10 hr, gave **3** in 71% yield on treatment with sodium benzoate in DMF at 100°.

On the basis of these findings, it is concluded that the principal route to **3** occurs by way of preliminary proton abstraction at C-4′ of **1c** to give its anionic conjugate base followed by unimolecular loss of mesylate anion from the conjugate base. This, then, is the E1cB mechanism[12] which is standard for the formation of α,β-unsaturated carbonyl compounds.[13] The same mechanistic interpretation may be applicable to the formation of **3** from **2** with the observed differences in the rate of formation of product from the corresponding anionic intermediate a consequence of the relatively poorer leaving group character of the thyminyloxy residue (in **2**) *vis-à-vis* mesylate anion.

The introduction of 3′,4′ unsaturation into **3** is accompanied by a hypsochromic shift of *ca.* 10 nm in the ultraviolet absorption $\lambda_{\max}$, which reverts to the value(s) characteristic of pyrimidine nucleosides, including the 2′,3′-unsaturated derivatives, on (selective) reduction of the carboethoxy function to **4**. Moreover, the 3′,4′-unsaturated nucleosides show a negative Cotton effect from which it may be concluded that these derivatives, like the 2′,3′-olefinic nucleosides,[14] but unlike the normal pyrimidine β-nucleosides, have the *syn* conformation in aqueous solution. Molecular models indicate the possibility of an effective overlap of π orbitals comprising the 2-carbonyl of the aglycon and the conjugated unsaturation of the sugar where **3** is in a *syn* conformation. As a consequence of orbital overlap, an anhydronucleoside-like structure would be approximated in an excited state and thereby account for the observed hypsochromic shift in **3**. This same interaction, though obviously less important in **4**, may also serve to explain the diamagnetic shift of H-6 (70–100 Hz) observed in the nmr spectra of **3**, **4**, and **5** relative to the parent structure.

On the other hand, there is little to suggest a steric barrier in the 3′,4′-unsaturated nucleosides that would restrict rotation about the glycosyl–nitrogen bond. Consequently, it is possible that in the ground state these structures exist in the opposite conformation. Moreover, molecular models indicate that in the *anti* conformation H-6 lies directly above the plane of the 3′,4′ double bond which would account for the observed shielding effect. By contrast, a corresponding anisotropic effect in the pyrimidine 2′,3′-unsaturated nucleosides is not indicated and apparently explains the normal chemical shift of H-6.

The possibility that the rotameric composition of a nucleoside, such as **3**, can differ in two low-lying energy states, which is suggested by the spectral data and which hetetofore has not been considered, has significant biochemical and biophysical implications.

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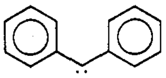
Steric Control in the Reaction of Diphenylcarbene with Olefins. Thoughts on the Structure of Diphenylcarbene in Solution[1]

Sir:

The development of the chemistry of triplet carbenes dates from the report of Etter, Skovronek, and Skell[2] that diphenylcarbene (**1**) added nonstereospecifically to olefins. These authors suggested a structure for **1** in which a central, sp-hybridized carbon atom was flanked by two perpendicular phenyl rings. Closs and Closs[3,4] later showed that addition was largely stereospecific and that the olefinic products of an abstraction–recombination process were the major compounds produced in the reaction. Nevertheless, the properties of diphenylcarbene have been generally regarded as both well known and archetypal of triplet carbenes. Neither is the case. Reports on the chemistry of **1** are rare and fragmentary, and the hydrogen abstraction–recombination process is not the path generally followed by triplets.[5–7]

The problem of the strangeness of **1** is accentuated by a comparison of properties with those of the related fluorenylidene (**2**) which reacts with olefins to give mainly cyclopropanes.[6] Abstraction–recombination is always a minor process. Esr spectroscopy on **1** and **2** initially indicated that a quite similar geometry was attained by both, at least at low temperature in rigid medium. In particular, both were bent, and **1** was thought to possess a structure in which the rings were more coplanar than perpendicular.[8] The question of why two such structurally similar molecules should react so differenlty was puzzling indeed.[9]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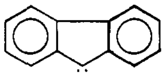
2

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[9] It has been pointed out[4] that **1** and **2** differ in their electronic structures, **1** being odd, alternant and **2** not.

More recently, structural evidence derived from endor experiments on **1** in crystalline 1,1-diphenylethylene has come forth which shows that, while **1** is bent, the rings are not very nearly coplanar.[10] The angle between the plane of each ring and the plane determined by the methylene and immediately adjacent carbons is 54°, and thus the structure is quite twisted.

We report here experiments which demonstrate that the mode of reaction of **1** with olefins is most sensitive to olefin structure. Either cycloaddition to give cyclopropanes or abstraction to give olefins can dominate the reaction. We feel that these results are well reconciled with a structure of **1** in solution similar either to that originally postulated by Skell[2] or to that shown to obtain in crystalline diphenylethylene,[10] but not with a structure similar to that of fluorenylidene.[9]

Almost any combination of cycloaddition and abstraction–recombination can be achieved simply by varying the structure of the olefin. As found by Closs and Closs,[3,4] reaction with the 2-butenes is primarily by abstraction. When the more substituted olefins are used abstraction becomes the sole path followed.[11] However, when the olefin contains a terminal methylene the pattern changes and cyclopropane formation becomes dominant. Two factors must influence this change in mechanism. One is of steric origin and simply reflects the reduced ease of entry of triplet **1** to the π electrons of the more highly substituted olefins. The other factor is electronic and involves the increased stability of the radicals formed from the di-, tri-, and tetramethylethylenes. We feel that the first factor is of more importance as methylenecyclohexane reacts primarily by cycloaddition. This parallels the behavior of isobutylene which has no alkyl groups which stabilize the allyl radical produced by abstraction. Were the electronic effect the more important, we would have expected methylenecylcohexane to react primarily by abstraction.

Table I. Mode of Reaction of Diphenylcarbene with Olefins[a]

Olefin	Cyclopropane	Abstraction–recombination
2,3-Dimethyl-2-butene	0	100
2-Methyl-2-butene	$\leqslant 8$	$\geqslant 92$
trans-2-Butene	22	78
3-Methyl-1-butene	52	48
Methylenecyclohexane	87	13
Isobutylene	100	0
Propylene	100	0

[a] Products were identified by nmr spectroscopy and elemental or mass spectral analysis. In the cases where we note 0 or 100% of one kind of product we were unable to detect any peaks which might correspond to the missing products, either in crude or purified material. Traces would have escaped us, but a few per cent could have been seen.

If the notion is accepted that steric factors determine the mode of reaction of **1**, then it becomes difficult to accept similar structures in solution for **1** and **2**. Compound **2** is not so influenced, but reacts in each instance to give cyclopropane.[6,9] A structure in solution approximating that originally proposed by Skell[2] or recently found to obtain in crystalline medium[10] seems appropriate to us.

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[11] Analysis of the cyclopropanes produced from **1** and the 2-butenes showed that the stereochemical relationship of the methyl groups in the olefin was largely maintained in the cyclopropane, although the exact result was temperature dependent.[4] This was attributed to reaction of singlet **1** in equilibrium with the more stable triplet which was thought to produce the compounds formed by abstraction–recombination.[4] Our work indicates that with the less substituted olefins either both spin states are giving cyclopropane or the rate of reaction of the singlet is enhanced in some way. We prefer the former explanation, but resolution of this point must await the results of work currently in progress.

[12] Alfred P. Sloan Research Fellow, 1967–1969.

Hydrogen Abstraction by Electronically Excited 1,1-Diphenylethylene

Sir:

The photoreduction of ketones in hydrogen–donating solvents has been thoroughly investigated.[1] The reactivity of the carbonyl group with respect to hydrogen abstraction depends dramatically on the configuration of the lowest lying triplet state.[2] The reactivity of n,π^* triplets approximates that of alkoxy radicals,[3] whereas hydrogen abstraction by π,π^* triplets is not observed or occurs at significantly lower rates.[4] The higher unpaired electron density on oxygen appears responsible for the greater reactivity in the former state.

In contrast to ketones, examples of hydrogen abstraction in the direct and sensitized photolysis of olefins are rare and are confined almost exclusively to cyclopentanes.[5] The intermediacy of the triplet state seems likely in these cases. Competitive decay processes are thought to be responsible for the general inability of triplet olefins to abstract hydrogen.[2]

In an earlier paper[6] we reported the formation of 2-(1,1-diphenylethyl)-2H,5,6-dihydropyran and 4-(1,1-diphenylethyl)-2H,5,6-dihydropyran during the photolysis of 1,1-diphenylethylene (DPE) in 2,3-dihydropyran. We postulated that these products occurred *via* allylic hydrogen abstraction by the π,π^* DPE triplet followed by free-radical coupling reactions. Subsequently, it has been reported that 9,9′-bifluoroenylidene abstracts hydrogen during direct and sensitized photolysis.[7] We were therefore motivated to conduct a more detailed investigation of the photolysis of DPE.

Irradiation of DPE in 2-propanol at 2537 Å produced 2-methyl-3,3-diphenyl-2-butyl alcohol, 2,2,3,3,-tetraphenylbutane, and 2,3-dimethyl-2,3-butanediol in molar ratio 1:2.1:2.7, in addition to small quantities of

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