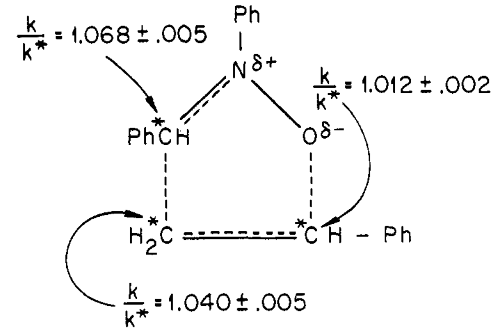
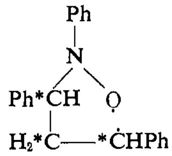


Figure 1.

cyclic transition state such as that symbolized. If the mechanism were to proceed instead through one of the diradicals **1** or **2**, the carbon atoms containing the odd



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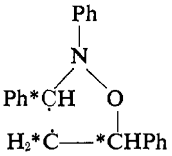

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electrons at the diradical stage would remain sp^2 hybridized, as they were in the reactants, and we would expect two carbon-14 isotope effects for one bond in the formation of **1**, or a single carbon-14 isotope effect[15] for the other bond in the formation of **2**. In the diradical mechanism, however, we would not expect carbon-14 isotope effects during the formation of both bonds except under circumstances requiring *both* **1** and **2** as intermediates, a condition rejected unequivocally by Firestone,[1] who states that nitrones react through diradicals of type **1**. The smallest ($k/k^* = 1.012 \pm 0.002$) of the three ratios shown in Figure 1 is larger than any known *secondary* isotope effect[14] of carbon-14 and, in addition, is not less than unity, but in the normal direction.

It is interesting, but not unexpected,[2,16,17] that the isotope effects exhibited at each of the two carbons involved in making the single C–C bond (Figure 1) are substantially different. The difference in k/k^* for the α-^{14}C- and β-^{14}C-labeled styrenes does not necessarily mean that bond formation associated with the smaller value lags formation of the other bond. The situation is more complicated than this, and has been discussed by Fry[2] and Van Hook[16] in terms of the Bigeleisen–Mayer expressions.[17]

Acknowledgment. We wish to thank Dr. Vernon F. Raaen for independent analyses of certain of the labeled samples.

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(15) For the same reason, no secondary deuterium isotope effects are exhibited at new radical centers during radical additions to olefins: W. A. Pryor, R. W. Henderson, R. A. Patsiga, and N. Carroll, *J. Amer. Chem. Soc.*, **88**, 1199 (1966); M. Matsuoka and M. Swarc, *ibid.*, **83**, 1260 (1961); M. Feld, A. P. Stephani, and M. Swarc, *ibid.*, **84**, 4451 (1962).

(16) W. A. Van Hook, "Isotope Effects in Chemical Reactions," American Chemical Society Monograph No. 167, C. J. Collins and N. S. Bowman, Ed., Van Nostrand Reinhold, New York, N. Y., 1971, Chapter 1.

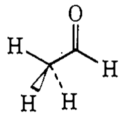
(17) J. Bigeleisen and M. Goeppert-Mayer, *J. Chem. Phys.*, **15**, 261 (1947); J. Bigeleisen, *ibid.*, 17, 675 (1949).

Orbital Factors and Asymmetric Induction

Sir:

We suggest that, *at least partially*, orbital factors may be responsible for asymmetric induction. An asymmetric center induces a hybridization change in a vicinal unsaturated system. A dissymmetric π-electron cloud results and the reactivity of the two diastereotopic faces toward an ionic reagent will not be the same.

Ab initio (STO-3G) calculations[1] have been performed for the following molecules: acetaldehyde, propanal, 2-chloropropanal, butan-2-one, butanal, and ethyl glyoxylate. Two fixed conformations are considered for acetaldehyde (**1** and **2**), propanal (**3** and **4**), 2-chloropropanal (**5** and **6**), butan-2-one (**7** and **8**), four fixed conformations for butanal (**9**–**12**), and one for ethyl glyoxylate (**13**). Standard geometries are used throughout.



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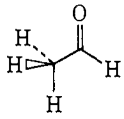

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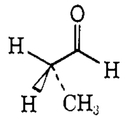

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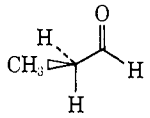

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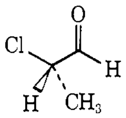

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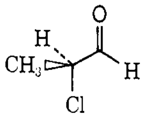

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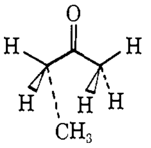

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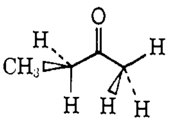

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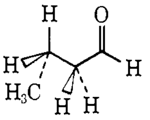

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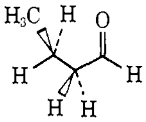

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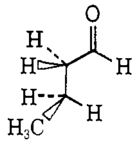

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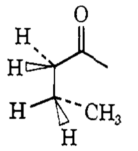

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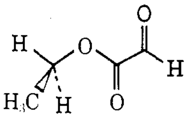

13

The principal results are the following. (1) A σ–π mixing occurs in the carbonyl group of compounds **3**–**13**. For example, whereas the π orbital of acetaldehyde contains only 10^{-10} 2s character, the same orbital in **3** incorporates up to 10^{-3} 2s character. In some other orbitals, the σ–π mixing is even greater. Thus, in the 11th occupied molecular orbital (MO) of **3**,[2] the coefficients of the carbonyl group are: 0.354 (2s) and 0.104 ($2p_z$) for the oxygen atom and −0.160 (2s) and 0.134 ($2p_z$) for the carbon atom.

(2) As anticipated, the π-electron cloud becomes dissymmetric: the electron density is greater on one diastereotopic face than on the other. It seems reasonable to suppose that a nucleophilic reagent would attack preferentially on the positive face. An aldehyde may react under several conformations. In accordance

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(1) It is known that *ab initio* calculations with the minimal basis set give fairly good results for charge distribution; the calculated dipoles are usually smaller than the experimental values but the general trends are well reproduced. See, for example, W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2191 (1970); W. J. Hehre, L. Radom, and J. A. Pople, *ibid.*, **94**, 1496 (1972).

(2) The numbering starts from the lowest MO.

with the Curtin–Hammett principle,[3] we also assume that the conformer having the greatest dissymmetry between the two faces will give the greatest relative ratio of diastereoisomers. Thus, for example, although **3** is more stable than **4** in the ground state, the latter might play a predominant role as far as asymmetric induction is concerned.

As can be seen from Table I, our method predicts the same stereochemical course as Cram's rules[4] for propanal, butan-2-one, and butanal, as Cornforth's rule[5] for 2-chloropropanal, and as Prelog's rule[6] for ethyl glyoxylate. We would like to emphasize *that steric factors have been completely neglected* in our reasoning. Also noteworthy is the fact that our "most reactive conformers" are those adopted in Cram's rules.

Table I

Compd	Rel energies in the ground state[a]	Charge density on carbon atom[b]	Direction of preferential attack[c]
3	0	-1.0441×10^{-3}	F
4	0.97	1.9537×10^{-3}	R predominant term
5	0.89	-1.5025×10^{-3}	F
6	0	1.8103×10^{-3}	R predominant term
7	0.07	-1.1739×10^{-3}	F
8	0	1.9805×10^{-3}	R predominant term
9	0.39	-2.6641×10^{-4}	F
10	0.75	-7.9986×10^{-5}	F
11	2.09	2.5184×10^{-4}	R
12	0	-1.4545×10^{-3}	F predominant term
13		$+5.7762 \times 10^{-4}$	R

[a] In kcal/mol. [b] A + sign means a negative charge above the carbonyl plane, *i.e.* front side, and a − sign a negative charge below the same plane, *i.e.* rear side. [c] F = front side, R = rear side.

(3) It remains to be seen whether this hybridization effect is dominant. The energies of the "supermolecule" formed by a molecule of propanal and a hydride ion located on the vertical of the carbon atom at a distance of 1.5 Å have been determined by *ab initio* calculations. We found that in both conformers **3** and **4**, attack on the hydrogen side is preferred to attack on the methyl side by 4.6 and 4.3 kcal/mol, respectively. Thus, in effect, conformer **3** gives rise to one diastereoisomer whereas **4** gives rise to the other. Interestingly, the "right" isomer deriving from **4** is preferred to the "wrong" isomer deriving from **3** by 0.38 kcal/mol. This value is of the order of magnitude of the asymmetric induction caused by the difference between a hydrogen and a methyl group.[7]

Although those numbers are not to be taken at their face values, they show clearly that orbital factors cannot be neglected in comparison with steric factors. It seems reasonable to consider that asymmetric induction is controlled by both factors.[8]

When the distance between the reaction center and the inductive center is increased, both orbital and steric factors decrease. However, the rate of decrease of the former seems to be relatively small (*cf.* Table I) while it is usually considered that steric repulsion diminishes quite rapidly.[9] It seems then that at longer distances, orbital factors might be more effective than steric factors.

Acknowledgments. We thank Professors L. Salem and H. B. Kagan for many helpful suggestions, W. J. Hehre for the *ab initio* program, and M. Fétizon for his interest. A generous computer time donation by the C.N.R.S. is gratefully acknowledged.

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(3) D. Y. Curtin, *Rec. Chem. Progr.*, **15**, 111 (1954).

(4) D. J. Cram and F. A. Abd Elhafez, *J. Amer. Chem. Soc.*, **74**, 5828 (1952); T. J. Leitereg and D. J. Cram, *ibid.*, **90**, 4011 (1968).

(5) J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 112 (1959).

(6) V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953); *Bull. Soc. Chim. Fr.*, 987 (1956).

(7) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood-Cliffs, N. J., 1971, p 92.

(8) This hybridization effect may also intervene in the so-called "product development control."

(9) The repulsion energy is usually approximated by $\exp(-ar)$ or by r^{-12} (E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 449).

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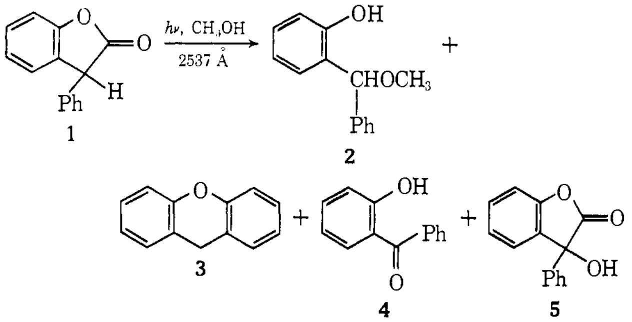
Tautomeric Control of the Photochemistry of 3-Phenylbenzofuran-2-one[1]

Sir:

The photochemical reactivity of β,γ-unsaturated lactams[2] and lactones[3,4] is a subject of current interest. These compounds undergo a facile photodecarbonylation producing unstable *o*-quinyl methide intermediates which can be trapped by protic solvents. Similar decarbonylation processes have been observed to occur with excited sultones,[3] carbonates,[3] and related substituted 2-indanones.[5] We now wish to report some fascinating variations to this behavior in the 3-phenylbenzofuran-2-one (**1**) system. Our observations indicate that this system displays a remarkable dependence on the tautomeric composition of **1** in solution.

Irradiation of **1**[6] in methanol with a low-pressure mercury arc (2537 Å) led to the formation of four major products (**2**–**5**) whose relative yields varied as a function of the reaction conditions. Careful exclusion of oxygen from photolyzed solutions resulted in the formation of only *o*-hydroxybenzhydryl methyl ether (**2**) and xanthene (combined yield 40%). The ratio of **2**:**3** de-



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(1) Photochemical Transformations of Small Ring Heterocyclic Compounds. L. For part XLIX see A. Padwa and J. Smolanoff, *J. Chem. Soc., Chem. Commun.*, 342 (1973).

(2) M. Fischer and F. Wagner, *Chem. Ber.*, **102**, 3486, 3495 (1969).

(3) O. L. Chapman and C. L. McIntosh, *Chem. Commun.*, 383 (1971).

(4) A. Yogev and Y. Mazur, *J. Amer. Chem. Soc.*, **87**, 3520 (1965).

(5) G. Quinkert, W. W. Wiersdorff, M. Finke, and K. Optiz, *Tetrahedron Lett.*, 2193 (1966).

(6) A. Bistryzycki and J. Flatau, *Chem. Ber.*, **28**, 989 (1895).