of **3** to a solution of 1.46 g of $AgBF_4$ and 1 ml of cyclohexene in 10 ml of dry CH_2Cl_2 at −60° and slowly warming the mixture to room temperature (no cycloaddition occurred at −60°). After filtration of AgCl (1.1 g, *ca.* 100%) and evaporation of the solvent, a residue was obtained which contained essentially the adduct **8** (>90%) contaminated with *N*,*N*-dimethylisobutyramide (<10%). Recrystallization from chloroform–ether gave pure **8** in 83% yields. The cycloadducts obtained with various olefins and dienes are summarized in Table I. They have been characterized by ir and nmr spectroscopy. The structures were confirmed by hydrolysis of the adducts to the corresponding cyclobutanones.

Several characteristic features of these cycloadditions should be mentioned: (1) Reactions with conjugated dienes give only the (2 + 2) cycloadducts; no Diels–Alder adducts are observed. Thorough examination of the crude reaction mixtures showed that *N*,*N*-dimethylisobutyramide was the sole side product of the reaction, resulting probably from the hydrolysis of unreacted **4** during work-up. (2) With *cis*- or *trans*-piperylene, the addition occurred at the less-substituted double bond (**6** and **7**) in the same manner as the corresponding reactions with ketenes.[6] (3) *cis*- and *trans*-cyclooctenes reacted stereospecifically, giving isomeric adducts (**9** and **10**, respectively). They showed distinct ir and nmr spectra. However, the configurational assignments were more readily made on the corresponding ketones. *cis*-10,10-Dimethylbicyclo[6.2.0]decan-9-one (**15**) obtained from the hydrolysis of **9** showed indeed the two net ir absorptions at 1462 and 1450 cm^{-1} which appear to be typical for an eight-membered ring cis fused to three- or four-membered rings.[7] The protons of the *gem*-dimethyl groups gave two singlets (δ 1.23 and 0.93). On the other hand, *trans*-10,10-dimethylbicyclo[6.2.0]decan-9-one (**16**) obtained from the hydrolysis of **10** showed only one signal for the six methyl protons at δ 1.08. Finally, **15** and **16** were compared with authentic samples prepared from the (ketene + olefin) reactions.[8] For both cycloadditions the degree of intercontamination was checked by hydrolyzing the crude salts **9** or **10** under controlled conditions[9] and examining the resulting mixtures by vpc; less than 5% intercontamination was observed. These data appear fully consistent with the mechanistic hypothesis of a $({}_{\pi}2_s + {}_{\pi}2_a)$ concerted cycloaddition.

Finally, the synthetic utility of the reaction should be emphasized; it is indeed suggested that tetraalkyl-substituted keteneimmonium ions should be superior to the corresponding ketenes for the building of four-membered rings by (2 + 2) cycloadditions. The conditions are very mild, the yields are excellent, and the starting material is cheap and readily available. Clearly more synthetic uses of these reactions have to be expected; our more recent studies on the cycloadditions of keteneimmonium ions to other substrates such as acetylenes or imines will be reported later.

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[9] The hydrolysis has been shown to cause epimerization of the salts 9 or 10. Short reaction times and buffered solutions were used to prevent isomerization. However, it is highly probable that the small amount of intercontamination still resulted from the hydrolysis.

Characterization of the Triplet State of Aromatic Esters. Electron Spin Resonance Spectrum of the Triplet State of Substituted Methyl Benzoates[1]

Sir:

In comparison with the many, extensively studied photochemical reactions of aldehydes and ketones, the carboxyl carbonyl of esters is, in general, much less reactive and has received correspondingly little attention. Since many of the reactions of the carbonyl group are known to involve the n,π^* excited state, the lack of reactivity of the carboxyl carbonyl has been taken as an indication that in these molecules the lowest states have π,π^* character. Such generalizations are being challenged with increasing frequency and, in fact, two groups of workers have recently reported efficient photochemical reactions from the triplet state of some benzoate esters and the character of the lowest excited triplet state of these molecules was opened to question.[2,5] We report here electron spin resonance and phosphorescence emission spectral data (Table I) which characterize the lowest triplet state of the benzoate esters studied as π,π^* (that is, a perturbed $^3B_{1u}$ state of benzene). The zero-field splitting parameter (D) indicates that a considerable spin density is distributed onto the carboxyl group and thus the carboxyl carbonyl oxygen should have some radical reactivity. The results also give an indication of two other correlations: (1) there is a relationship between the zero-field splitting parameter (D) and the triplet energy (E_T); (2) the zero-field splitting parameters vary with substitution in a way which may indicate differing contributions of the diallyl radical and paraquinoidal structures of the triplet (*vide infra*).

The phosphorescence emission of all the esters studied (with the exception of dimethyl phthalate where interaction of the adjacent carboxyl groups offers a plausible explanation for anomalous behavior) had

[1] Contribution No. 28 from the Photochemistry Unit.

[2] Alkyl benzoate esters undergo the Norrish type II cleavage with very low quantum yield.[3] The suggestion has been made that the inefficiency is due mainly to reversal of the hydrogen-transfer step.[3a] This seems untenable with the expected behavior of the 1,4 diradical; alternatively, vibronic coupling of the carboxyl group with the γ-hydrogen[4] should be considered.

[3] (a) J. A. Barltrop and J. D. Coyle, *J. Chem. Soc. B*, 251 (1971); (b) M. Day and D. M. Wiles, *Can. J. Chem.*, **49**, 2916 (1971); (c) H. Morrison, R. Brainard, and D. Richardson, *Chem. Commun.*, 1653 (1968).

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[5] Benzoate esters substituted with electron-withdrawing groups (Table I; 2, 4, 5, 7, and 8) undergo photocycloaddition to 1,1-diphenylethylene.[6a] The authors first proposed a mechanism involving the n,π^* triplet state of the ester.[6a] This was later withdrawn in favor of an exciplex pathway[6b] which is consistent with the results reported here.

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Table I. Some Spectral Characteristics of Substituted Benzoate Esters[a]

Ester	τ_{phos}, sec	Triplet energy,[b] kcal/mol	Zero-field splitting: D/hc, cm^{-1} [c]	E/hc, cm^{-1} [d]	D/hc^*,[e] cm^{-1}
Methyl benzoate (**1**)	2.7	77.9	0.133 ± 0.001	0.011 ± 0.001	0.134 ± 0.002
Methyl *o*-cyanobenzoate (**2**)	2.9	73.4	0.134 ± 0.002	0.030 ± 0.002	0.142 ± 0.003
Methyl *m*-cyanobenzoate (**3**)	3.4	76.2	0.141 ± 0.003	0.021 ± 0.005[g]	0.145 ± 0.006
Methyl *p*-cyanobenzoate (**4**)	2.4	72.0	0.127 ± 0.001	0.007 ± 0.001	0.126 ± 0.002
Dimethyl phthalate (**5**)	0.7	*f*	0.121 ± 0.003	0.034 ± 0.003	0.140 ± 0.005
Dimethyl isophthalate (**6**)	2.6	76.9	0.136 ± 0.002	0.036 ± 0.002	0.149 ± 0.003
Dimethyl terephthalate (**7**)	2.4	72.9	0.122 ± 0.001	0.005 ± 0.001	0.122 ± 0.002
Trimethyl 1,3,5-benzenetricarboxylate (**8**)	2.7	76.5	*h*		0.146 ± 0.002

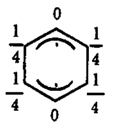
[a] Ethanol–methanol (4:1), *ca.* 77°K. [b] Taken as the maximum of the 0–0 band. [c] $D = {}^1/_2 g\beta(H_{2z} - H_{1z}) - E^2(H_{2z} - H_{1z})/4g\beta H_{2z}H_{1z}$. [d] $(D \mp 3E) = g\beta(H_{2\mu} - H_{1\mu}) - (D \pm E)^2/8g\beta[(H_{2\mu} - H_{1\mu})/H_{2\mu}H_{1\mu}]$ (upper sign refers to $\mu = x$ and lower sign to $\mu = y$). [e] $D^* = (D^2 + 3E^2)^{1/2}$. [f] No distinctive vibrational fine structure (*ca.* 71 kcal/mol). [g] X and Y lines not observed; thus E was obtained from the Z lines plus the $\Delta M_s = 2$ line. [h] We have been unable to determine these values because of the reactivity of this ester upon irradiation. We attribute the reactivity to formation of the relatively stable radical anion of this ester.

similar vibrational structure[7] and lifetime.[8] The triplet energy of methyl benzoate is the highest of the esters studied; however, the substituent effect on triplet energy cannot be rationalized as being entirely a function of electron-withdrawing ability (compare **1**, **6**, and **8**) as is expected for an n,π^* state. The variation reflects the capability of the substituent(s) to delocalize the nonbonding electrons of a π,π^* triplet. Thus, the phosphorescence spectra are consistent with assignment of a perturbed π,π^* state for the lowest emitting triplet of these esters.[9]

Further support for these assignments comes from an analysis of the zero-field splitting parameters gleaned from the esr spectrum.[10] First we made certain the esr signal derived from the emitting triplet by comparing the decay of the $\Delta m = 2$ transition [ester ($\tau_{\Delta m=2}$, sec), **1** (3.0), **4** (2.6), and **7** (2.6)] with the phosphorescence lifetime. The zero-field splitting parameters (Table I) show a reasonable variation expected for a perturbed π,π^* triplet. There is no indication that the n,π^* triplet has been shifted to lowest energy by the electron-withdrawing substituents.

The more delocalized the nonbonding electrons of the triplet, the further they can get from one another, and thus, the smaller the D value. It seemed reasonable to expect that the smaller the D value the lower the triplet energy (assuming a greater influence due to electron delocalization on the excited state than on the ground state).[10h,i] Considering the methyl cyanobenzoate derivatives and the diesters (unfortunately, only two points), the expected trend is observed within each series; however, there is little correlation between D and E_T for all the esters studied. It may be possible to define more clearly the factors which influence triplet energy when additional derivatives have been studied.

Molecular orbital theory predicts two configurations, the "diallyl radical" I and "*p*-quinoidal" II structures, for the lowest unoccupied and highest occupied orbitals of benzene. (The numbers refer to the approximate normalized electron density at each position.) In the absence of substituents these two are degenerate; however, substituents can cause a removal of the degeneracy. A similar situation exists in the anion and cation radicals of benzene where substituents cause a removal of the degeneracy of the two states.[11]



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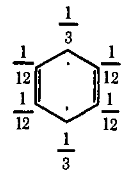

II

Clearly, an electron-withdrawing substituent will favor the *p*-quinoidal structure since electron density is best delocalized in that state. This is also true for para disubstitution. However, for ortho or meta disubstitution, the diallylic structure should be the most stable. We have calculated D and E values (Table II) for these two structures of the benzene triplet state using an SCF wave function.[12,13] Note that although the D values are similar, a large difference (in

Table II. Calculated Zero-Field Splitting Parameters for the Benzene Triplet

Structure	$\|D\|$, cm^{-1}	$\|E\|$, cm^{-1}
Diallyl radical (I)	0.1914[a]	0.0060[a]
p-Quinoidal (II)	0.0985	0.0054

[a] Reference 13.

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(7) (a) The gross features of the emission were similar to those of the methyl-substituted benzenes (R. V. Nauman, Ph.D. Dissertation, University of California, Berkeley, Calif., 1947); (b) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 96.

(8) The long lifetime is inconsistent with an n,π^* assignment; see, for example, ref 7b, p 246.

(9) Similar results were reported for related esters (ref 3a) and for benzoic acid and its salts (H. J. Maria and S. P. McGlynn, *J. Chem. Phys.*, **52**, 3399 (1970)).

(10) Esr is proving to be a powerful tool for assigning triplet character: (a) for a review with early references see; C. Thomson, *Quart. Rev., Chem. Soc.*, 45 (1967); (b) T.-M. Chen, *Photochem. Photobiol.*, 12, 81 (1970); (c) B. Smaller, E. C. Avery, and J. R. Remko, *J. Chem. Phys.*, **46**, 3976 (1967); (d) A. A. Lamola, *ibid.*, **47**, 4810 (1967); (e) D. R. Graber, M. W. Grimes, and A. Hang, *ibid.*, **50**, 1623 (1969); (f) S. Hotchandani and A. C. Testa, *ibid.*, **54**, 4508 (1971); (g) C. H. J. Wells, A. Horsfield, and J. Paxton, *Chem. Commun.*, 393 (1969); (h) J. S. Brinen and M. K. Orloff, *Chem. Phys. Lett.*, **1**, 276 (1967); (i) R. F. Riley and J. Rosenthal, *J. Chem. Phys.*, **50**, 1034 (1969).

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(13) For a triplet with exclusively the diallyl radical structure I, the measured values of D and E would require a change in axis in order to satisify the condition $|E| \leq |D|/3$. The calculated values then become $|D| = 0.1914$ and $|E| = 0.0060$. See also M. S. de Groot, I. A. M. Hesselmann, and J. H. van der Waals, *Mol. Phys.*, **16**, 45 (1969).

magnitude) is predicted for E between the two cases.[13] In particular, E is predicted to increase as the proportion of the diallyl radical structure increases.

The zero-field splitting parameters listed in Table I allow the esters to be divided into two categories. The mono and para substituted derivatives have smaller E values than do the ortho and meta derivatives. This is consistent with the triplet of the mono and para derivatives having a larger contribution of the p-quinoidal structure while the triplet of the ortho and meta derivatives assumes more of the diallyl radical structure. The variation of E for the mono and para substituted derivatives attests to the sensitivity of this parameter to asymmetry since the values decrease in the order **1** > **4** > **7**. Calculations which include the effect of the substituent and nonplanar structures are in progress.[14]

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(14) N. C. Baird, unpublished results.

(15) On leave from the University of Aarhus, Aarhus, Denmark.

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A Facile Method for Alkylation and Alkenylation of Heterocycles

Sir:

Despite the plethora of synthetic methods available for the introduction and manipulation of functional groups in heterocyclic systems,[1] there exists no general method for alkylation or alkenylation on carbon. We describe in this communication a facile procedure for the introduction of alkyl and alkenyl groups at positions activated toward nucleophilic substitution reactions, utilizing as starting materials halo-substituted heterocycles, which number among the most readily accessible derivatives of heterocyclic systems.

Existing methods for the direct introduction of alkyl substituents into heterocyclic nuclei appear to be severely limited in scope; these include reactions of parent heterocycles or their N-oxides with Grignard or organolithium reagents,[2-5] electrophilic alkylation of *in situ* produced dihydro derivatives,[6] the reaction of chloro derivatives with salts of active methylene compounds,[7-9] the reaction of certain parent heterocycles with methylsulfinyl carbanion to give methylated derivatives,[10] the reaction of pyrazines with aldehydes and ketones in the presence of a solution of an alkali or alkaline earth metal in liquid ammonia,[11] the reaction of protonated heteroaromatic bases with alkyl radicals,[12,13] and the Reissert reaction[14,15] and certain specialized variations thereof,[16,17] which seem to be largely restricted to quinolines, isoquinolines, and phenanthridines.

Our new procedure involves treatment of a chloroheterocycle with 2 equiv of an appropriate Wittig reagent. The new ylide which is formed *in situ* is either hydrolyzed to give an alkyl-substituted heterocycle, or subjected to the normal reaction of Wittig reagents with carbonyl compounds to elaborate an olefinic side chain.[18] Typical conversions are summarized in Tables I and II.

The general experimental procedure is as follows. To a suspension of the appropriate phosphonium salt (2.2 equiv) in anhydrous 1,2-dimethoxyethane (DME) under dry nitrogen at −30 to −35° was added 2.2 equiv of n-butyllithium in hexane, the reaction mixture was stirred for 1 hr, and the appropriate chloro-substituted heterocycle (1 equiv) was added. The reaction mixture was allowed to warm to room temperature and was then either stirred under reflux (for unreactive chloro derivatives) or at room temperature (for reactive chloro derivatives).

For hydrolysis to alkyl-substituted heterocycles, sodium carbonate (1 equiv) in water was added, and the mixture was refluxed for 3 hr, evaporated under reduced pressure, and then worked up by either of the two following procedures. (a) The mixture was suspended in chloroform or ether and extracted with dilute aqueous acid, the combined aqueous layers were made alkaline with sodium hydroxide, and the resulting mixture was then extracted with ether. The combined ether extracts were dried and evaporated and the product was purified by distillation or recrystallization. (b) The mixture was extracted with hot ether, the combined ether extracts were concentrated under reduced pressure, and the residual material was treated with an excess of mercuric chloride in 25% aqueous ethanol. The precipitated salt was then collected by filtration and washed, and the heterocycle was freed by treatment of the mercuric chloride salt with hydrogen sulfide followed by aqueous base.

For conversion to alkenyl-substituted heterocycles, the above reaction mixture was treated directly with an excess (about 4 equiv) of the appropriate aldehyde or ketone in anhydrous DME, and then stirred for 24 hr at room temperature. Excess solvent was removed by

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