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THE ASSIGNMENT OF CONFIGURATION TO THE PHOTOADDITION PRODUCTS OF UNSYMMETRICAL CARBONYLS TO FURAN USING PSEUDOCONTACT SHIFTS

E. B. WHIPPLE and G. R. EVANEGA

Contribution from the Union Carbide Research Institute, Tarrytown, New York

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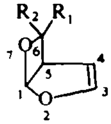
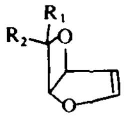
Abstract—The configuration of several 4'-pyridyl oxetanodihydrofurans was assigned from a study of the NMR pseudocontact shifts produced by the addition of cobalt (II) acetylacetonate. The results were used to infer the configurations of other oxetanodihydrofurans reported in the literature. Some additional information about the conformation of 3-pyridyl substituents is available from pseudocontact shift data.

THE photochemical addition of aldehydes and ketones to furan yields oxetanodihydrofurans[1] which have been shown to have the structure I.[2,3] Two alternative structures, II and III, are possible, and while only I and II were considered explicitly in the original work,[2,3] III can be ruled out along with II on the basis of the NMR evidence cited. One important question which was not considered is the geometrical isomerism possible when unsymmetrical carbonyl adducts are involved; i.e. when $R_1 \neq R_2$. While a number of such products are reported,[3,4] no mention of this point is made, although it would appear that in nearly all cases a single isomer resulted. If the proposed two-step photochemical addition occurs,[3] the isomer ratio would presumably reflect upon the conformational preference, internal rotation and inversion rate, and lifetime of the biradical IV. With some other oxetane systems, judicious choice of the reaction medium and other experimental conditions enables one to influence the isomer ratio.[5] Any attempt to understand these questions must begin with a knowledge of the structures of the products, and it was with this objective that the present work was undertaken.



I



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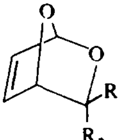

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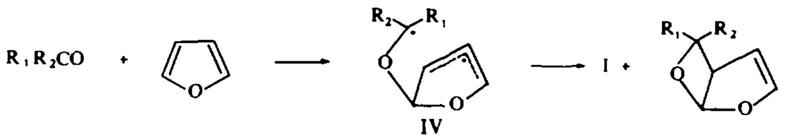

IV

While NMR can differentiate straightforwardly among the structural alternatives I through III, its extension to the present question requires more subtlety. When

R_1 or R_2 is a hydrogen atom one might attempt to interpret its vicinal coupling to the proton on C_5 in terms of the dihedral angle, although this is notoriously uncertain in 4-membered ring systems, particularly when only one isomer is available.[6,7] The invariance of this coupling over the series of aldehyde adducts reported[2,3] would indicate that all had the same configuration, and its small value ($J \sim 3{\cdot}0 \pm 0{\cdot}2$ c/s) suggests a *trans* arrangement of the protons, permitting a tentative assignment of I with $R_1 = H$ for the structures of the oxetanes derived from furan and aldehydes.

In the oextanes derived from ketones, no couplings are observed which differ significantly between the *cis-trans* isomers, so that one is forced to resort to chemical shift data. While prediction of the chemical shifts from first principles would be highly tenuous, one might reasonably hope for some variant of Shoolery's rules[8] to apply; i.e. that the shifts at the ring protons produced by the group R_1 might be largely independent of R_2, and *vice versa*. There is much evidence that long-range magnetic shielding effects by substituents on rigid molecules are characteristic of the substituent and the molecular geometry, and are additive.[9] Shielding effects of this type also have a firm theoretical basis, being most commonly attributed to anisotropy in the magnetic susceptibilities of substituent groups,[10] long known to be approximately additive.[9] In the present case, where the susceptibilities of the substituents R_1 and R_2 are not axially symmetric about the bonds to C_6, it becomes necessary to consider how the conformation of one group is affected by the presence of the other. This can introduce large uncertainties into semi-empirical correlations of the chemical shifts.

When R_1 or R_2 contains a strong coordinating group, it is possible to form paramagnetic chelates with transition metal ions in which the proton resonances of the ligand are affected profoundly.[11] When the lifetime of the paramagnetic complex is short compared to the electron spin–nuclear spin coupling, the shortening of the nuclear relaxation time is minimized and shifts in the nuclear resonance lines can be observed.[12] These shifts may be of two types known as contact shifts and pseudo-contact shifts.[13,14] The former is due to the presence of unpaired electron spin density at the nuclear positions, while the latter is due to a combination of electron–nuclear dipole interaction and electronic g-value anisotropy. When the g-tensor has axial symmetry and the electron is confined to the region of the metal nucleus, the pseudocontact shift is given[14] by equation (1), where the direction of $g_{\parallel}$ is the unique principal axis of the

$$\frac{\Delta H}{H_0} = \frac{-\beta^2 S(S+1)(g_{\parallel} - g_{\perp})(g_{\parallel} + 2g_{\perp})}{27\,kT} \cdot \frac{(3\cos^2\theta_i - 1)}{r_i^3} \qquad (1)$$

electronic g-tensor, and θ_i is the angle between this axis and the radius vector of length r_i from the metal to nucleus i. The ratio of pseudo-contact shifts for different nuclei in the same complex involves only the structural parameters constituting the last term in Eq. (1), and may be used as a test of structure provided that (a) the position of the metal ion can be defined, and (b) contact shifts are either precisely known or negligible. Since the protons in structure I are separated from the groups R_1 and R_2 by several σ-bonds, one can safely ignore contact shifts in a rough approximation of the structure. We have substantiated this claim by examining complexes in which pseudocontact shifts are largely absent due to nearly isotropic g-values, but in which contact shifts might be expected to persist.[12]

RESULTS AND DISCUSSION

All the conditions stated above can be satisfied when R_1 or R_2 is a 4′-pyridyl group and cobalt (II) acetylacetonate is chosen as the metal source.[12] A series of eight compounds (Table 6) were synthesized photochemically from furan and the unsymmetrical carbonyl compounds containing pyridyl, and phenyl, methyl or hydrogen, in good to excellent yields depending upon the reactant. Addition of small amounts of the metal chelate to deuterochloroform solutions of these compounds produces substantial shifts in the resonance conditions for all the protons,* while addition to the corresponding phenyl oxetane gave no significant shifts.

The protons on the pyridyl ring are subject to contact shifts and are hence not usable in Eq. (1) directly; however, they may serve to normalize the concentration when comparing shifts in different complexes containing 4′-pyridyl groups. This assumes that the complex between the metal and the pyridyl ring is unaffected by the remainder of the molecule. This assumption is not strictly justified, and probably leads to small (~20%) errors in comparisons of pseudocontact shifts in different molecules. Figure 1 shows some typical linear plots of the skeletal proton shifts

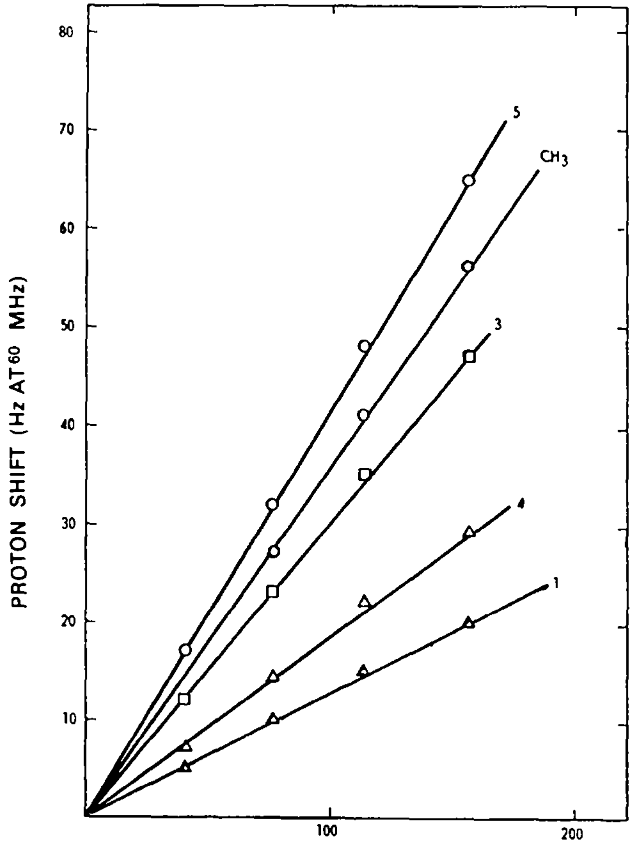

FIG. 1. Observed skeletal proton shifts *vs* α-pyridyl proton shifts of *syn*-6-methyl-anti-6-(4′-pyridyl)2,7-dioxabicyclo[3.2.0]hept-3-ene at various concentrations of Co (II) acetylacetonate.

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* This method is useful in resolving the spectra of a mixture of isomers, since each isomer has a unique shift for related protons.

against the α-proton shifts of the pyridyl ring at various metal concentrations. The slopes from several such plots are collected in Table 1 and compared with pseudocontact shifts calculated from Eq. (1) in the following way. A base structure was assumed from reasonable bond distances and angles, leading to the proton coordinates listed in Table 2. Assuming g in the metal complex to be symmetrical about the metal–nitrogen bond which coincides with the rotation axis of the pyridyl rings, these vectors were oriented so that their plane bisects the angle C_5–C_6–O_7 (Table 2), and each axis is 60° out of the plane of the oxetane ring. The distance of the metal ion along either of these vectors was treated as an independent variable to yield the calculated shieldings in Fig. 2. Only the relative shifts are meaningful since no effort has been made to include the first term on the right-hand side of Eq. (1) or to measure the concentration of the complex in solutions. It is apparent from Fig. 2 that the ratios of the pseudocontact shifts are rather insensitive to the distance when the pyridyl ring is *anti* to the fused dihydrofuran ring (R_2 position in I), and are in reasonable agreement with the observed values for three of the four compounds in Table 1. The order of the shifts for the *syn* (R_1) configuration depends on the distance, since the broken curves in Fig. 2 cross near $r = 6{\cdot}2$ Å, and 7·2 Å. The shift ratios listed in Table 1, which agree closely with the observed values for the remaining isomer, were obtained for $r = 6{\cdot}0$ Å which, allowing for the dimensions of the pyridyl ring, correspond to a metal–nitrogen distance of 1·7 Å.

TABLE 1. OBSERVED AND CALCULATED RATIOS OF PSEUDOCONTACT SHIFTS TO α-PYRIDYL PROTON SHIFT

Substituents		Proton shift*			
R_1	R_2	H_1	H_3	H_4	H_5
		Observed			
Methyl	4'-pyridyl	0·301	0·128	0·186	0·416
Phenyl	4'-pyridyl	0·287	0·111	0·185	0·357
4'-pyridyl	Phenyl	0·190	0·170	0·330	0·260
H	4'-pyridyl	0·265	0·118	0·185	0·355
		Calculated			
—	4'-pyridyl	0·27	0·12†	0·19	0·43
4'-pyridyl	—	0·19	0·17†	0·35	0·26

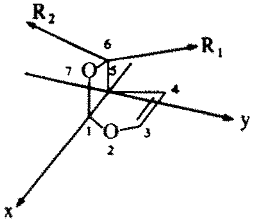
* Positive values indicate shifts to higher applied field, or increased shielding.

† Adjusted to fit.

These results make it possible to assign unambiguous structures to all the available oxetanes containing 4'-pyridyl groups, and these might then serve as a basis for systematic investigation of how the skeletal proton shifts are affected by functional group replacement at R_1 and R_2. Some illustrative data are given in Table 3 in the form of incremental shifts caused by replacing the phenyl groups in the oxetane structure I (R_1, R_2 = Ph).

The increments caused by 4'-pyridyl groups in both *syn* and *anti* positions were determined by direct comparisons of shifts in known structures, and the increment

TABLE 2. COORDINATES AND DIRECTION COSINES OF TRIAL STRUCTURE



	x (Å)	y (Å)	z (Å)
H_1	2·00	−0·58	−0·77
H_3	0·76	3·30	0·0
H_4	−1·40	1·87	0·0
H_5	−0·46	−0·59	−0·76
C_6	0·04	−0·65	1·40
R_1	$\alpha = -0·26$	$\beta = 0·63$	$\gamma = 0·70$
R_2	$\alpha = -0·26$	$\beta = -0·95$	$\gamma = -0·04$

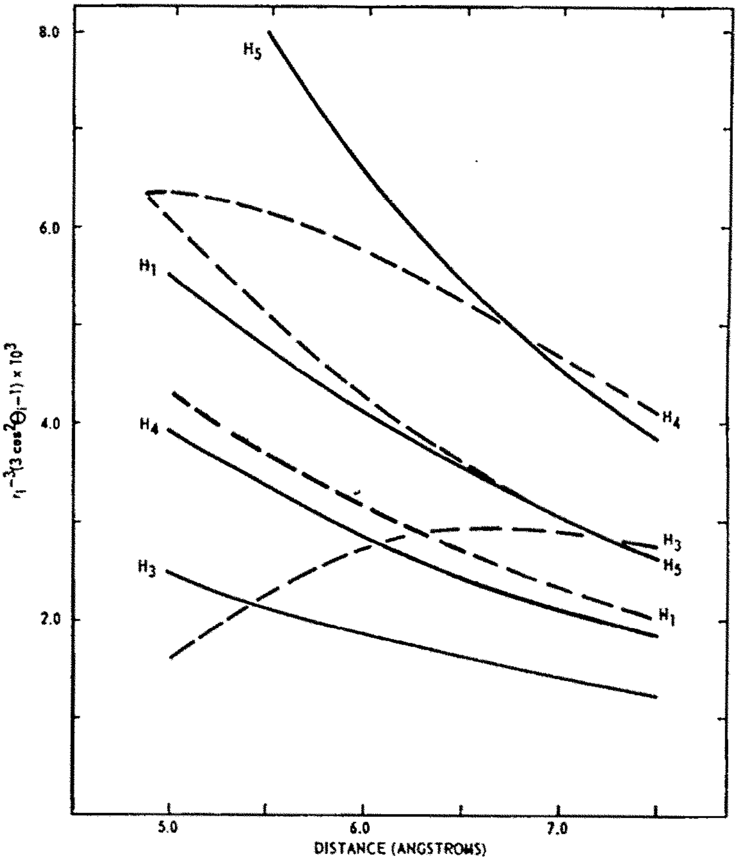


FIG. 2. Calculated pseudocontact shifts *vs* the metal distance from C_6 along R_1 (solid curves) and R_2 (broken curves) in the calculated structure of Table 2.

TABLE 3

PART (A). CHEMICAL SHIFTS[a] IN 6,6-DIPHENYL-2,7-DIOXABICYCLO[3.2.0]HEPT-3-ENE
PART (B). INCREMENTAL SHIFTS CAUSED BY SUBSTITUTION OF PHENYL GROUP IN 6-POSITION

	R_1 (*syn*)	R_2 (*anti*)	H_1	H_3	H_4	H_5
A	phenyl	phenyl	6·31[b]	6·39	4·93	4·38
B		4′-pyridyl	−0·01	+0·01	+0·07	−0·06
	4′pyridyl		−0·01	+0·03	−0·03	+0·04
	hydrogen		+0·20[c]	+0·32	+0·50	−0·69
	methyl		−0·01[d]	+0·30	+0·30	−0·52
		methyl	−0·04[d]	−0·11	−0·10	−0·32

[a] δ values in $CDCl_3$ solution. [b] See Ref. 2. [c] See Ref. 3. [d] See Ref. 4.

TABLE 4. CALCULATED AND OBSERVED[4] CHEMICAL SHIFTS FOR PHOTOADDITION PRODUCT OF ACETOPHENONE TO FURAN

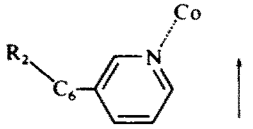
	δ_1	δ_3	δ_4	δ_5
Calculated R_1 = Me	6·21	6·29	5·23	3·86
Calculated R_2 = Me	6·27	6·28	4·83	4·02
Observed[4]	6·21	6·29	5·30	3·82

from *syn* 6-methyl substitution by comparison of the compounds with 4′-pyridyl groups in the *anti* position. The shift increment for *anti* methyl substitution was determined indirectly, using available data[4] for the dimethyl derivative (I, $R_1 = R_2 =$ —Me) and the increments for *syn* methyl substitution determined above. Assuming the increments in Table 3 to be approximately constant, chemical shifts could be predicted for both possible isomers formed by photoaddition of acetophenone to furan, and comparison with the known values[4] for the one isomer available permits one to assign its methyl group to the *syn*-position (Table 4).

Despite appearances, the example of acetophenone and 4-acetylpyridine does not portend a general additivity of group contributions to the chemical shift. A counterexample is found among available data[3] from aldehyde adducts. By virtue of the close correspondence of vicinal couplings between protons on C_5 and C_6, these can all be assumed to have the same configurations which is demonstrably *syn*-H_6 in the case of the 4′-pyridyl derivative (Table 1). Comparison of the reported shifts[3] yields increments for replacement of *anti*-phenyl by methyl of −0·19, −0·03, −0·05, and −0·08 ppm at ring positions, 1, 3, 4, and 5, respectively. These correspond with neither of the last two rows in Table 3, although that corresponding to substitution of the *anti*-position would correctly seem the better choice. It appears then that *anti*-phenyl groups cause less shielding at position 1, and more at position 5, where R_1 = H than when R_1 = Me. This is most likely due to a change in conformation of the aryl substituent.

We can demonstrate by means of pseudocontact shifts on cobalt complexes of 3′-pyridyl substituents that replacement of a phenyl by hydrogen or methyl at the R_1 position does change the conformation of the pyridyl group in the R_2 position of structure I. Although the 4'-pyridyl oxetanodihydrofurans could be treated in a straightforward manner, the case in which R_1 or R_2 is 3'-pyridyl is complicated, since the position of a metal ion complexed to the nitrogen atom of a 3'-pyridyl ring depends upon the angle of rotation about the bond connecting the pyridyl substituent to C_6. In these cases the distance r_i and the angle of rotation θ_i of Eq. (1) will be less accurately defined but can be confined within certain limits.

In order to evaluate the pseudocontact shifts from 3'-pyridyl oxetanodihydrofurans we have approached the problem in the following manner. Using the structure of the oxetanodihydrofuran skeleton given in Table 2, the metal ion is assumed to be on an axis bisecting the C–N–C angle and in the plane of the pyridyl ring, at a distance of 1·7 Å from the nitrogen atom. The dihedral angle is measured between the planes defined by the three adjacent atoms R_2, C_6, R_1, and the pyridyl ring, the zero point being the planar arrangement V and the positive sense of rotation being such that at 120° the pyridyl and oxetane rings are approximately coplanar.



V

The arrows in Fig. 3 point in the direction of the pyridyl nitrogen atom, as indicated in V, and the calculated variations of pseudocontact shift with dihedral angle are plotted in Fig. 3.

The experimentally observed pseudocontact shifts in several cobalt II complexes of oxetanodihydrofurans containing 3'-pyridyl groups attached to the 6-position are collected in Table 5. In each case the shifts are referred to the higher field of the two α-pyridyl proton shifts. This procedure attempts to normalize the concentrations of the complexes, but probably leads to errors as large as 20% due to effects by the substituent R_1 on the contact and pseudocontact shifts of the α-pyridyl hydrogen chosen as a reference. However, the ratio of shifts at different ring position in the same molecule are not affected by this error. Both geometrical isomers were available in only one of the cases listed in Table 5. A rough correspondence among the observed pseudocontact shifts supports the contention that the first three entries in Table 5 have their 3'-pyridyl groups in the same configuration, and the vicinal coupling to

TABLE 5. OBSERVED PSEUDOCONTACT SHIFTS (RELATIVE TO α-PYRIDYL PROTON SHIFTS) FOR Co (II) COMPLEXES OF *anti*-6-(3'-PYRIDYL)-2,7-DIOXABICYCLO[3.2.0]HEPT-3-ENE WITH VARIOUS SUBSTITUENTS IN THE *syn*-6-POSITION

		Proton position			
R_1	R_2	1	3	4	5
hydrogen	3'-pyridyl	0·166	0·052	0·086	0·350
methyl	3'-pyridyl	0·257	0·061	0·051	0·390
phenyl	3'-pyridyl	0·303	0·052	0·042	0·350
3'-pyridyl	phenyl	0·155	0·149	0·228	0·165

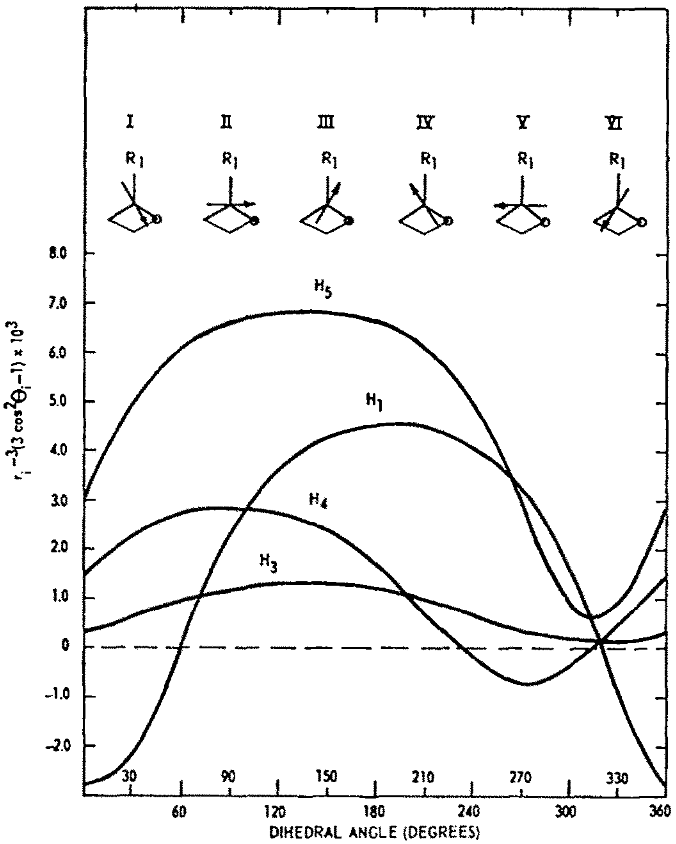


FIG. 3. Calculated pseudocontact shifts at the skeletal protons as a function of pyridyl group rotation in Co (II) complexes of *anti*-3′-pyridyl oxetanodihydrofurans.

the 6-proton in the first compound listed indicates that the pyridyl configuration is 6-*anti*. Comparing Table 5 with Fig. 3, it appears that when bulky groups such as phenyl or methyl occupy the R_1 position, the observed pseudocontact shift ratios best correspond to dihedral angles in the range 210–270°. Only in this region do the calculated pseudocontact shifts occur in the same order as the observed. When R_1 is a proton, the range of preferred dihedral angles extends to about 150–330°, increasing the pseudocontact shift at H_4 and decreasing it at H_1. The conformational preferences indicated would be about those expected were the determining factors steric hindrance between vicinal groups, and a tendency for opposite alignments of the dipole moments in the pyridyl and oxetane rings, the metal ion being neglected.

CONCLUSIONS

The pseudocontact shift method has been used here to assign the structure of various 3′- and 4′-pyridyl oxetanes, but could be applied to other heterocyclic systems by the proper choice of coordinating cation and ligand. However, it is only useful for those isomer problems in which the contact shifts are minimized, that is, for resonance signals from nuclei which are remote from the ligand–metal bond. Careful application of this method can lead to information on molecular confirmation as well as structure.

TABLE 6. OBSERVED COUPLING CONSTANTS (Hz)

	R_1	R_2	J_{13}	J_{15}	J_{16}	J_{34}	J_{35}	J_{45}	J_{56}
I a	phenyl	4′-pyridyl	±0·6[a]	±4·4[a]	—	±3·0[a]	∓1·2[a]	±3·0[a]	—
I b	4′-pyridyl	phenyl	0·7	4·1	—	2·9	1·3	3·0	—
I c	phenyl	3′-pyridyl	0·7	4·4	—	3·0	1·3	3·0	—
I d	3′-pyridyl	phenyl	0·7	4·2	—	2·9	1·3	3·0	—
I e	methyl	4′-pyridyl	0·7	4·4	—	3·0	1·2	3·0	—
I f	methyl	3′-pyridyl	0·7	4·4	—	3·0	1·0	3·0	—
I g	hydrogen	4′-pyridyl	0·7	4·4	0·7	2·9	1·2	3·0	3·1
I h	hydrogen	3′-pyridyl	0·6	4·4	0·6	3·0	1·0	3·0	3·3
I i	hydrogen	phenyl	0·7	4·4	0·7	3·0	1·1	2·9	3·2

[a] Relative signs established by double resonance; also reported by D. Gagnaire, E. Payo-Subiza and A. Rousseau, *Nuclear Magnetic Resonance in Chemistry* p. 169 (Edited by B. Pesce). Academic Press (1965).

In the particular case of oxetanodihydrofurans, all the structures listed in Table 6 have been assigned. Using chemical shift and coupling constant data thus accumulated, most of the remaining oxetanodihydrofurans reported in the literature[3,4] can be assigned probable configurations, although with less certainty than those in Table 6. All the known products of the photochemical addition of aldehydes to furan appear to have the original aldehyde proton in the *syn*-position, although this conclusion rests on the assumption that the difference between cis and trans proton couplings in the fused oxetane rings is greater than the variation of the trans coupling over the range of R_2 substituents reported. It also appears consistently true that methyl groups occupy the *syn*-position, and aromatic rings the *anti*-position (see the intermediate IV), so that all known cases have the less bulky group in the least hindered position.[*] That steric factors play the predominant role is also suggested by the fact that both 4-benzoylpyridine and 3-benzoylpyridine give essentially 50:50 mixtures of both isomers.

EXPERIMENTAL

The pyridyl ketones and aldehydes were obtained from Aldrich Chemical Co.; the 3- and 4-benzoylpyridines were used without further purification; the 3- and 4-acetylpyridines and the 3- and 4-pyridine aldehydes were distilled immediately before use. The oxetanodihydrofurans were synthesized photochemically from the corresponding ketone or aldehyde and furan as follows: a magnetically stirred solution of 0·1 mole ketone or aldehyde in 250 cc furan was purged with N_2 for 30 min and irradiated with a 450 W Hanovia Hg HP immersion lamp (Pyrex filter) until the IR carbonyl stretch disappeared or decreased markedly. 3-Acetyl pyridine and the pyridine aldehydes were especially prone to polymer or tar formation on the immersion well. Thus it was necessary to stop the irradiation daily, clean the immersion well and repurge with N_2 before irradiating. The products were isolated and identified by IR (by the presence of vinyl CH stretch, which disappeared on hydrogenation of the double bond, and the oxetane C—O stretch and by the absence of C═O and O—H stretch), by NMR spectra (the spectra, chemical shifts and coupling constants were in agreement with the spectra of analogous oxetanodihydrofurans[2–4]) and by elemental analyses. The various coupling constants are tabulated in Table 6.

syn-6-*phenyl*-anti-6-(4′-*pyridyl*)2,7-*dioxabicyclo*[3.1.0]*hept*-3-*ene* (Ia) *and* anti-6-*phenyl*-syn-6-(4′-*pyridyl*)-2,7-*dioxabicyclo*[3.1.0]*hept*-3-*ene* (Ib). The irradiation was stopped after 43 hr and the soln was concentrated in vacuum to give a red-brown paste. This was swirled with ether and filtered to give a pink solid, 9·85 g Ia, m.p. 154–156°, 39% yield; recrystallized from benzene–hexane, colorless needles, m.p. 159–160°; (Found: C, 76·25; H, 5·12; N, 5·54. $C_{16}H_{13}NO_2$ requires: C, 76·47; H, 5·22; N, 5·57%.) IR/KBr ν_{max} 950–1050 cm^{-1} (s) (oxetane C—O str), 3100 cm^{-1} (w) (vinyl C—H str). The ether wash was concentrated to give 14·8 g of a red-brown oil. This was dissolved in dry ether and a 2N HCl ether soln was added in small portions with stirring; 5 fractions were collected, each was filtered, neutralized immediately with 10% $NaHCO_3$aq, extracted with ether, and the ether dried with $MgSO_4$ and concentrated. Fractions 3 and 4 crystallized immediately 5·75 g Ib; recrystallized from hexane, m.p. 104–105°, 23% yield. (Found: C, 76·64; H, 5·08; N, 5·76. $C_{16}H_{13}NO_2$ requires: C, 76·47; H, 5·22; N, 5·57%.) The IR/KBr of Ib was distinctly different from that of Ia: IR/KBr ν_{max} 950–1050 cm^{-1} (s) and 3100 cm^{-1} (w). Fractions 1, 2 and 5 were oily residues that contained carbonyl material (IR, C═O str), and were not looked at further. The NMR of the crude irradiation mixture upon addition of cobalt (II) acetylacetonate indicated that Ia and Ib were present in a 50:50 ratio.

syn-6-*Phenyl*-anti-6-(3′-*pyridyl*)2,7-*dioxabicyclo*[3.1.0]*hept*-3-*ene* (Ic) and syn-6-(3′-*pyridyl*)anti-6-*phenyl*-2,7-*dioxabicyclo*[3.1.0]*hept*-3-*ene* (Id). The irradiation was stopped after 72 hr and the soln was concentrated to give 24·6 g of a brown oil. The NMR of the crude oil in $CDCl_3$ with cobalt (II) acetylacetonate indicated a 50:50 mixture of Ic and Id. The brown oil was extracted several times with hot hexane to give

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[*] On the other hand, the addition of acetylpyridines to norbornene leads to a single product—an exo-oxetane—that has the methyl group *anti* to the fused norbornane ring, suggesting that although methyl appears to be larger than pyridyl in some cases, it is necessary to consider the geometry of the diradical IV in detail. These results and their interpretation will be presented elsewhere.[5]

21·2 g of a yellow solid. Five recrystallizations of this material from hexane gave 3·9 g of Id, m.p. 106–108° (greater than 95% one isomer by NMR). (Found: C, 76·37; H, 5·34; N, 5·45. $C_{16}H_{13}NO_2$ requires: C, 76·47; H, 5·22; N, 5·57%.) IR/KBr ν_{max} 940 cm^{-1} (s), 960 cm^{-1} (s) and 3100 cm^{-1} (w). The mother liquors of the above were combined, and concentrated to give 16·3 g of a yellow solid. This was dissolved in ether, filtered and an ethereal solution of HCl added. The first portion of ppt was filtered off, washed with ether, and dried in vacuum. It was then dissolved in hot acetone, filtered to remove some insoluble material, allowed to stand in the refrigerator in order to obtain 3·1 g of the hydrochloride. The needles were neutralized with 10% NaOHaq and the free base was extracted with CH_2Cl_2; the soln was dried with $MgSO_4$ and concentrated to give 2·9 g of Ic; recrystallized from ether, m.p. 125–126°, NMR indicates only one isomer. (Found: C, 76·65; H, 5·13; N, 5·47. $C_{16}H_{13}NO_2$ requires: C, 76·47; H, 5·22; N, 5·57%.) IR/KBr ν_{max} 925 cm^{-1} (s), 950 cm^{-1} (s), 960 cm^{-1} (s) and 3100 cm^{-1} (w). The IR spectrum of Ic and Id were distinctly different.

syn-6-*Methyl*-anti-6-(4'-*pyridyl*)2,7-*dioxabicyclo*[3.1.0]*hept*-3-*ene* (Ie). The irradiation was stopped after 60 hr and the soln was concentrated to give a brown oil. This was extracted with hot hexane several times and the extract was cooled to give 13·68 of light yellow needles (Ie), m.p. 71–72°, 72% yield; sublimation and recrystallization gave colorless needles, m.p. 73–74°; IR/KBr ν_{max} 3095 cm^{-1} (w) (vinyl C—H str), 960 cm^{-1} (s) (oxetane C—O str). (Found: C, 69·67; H, 5·81; N, 7·46. $C_{11}H_{11}NO_2$ requires: C, 69·82; H, 5·86; N, 7·40%.) The NMR of the crude irradiation mixture was almost identical with the NMR of Ie, indicating less than 5% of the other isomer.

syn-6-*Methyl*-anti-6-(3'-*pyridyl*)2,7-*dioxabicyclo*[3.1.0]*hept*-3-*ene* (If). The irradiation was stopped after 7 days since even though the neat IR of the C═O str of 3-acetylpyridine had diminished, no further change occurred over the last 24 hr. After concentration to a dark brown oil, extraction with hexane gave a light yellow oil, 14·35 g, that contained a significant amount of 3-acetylpyridine (neat IR). This oil was dissolved in hot hexane and allowed to stand overnight at room temp; 4·78 g, 25% yield, colorless prisms (If), m.p. 47–48° was obtained; IR/KBr ν_{max} 3090 cm^{-1} (w) (vinyl C—H str) and 940 cm^{-1} (s) (oxetane C—O str). (Found: C, 69·68; H, 5·86; N, 7·46. $C_{11}H_{11}NO_2$ requires: C, 69·82; H, 5·86; N, 7·40%.)

The NMR of the light yellow oil (14·35 g) indicated the presence of If (ca. 64% overall yield) along with 3-acetylpyridine. In addition, the presence of another isomer was suggested by the Me resonance at 2·12 δ. The ratio of Me areas of If and the other product is 8·1/1·0. All attempts to isolate this material and verify this suspicion were unsuccessful.

anti-6-(4'-*Pyridyl*)2,7-*dioxabicyclo*[3.2.0]*hept*-3-*ene* (Ig). After 2 weeks of irradiation during which time the soln was purged with N_2 continuously, the irradiation mixture was concentrated to a brown liquid and then distilled through a vigoreaux column under high vacuum. The fraction which distilleed at 110° (5 μ) was dissolved in 20 ml CH_2Cl_2 and extracted with 25 ml standard bisulfite soln. The CH_2Cl_2 layer was dried over $MgSO_4$, concentrated to an orange oily solid (8·2 g), sublimed (52° and 10 μ), and the yellow sublimate recrystallized from ether at −70°; 4·8 g (27% yield) colorless solid (Ig), m.p. 54·0–55·5°. (Found: C, 68·54; H, 5·29; N, 7·93; O, 18·22. $C_{10}H_9NO_2$ requires: C, 68·56; H, 5·18; N, 8·00; O, 18·27%); IR neat, 943 cm^{-1} (s) (oxetane C—O str) 3092 cm^{-1} (w) (vinyl C—H str).

anti-6-(3'-*Pyridyl*)2,7-*dioxabicyclo*[3.2.0]*hept*-3-*ene* (Ih). After 3 weeks of irradiation, during which time the soln was purged with N_2 continuously, the soln was concentrated to a brown oil which was dissolved in CH_2Cl_2, extracted with bisulfite soln, dried and concentrated to give 3·50 g orange oil. The oil was evaporatively distilled at 110° (10 μ) to yield 2·22 g (13% yield) of a colorless oil (Ih). (Found: C, 68·69; H, 5·23; N, 7·77; O, 18·23. $C_{10}H_9NO_2$ requires: C, 68·56; H, 5·18; N, 8·00; O, 18·27%); IR neat, 939 cm^{-1} (s) (oxetane C—O str) and 3096 cm^{-1} (w) (vinyl C—H str).

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REFERENCES

[1] G. O. Schenck, W. Hartmann and R. Steinmetz, *Chem. Ber.* **96**, 498 (1963).

[2] D. Gagmaire and E. Payo-Subiza, *Bull. Soc. Chim. Fr.* 2623 (1963).

[3] S. Toki, K. Shima and H. Sakurai, *Bull. Chem. Soc. Japan* **38**, 760 (1965).

[4] K. Shima and H. Sakurai, *Ibid.* **39**, 1806 (1966).

[5] G. R. Evanega and D. R. Arnold, to be published.

[6] A. A. Bothner-by, *Advances in Magnetic Resonance* (Edited by J. S. Waugh) Vol. I; p. 244. Academic Press (1965).

[7] H. Weitkamp and F. Korte, *Tetrahedron* Suppl. No. 7, 75 (1966).

[8] J. N. Schoolery, *Technical Information Bulletin* Vol. 2; No. 3. Varian Associates, Palo Alto, California (1959).

[9] N. S. Bhacca and D. N. Williams, *Applications of NMR Spectroscopy in Organic Chemistry*. San Francisco, Holden-Day (1964).

[10] H. M. McConnell, *J. Chem. Phys.* **27**, 226 (1957).

[11] D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *J. Chem. Phys.* **37**, 347 (1962).

[12] J. A. Happe and R. L. Ward, *J. Chem. Phys.* **39**, 1211 (1963).

[13] N. Bloembergen and W. C. Dickinson, *Phys. Rev.* **79**, 179 (1950).

[14] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.* **29**, 1361 (1958).