysis are stored with the reflexion data on magnetic tape. Most programmes,

Table 1. Typical set of directives for Fourier summation.

TITLE	Trilaurin first trial;	
SPACE GROUP	2	
SECTIONS	Y	0,20:20
RANGES	X	0,30:30
	Z	0,30:60
DIFF		
SF	Tape 1	Block 75
SORTED	Tape 2	Block 15
RESULT	Tape 1	Block 105
START		

therefore, need a minimum of input parameters particularly if use is made of the fixed area in the core memory where other parameters common to several programmes (atomic coordinates etc.) are also stored. It is, for example, possible to calculate interatomic distances and angles after structure factor calculation without any parameter input. The programme system is designed to make it possible — if the structure allows — to perform a complete structure determination including refinement in one session at the computer. The programmes are therefore fully compatible with each other and their input from magnetic tape is controlled by a special monitor routine.

Machine. The programmes have been written for the D21 computer.* It is a binary, fixed-point, single address machine with a 24 bit word. The addition and multiplication times are 9.6 μ s and 35.6 μ s, respectively. An automatic interrupt system allows slow peripheral units to work at the same time as computations are performed by the central processor.

The programmes require a core memory of at least 16 384 words and four magnetic tape drives. Input is five or eight channel punched paper tape (500 ch/sec), whereas output can be obtained on both paper tape (150 ch/sec) and on a line printer (1000 lines/min). The programme system now handles three different paper tape codes but others are easily incorporated.

Fixed point operation is used in all programmes where high computing speed is essential as floating point arithmetic is not included in the hardware but as compiler subroutines. Great care has therefore been taken in scaling the data to ensure

* Manufactured by Svenska Aeroplan AB (Saab), Sweden.