ing acids and that the contact time must be controlled carefully to maximize the yield of ketone. It may be that 4 is more labile to the acid medium than 5.

Unfortunately, experimental verification for both hypotheses is lacking since no mass balance was reported for the reaction.

Experimental Section

Hydroboration of 1-Chloronorbornene (1).[1] Aldrich 1 *M* diborane in THF (13.8 ml) was added to a stirred solution of 6.9 g (0.0537 mol) of **1** in 13.8 ml of freshly distilled THF under nitrogen. After 20 min, 5.7 ml of 3 *N* sodium hydroxide was added dropwise (caution, frothing) to the stirred solution followed by 4.2 ml of 50% hydrogen peroxide (slowly, reaction exothermic). The reaction mixture was stirred for 2 hr.

Water (20 ml) and some sodium chloride were added and the mixture was extracted three times with ether (30 ml, 2 × 20 ml). The combined ether extracts were washed with water (3 × 50 ml) and dried over magnesium sulfate. The ether solution was concentrated to about 30 ml by slow distillation through a small Vigreux column and examined by glpc (Perkin-Elmer Column K, 15% Carbowax 20M, 170°, 40 psi). The analysis showed, in order of increasing retention time, 8% **1**, 57% **2**, 1% of an unidentified substance, and 34% **3**.

The chloro alcohol mixture was separated by preparative glpc (column: 20 ft × 0.375 in. 20% SE-30 on Chromosorb P 45/60, 185°, 29 psi): 1-chloro-2-*exo*-norbornanol (**2**), mp 84.5–85.5°, ir (CCl_4) hydroxyl 3550 cm^{-1}, the nmr ($CDCl_3$) consisted of a multiplet centered at τ 6.36 (α-hydroxy proton) and a multiplet between τ 7.65 and 9.0, in the ratio of 1:10; 1-chloro-3-*exo*-norbornanol (**3**), mp 76.5–77.5°, ir (CCl_4) hydroxyl 3590 cm^{-1}, the nmr ($CDCl_3$) consisted of a multiplet at τ 6.1 (α-hydroxy proton) and a very complex multiplet between τ 7.7 and 8.95, in the ratio of 1:10.

Oxidation of 1-Chloro-3-*exo*-Norbornanol (3).[8] Ruthenium tetroxide [2.9 ml of *ca* 0.137 *M* solution in Freon 11 (Matheson)] was added with a chilled syringe to a stirred solution of 50 mg *(0.00034 mol) of 3 in 2 ml of Freon 11 and 2 ml of pentane* at 5–10°. It was necessary to add an equal volume of pentane to bring the chloro alcohol into solution; at 0° the chloro alcohol was only partially soluble. The reaction mixture was stirred at 0° for 20 min.

The excess oxidant was consumed by addition of 2 ml of anhydrous ether and the black ruthenium dioxide was removed by filtration. The solvent was removed by careful evaporation with nitrogen and sublimation of the residue afforded 25 mg of **5**, ir (CCl_4) carbonyl 1775 cm^{-1}, the nmr ($CDCl_3$) showed three multiplets centered at τ 7.3, 7.47, and 7.87.

Oxidation of 1-Chloro-2-*exo*-norbornanol (2).[8] Alcohol **2** (30 mg) in 2 ml of Freon 11 (**2** was completely soluble in Freon 11 at 0°) was oxidized with 1.9 ml (0.00026 mol) of 0.137 *M* ruthenium tetroxide solution at 0° as in the procedure above except that the reaction mixture was stirred at room temperature for 18 hr.[9] Work-up identical with that given above afforded 17 mg of **4**, ir (CCl_4) carbonyl 1780 cm^{-1}, the nmr ($CDCl_3$) showed two multiplets, one centered at τ 7.33 and the other between τ 7.5 and 8.8, with the relative areas of 1:9.4.

Acknowledgment. We wish to thank the National Science Foundation for financial suppcrt. We are grateful to Professor A. J. Fry for sending us copies of private correspondence and a number of spectra which were helpful in making this clarification. Gratitude is also expressed to Dr. Raymond Weglein for consultation on several aspects of this work.

Registry No.—**1**, 15019-71-3; **2**, 19916-70-2; **3**, 19916-71-3; **4**, 51417-65-3; **5**, 51417-66-4.

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(6) The reduction of 1-chloronorcamphor with sodium borohydride gave a 3:1 mixture of 1-chloro-2-*endo*-norbornanol and 1-chloro-2-*exo*-norbornanol. Satisfactory analyses were obtained for both chloro alcohols. R. J. Muller and B. L. Murr, unpublished results.
(7) The ir spectra of the major and minor chloro alcohols were identical with those of the first and second chloro alcohol peaks, respectively, from the preparative glpc carried out by Fry and Farnham. We are grateful to Professor Fry for sending copies of these spec*tra*.
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(10) We are grateful to Professor R. Sauers for sending copies of these spectra.
(11) The ir spectra of **4** and **5** (prepared from **1** by hydroboration and chromic acid oxidation) sent to us by Professor Fry were identical with the ir spectra of the chloro ketones prepared from the oxidation of **2** and **3**, respectively.
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Conformation of Acyloxy Groups in *I,I*-Diacyloxyiodobenzenes. A Dipole Moment Study

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In the compounds of general formula R-X-Y-X-R, where X and Y stand for any divalent group, the two bonds Y-X are equivalent and *a priori* the same conformation on both may be expected. Summarizing the results of our dipole moment studies and those obtained from other methods, we reached the conclusion[1] that the actual conformation can be predicted from the conformation of the simpler model compound R-Y-X-R. If it is planar, the electronic configuration on the central atom Y is usually sp^2 and the bonds Y-X acquire partial double bond character. The whole molecule R-X-Y-X-R is then also planar, or nearly planar (carbonates and their analogs, anhydrides,[2] diacyl sulfides,[1] boronic esters[3]). When the central atom Y has a tetrahedral sp^3 configuration, the model molecule R-Y-X-R as well as the bifunctional molecules R-X-Y-X-R are nonplanar. The latter has more frequently C_2 than C_s symmetry (acetals,[4] *gem*-disulfones,[4] sulfonic acid anhydrides,[1] dialkylphosphinic esters,[5] trisulfides).

Table I
Polarization Data of *I,I*-Diacyloxyiodobenzenes (Benzene, 25°)

Compd	$P_2(\infty)$, cm³	R_D,[a] cm³	$\mu(5\%)$,[b] D	$\mu(15\%)$,[b] D
Ia $C_6H_5I(OCOCH_3)_2$	514.6	63.3	4.68[c]	4.61
Ib 4-$ClC_6H_4I(OCOCH_3)_2$	338.0	68.2	3.61	3.56
Ic $C_6H_5I(OCOC_6H_5)_2$	570.2	105.1	4.74	4.69
Id $C_6H_5I(OCOC_6H_4CH_3$-4$)_2$	561.8	114.4	4.65	4.59
Ie $C_6H_5I(OCOC_6H_4F$-4$)_2$	634.8	104.7	5.06	5.02
If $C_6H_5I(OCOC_6H_4Br$-4$)_2$	660[d]	120.8	5.1[d]	5.1[d]

[a] Calculated using Vogel's atomic increments[9] including the common value for iodine. Suitable exaltations, 1.25 and 0.1 cm³, were added to account for Ph–CO and Ph–Hal conjugation, respectively. [b] Correction for the atomic polarization of 5 or 15% of the R_D value, respectively. [c] Reference 10 gives 4.9 D without correcting for the atomic polarization. [d] These values are less precise owing to the unexplained instability of the solutions.

The polyvalent iodine derivatives offer the rare opportunity to study compounds with the dsp³ configuration on the central atom Y and with the two X–Y bonds practically collinear, oriented to the two apices of the trigonal dipyramid.[6,7] Since the alkyl derivatives are not available, we used in this study the *I,I*-diacyloxyiodobenzenes Ia–f (Table I). We are aware that the replacement of alkyl by acyl may influence the results; *e.g.*, the conformations of acylals[8] and acetals[4] are not the same. Since the two rotating groups are relatively distant (Figure 1) we may anticipate that the conformation is controlled by the interactions on each I–O bond (see the Newman projection II); any comparison with simpler model compounds does not seem to be possible.

We followed the same experimental approach as previously.[1-5] The experimental dipole moments (Table I) are also influenced by the estimated molar refraction, which is uncertain owing to an unknown increment for tervalent iodine atom. Since the measured moments are large, they would be not affected even by an inaccuracy of 1 cm³ in molar refraction. The expected dipole moments for individual conformations have been calculated assuming the exactly linear conformation O–I–O and common geometry of the acyl group (∠O–C═O = 124°, ∠C–C═O = 116°, ∠C–O–I = 113° as in esters). We used the bond moments well tried in previous work[1-5,8] on similar compounds, *viz.*, C_{al}–H 0.3 D, C_{ar}–H 0 D, C–O 0.74 D, C═O 2.5 D, C_{ar}–Cl 1.60 D, C_{ar}–Br 1.58 D, C_{ar}–F 1.35 D. In the actual conformation the bond moments C–Hal are almost insignificant and the I–O moment is completely irrelevant; the C═O and C–O bonds have been confirmed on many acyl derivatives.[1,2,8] Most problematic is the formal moment C–I, including also the two lone electron pairs. Its value should be intermediate between that in iodobenzene dichloride (equal to its dipole moment,[10] 2.6 D) and aliphatic iodides (*ca.* 1.45 D). We got reasonable results with the moment of 1.9 D, but the final conclusions are not affected by its exact value.

The expected moments have been calculated for various dihedral angles $\tau_{1,2}$ = ∠C–I–O–C in the two moieties and for various planar conformations on the C–O bond, *i.e.*, *E* or *Z*. From these only the *Z* conformation in both moieties (Figure 1) yielded dipole moments comparable to the experimental ones. The *Z* conformation is clearly the only reasonable one, since it is found in all compounds containing the COO– grouping (see, *e.g.*, ref 1, 2, and 8). The computed and experimental values are compared using the previously introduced[8] graphical method (Figure 2). In Figure 2 only the symmetrical conformations are shown: $\tau_1 = \tau_2$, *i.e.*, the two acyl groups symmetrically situated when looking along the O–I bond (full lines), and $\tau_1 = -\tau_2$, *i.e.*, the two acyl groups eclipsed (broken lines).

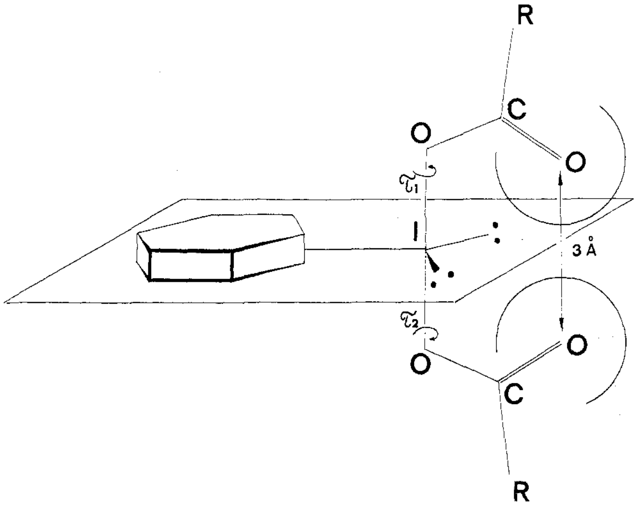


Figure 1. Steric arrangement of the molecule of *I,I*-diacyloxyiodobenzene. The actual conformation with $\tau_1 = \tau_2 = 0$ is shown.

Figure 2 shows in a convincing manner that only the planar conformation IIa with $\tau_1 = \tau_2 = 0$ in which the dipole moment is a maximum is compatible with experiment. The dipole moment method is, of course, unsufficiently sensitive to the presence of other, little populated

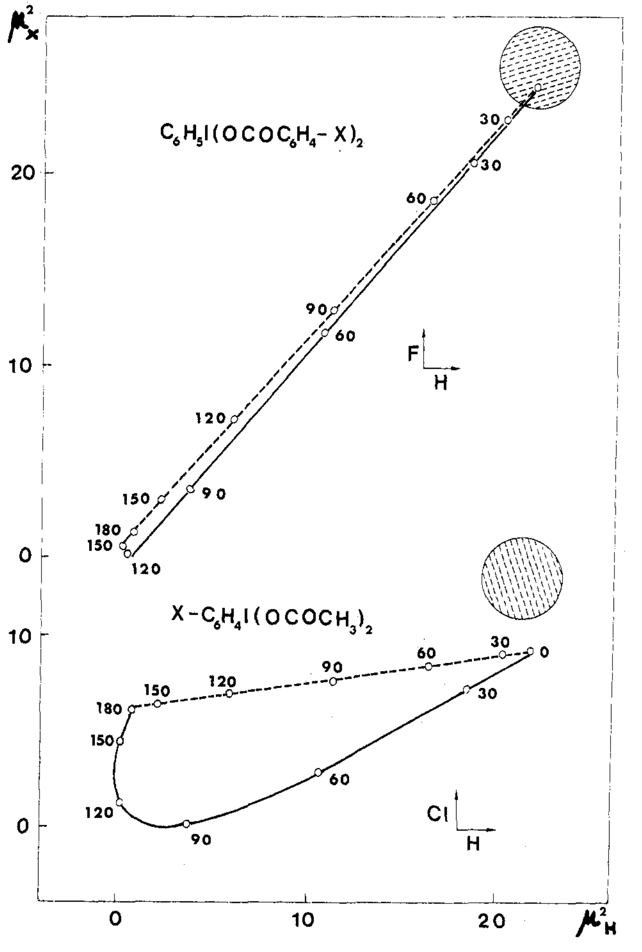
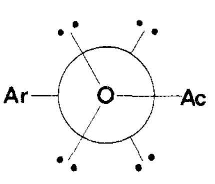
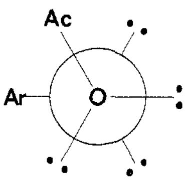


Figure 2. Comparison of dipole moments of *I,I*-diacyloxyiodobenzenes, experimental and calculated for various conformations. Values of μ^2 for the unsubstituted compounds (Ia, Ic) are plotted on the *x* axis, and values for the para derivatives (Ib, Ie) on the *y* axis. Computed values are plotted as a function of the dihedral angle τ = ∠C–I–O–C; the experimental points are shadowed.



IIA



IIB

forms. Neither have such forms been revealed by the nmr spectra of several derivatives from Table I. Within the temperature interval −50 to 55°, which was limited by the solubility and stability of the compounds, no additional signals or shifts were observed. We conclude that the conformation IIa is the prevailing one, or even the only one present.

The result shows that the interaction of the two acyl groups is negligible as anticipated, but it is somewhat surprising with respect to the interactions about the I–O bonds. If we compare the two staggered conformations IIa and IIb in terms of Wolfe's theory[11] of gauche interaction, we would give IIb the preference. It has the bonds I–C and O–C in the gauche positions and in addition there is a double Edward–Lemieux effect[11] (a polar bond between two electron pairs) destabilizing the form IIa. We could conclude that Wolfe's concept is not applicable to dsp^3-hybridized atoms;[12] *e.g.*, the C$_1$–I–O angle of 90° could produce greater repulsion between phenyl and carbonyl groups, not fully compensated by the C–I and I–O bond lengths. Alternatively, the apparent exception could be caused by the presence of acyl groups. On the other hand, we do not find any clear reason why the repulsion between phenyl and carbonyl should exceed that between phenyl and, *e.g.*, alkyl. In addition, disagreement was found even with other compounds[13] where similar arguments do not apply. Hence, there is a more probable explanation that the whole theory,[11] although promising, is not valid without exceptions in its simplified form.

Experimental Section

Materials. *I,I*-Diacyloxyiodobenzenes were prepared by the known procedure[14] and found to be 99% pure by iodometry.

Physical Measurements. The same method was used as previously,[1-5,8] except that the concentration of benzene solutions was lowered to 10^{-3}–10^{-2} *M* owing to the low solubility.

Acknowledgment. Thanks are due to Mrs. M. Kuthanová for technical assistance in physical measurements and to Dr. V. Jehlička for the control.

Registry No.—Ia, 3240-34-4; Ib, 6973-73-5; Ic, 6597-18-8; Id, 51716-26-8; Ie, 38469-36-2; If, 38469-37-3.

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A Facile Method for the Transformation of Ketones into α-Substituted Aldehydes

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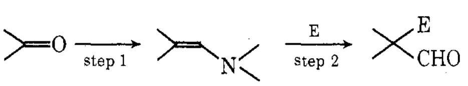
The introduction of dissimilar geminal substituents with concomitant creation of a quaternary carbon center remains a problem in the synthesis of natural products, where fully substituted carbon atoms commonly occur. Recent approaches to geminal alkylation involve the use of the thio-Claisen rearrangement,[2] the base-induced decomposition of methyl dialkylcyanodiazenecarboxylates,[3] the acid-catalyzed rearrangement of cyclopropyl ethers,[4] the [2,3] sigmatropic rearrangement of allylic sulfonium ylides[5] and allylic ammonium ylides,[6] the [2,3] sigmatropic rearrangement of sulfur-stabilized carbenoids,[7] the addition of organocopper or organolithium reagents to α, β-ethylenic sulfur compounds,[8] and the spiro annelation procedure based upon the rearrangements of oxaspiropentanes.[9] Unfortunately, these methods typically involve multistep procedures with the isolation of intermediates. We now wish to report an efficient, one-pot procedure for the one-carbon homologation of ketones to α-allyl aldehydes which may, in principle, be extended to the synthesis of other α-substituted aldehydes and ketones.

It is well known that enamines of aliphatic α-disubstituted aldehydes react readily with electrophilic reagents such as allyl bromide to afford, upon hydrolysis, α-allyl dialkylaldehydes.[10] It occurred to us that the conversion of a ketone with one-carbon homologation to the enamine of an α-disubstituted aldehyde, and the subsequent reaction of the thus formed enamine *in situ* with an appropriate electrophilic reagent (E), would provide an efficacious synthesis of a quaternary carbon atom possessing two substituents of differing functionality (eq 1). We envisioned that a

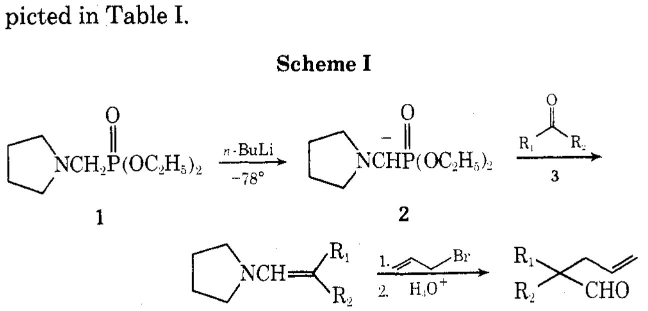


(1)

modified Wittig reaction of a dialkylaminomethylphosphonic acid ester with a ketone would effect the conversion indicated in step 1.[11]

Treatment of diethyl pyrrolidinomethylphosphonate[12] (1) with 1 equiv of *n*-butyllithium in tetrahydrofuran at −78° afforded the anion 2, which reacted smoothly with ketones 3 to give the corresponding enamines 4 (Scheme I). Subsequent reaction of 4 with an excess of allyl bromide and hydrolysis of the intermediate immonium salt afforded the α-allyl aldehydes 5 in good yields. These results are depicted in Table I.

Scheme I



The enamines **4a–e** which were generated are very useful synthetic intermediates which undergo a wide variety of transformations.[13] For example, in a preliminary experi-