for the synthesis of the Young peptide, ethyl benzoylleucylglycinate (**3**), and the Anderson peptide, ethyl benzyloxycarbonylglycylphenylalanylglycinate (**4**), are given in Table I.

The most striking result of Table I is the isotope effect of unity observed for all benzoylleucine couplings. Since methyl benzoyl-L-leucinate is observed to racemize in methanol containing potassium methoxide with an isotope effect of 3.8, one can conclude that appreciable isotope effects should be observed for the simple enolization mechanism; the oxazolone route, A, therefore appears to account for the major part of racemization observed for benzyolleucine couplings. It should be noted that two of the cases of Table I appeared as likely candidates for simple enolization: method 1i involves intermediacy of a catechol monoester anion, for which racemization *via* an internal proton transfer may now be excluded; method 2 involves conditions (tertiary amine, high conjugate acid concentration) for which the normal specific base catalysis mechanism is suppressed.[2b] We now attribute the racemization observed with method 2 to general base catalyzed oxazolone formation.

Isotope effects observed for the Anderson couplings are perhaps within experimental error of unity for methods 1ii and 1iii,[7] 3, and 4iv, but reflect substantial isotopic selectivity for most of the azide couplings. Before the oxazolone route can be excluded for these cases, it must be established that for the Anderson oxazolone, 2-benzyloxycarbonylaminomethyl-4-benzyloxazol-5-one (**5**), under the reaction conditions 4i–iii, k_1 in fact greatly exceeds k_2.

In accord with the study of Goodman and McGahren[8] L-**5**[9] was found to react with ethyl glycinate under condition 4i to yield tripeptide which was only 54% racemic, and an isotope effect of *ca.* 3.5 was observed; under condition 4iii the corresponding numbers were 80% and *ca.* 5–7. On the other hand, complete racemization ($k_H/k_D = 1.0$) was observed with **5** under conditions 4ii or 4iv. The isotope effect in case 4ii is therefore inexplicable by the oxazolone mechanism, and in the presence of triethylamine the acyl azide of **2** in ether must racemize largely by the direct enolization mechanism. The evidence does not permit clear-cut assignment of mechanism for the three remaining azide cases, but they seem best interpreted as involving contributions from both mechanisms.

Thus with the benzamido group (or its anion) the oxazolone pathway appears to be the major contributor to racemization. With a less nucleophilic peptide amide the competition is more delicately balanced, and in at least one azide coupling direct enolization is competitive.

---

ethylamine; the sample was mixed with Z-Gly-L-[*3*-^{3}*H*]PheOH and diluted with unlabeled DL.[4]

(6) Though not strictly valid for all mechanistic cases, calculations of Table I assume that $k_H/k_D = ([^3H_{prod}]/[^{14}C_{prod}])\ ([^{14}C_{sm}]/[^3H_{sm}])$.

(7) The value of 1.5 for the anhydride case is significantly larger than unity and may reflect either a contribution from path B or a finding of $k_2 \sim k_1$ for THF.

(8) M. Goodman and W. J. McGahren, *Tetrahedron*, **23**, 2031 (1967).

(9) L-**5** was prepared in *ca.* 10% yield by reaction of **2** in MeCN with the ketoketenimine obtained from Woodward's reagent K and triethylamine.[10] By-products were removed by extraction with water. Optical purity of **5** was established by a cleavage with hydrazine[8] at 0° in methanolic THF which yielded hydrazide of **2**, >95% L, assessed by isotopic dilution.

(10) R. B. Woodward and D. J. Woodman, *J. Org. Chem.*, **34**, 2742 (1969).

(11) A. P. Sloan Fellow, 1968–1970; financial support from National Institutes of Health Grant GM 13453 is gratefully acknowledged. Address correspondence to this author.

(12) National Science Foundation Predoctoral Fellow, 1967–1970.

D. S. Kemp,[11] Julius Rebek, Jr.[12]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received April 15, 1970

A Radical Intermediate in the Photolysis of *o*-Phthalaldehyde at 77°K

Sir:

Following our report,[1] two papers[2,3] discussed the mechanism of the photochemical isomerization of *o*-phthalaldehyde (**1**) to phthalide (**3**), and both proposed an intermediate hydroxyketene (**2**). We now wish to report that the mechanism of the photochemical reaction is strongly temperature dependent and that we have secured evidence for a free-radical intermediate in the photolysis of **1** at low temperature.

When a sample of **1** (carbonyl at 1670 cm^{-1}), neat or as a mull in Nujol, was irradiated at 77°K,[4] a minute ir absorption at 2060 cm^{-1} appeared almost immediately, and its intensity remained constant while a phthalide-like carbonyl peak at 1755 cm^{-1} slowly increased with the irradiation time.[5] The 2060 peak was stable at

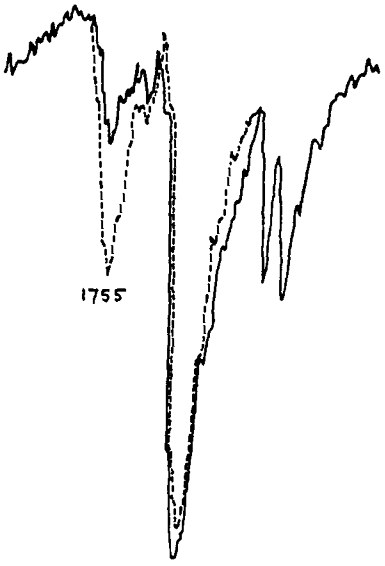


Figure 1. Infrared spectra of **1** (neat): after 5-min irradiation at 77°K with a 450-W Hanovia lamp (solid line), and after warm-up of that sample to room temperature in the dark (dotted line). Considerable scale expansion was required for seeing the 2060-cm^{-1} peak in the first spectrum.

---

(1) J. Kagan, *Tetrahedron Lett.*, 6097 (1966).

(2) S. P. Pappas and J. E. Blackwell, Jr., *ibid.*, 3337 (1968).

(3) K. F. Cohen, J. T. Pinhey, and R. J. Smith, *ibid.*, 4729 (1968).

(4) We used a variable-temperature cell (No. VLT-2, Beckman) which was placed in a Rayonet reactor at 253.7 nm, or in front of a 450-W Hanovia lamp housed in a water-cooled quartz well with a Vycor filter.

(5) Very significant conversion took place upon prolonged irradiation at 77°K, especially with the Hanovia lamp.

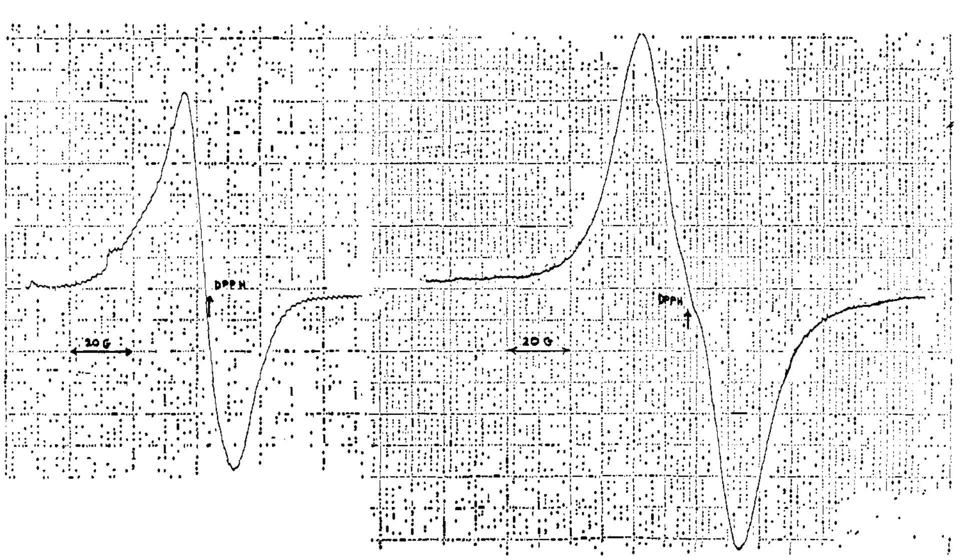
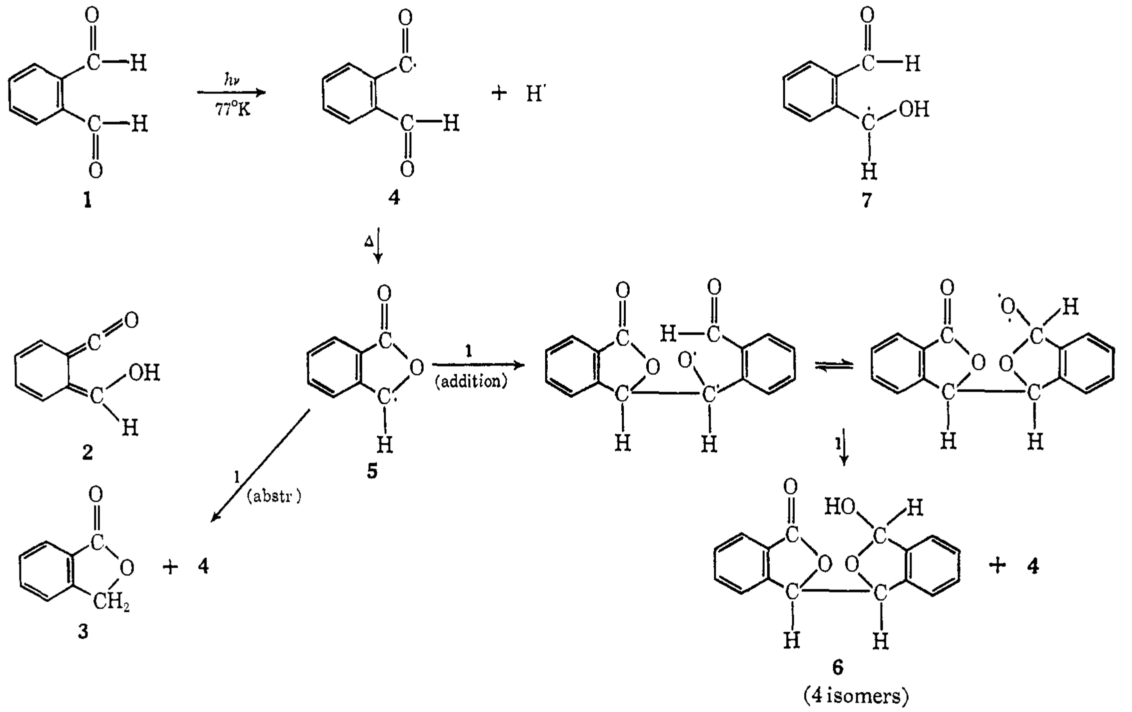


Figure 2. Benzaldehyde (left) and *o*-phthalaldehyde (right) radicals, produced and observed at 77 °K.

77 °K in the dark. Upon slow warm-up in the absence of light there was a gradual increase of the 1755 peak following the almost immediate disappearance of the 2060 peak (Figure 1).[6] Glc analysis of the products[7] confirmed the formation of **3** and of the dimers **6** usually obtained at room temperature.[8] These are two pairs of epimeric hemiacetals, which can be oxidized to *d,l*- and *meso*-dihydrobiphthalide.[9] No benzaldehyde was detected.

Even if the peak at 2060 cm^{-1} corresponded to **2**, its disappearance prior to the formation of most of **3** during warm-up indicated that **2** could not have been an important precursor to **3** in the dark reaction. Irradiation of **1** as a powder in a sealed quartz tube at 77 °K darkened the sample considerably and yielded a single esr line with a *g* value almost identical with that of DPPH ($g = 2.0036$). Both color and signal disappeared upon warming to room temperature. The signal was almost identical with that obtained by irradia-



---

(6) The relative intensities of the 1755 and 1670 peaks depended upon the reaction conditions, but conversion in excess of 50% could be observed.

(7) After trimethylsilylation.

(8) The ratio of dimers to **3** shows a concentration dependence, which is also solvent dependent. There appears to be a heavy atom solvent effect on the dimer formation, the extreme case being in 1-bromobutane, where the photolysis of a saturated solution of **1** yielded no dimer. The abnormality of that solvent was further demonstrated by the room-temperature irradiation of **1** in 1-bromobutane containing CH$_3$OD, which yielded **3** free from deuterium. The ionic mechanism, therefore, did not operate in those conditions. Further work is in progress to determine the extent of participation of the free-radical process in other solvents at room temperature.

(9) The ratio of erythro to threo is solvent dependent, but both were formed when the dimer was formed. The discrepancy between our results and those of the Australian group may be attributed to differences in the rates of oxidation of the dimers, resulting in preferential formation of the meso product, which was detected by tlc. We are grateful to Dr. Pinhey for communicating to us the detailed oxidation procedure.

tion of benzaldehyde (Figure 2), and supported a carbonyl radical **4**. Cocivera and Trozzolo have recently suggested the intermediacy of a radical pair ($C_6H_5\dot{C}{=}O + C_6H_5\dot{C}HOH$) in the room-temperature photolysis of benzaldehyde.[10] Our results, however, show that the hydroxybenzyl radical is absent in the low-temperature photochemistry, which must simply involve the formation of a benzoyl radical. Furthermore, hydrogen transfer in **1** taking place intramolecularly (yielding **2** or its diradical equivalent) or intermolecularly (yielding a mixture of **4** and **7**) is not compatible with our results, which are best explained by a radical chain mechanism.[11] For the sake of simplicity we assumed that both **3** and **6** were derived from **5**, but **6** could also have been formed by reaction of **4** with **1**.

Additional evidence for a second radical, such as **5**, in the thermal conversion of **4** to products was obtained by esr during warm-up of the photolyzed sample, whereby the formation of a radical showing hyperfine structure became visible (Figure 3).[12] Our mechanism predicts that a solvent which is a poorer hydrogen donor than **1** should not participate chemically in the conversion of **1** to **3**. Indeed, irradiation of **1** at 77°K in benzene containing CD_3OD and warm-up yielded **3** which was free from deuterium (mass spectrum),[13] in contrast with the results of Pappas and Blackwell,[2] who obtained mostly **3**-d_1 by photolyzing **1** at room temperature in solvents containing CH_3OD[14] or D_2O. The mechanism of the photochemical conversion of **1** to a phthalide-like product (**3** and/or **6**) at 77°K will remain unclear at least until a direct product analysis can be performed at that temperature. We note, however, that since the radical **4** is stable at 77°K, neither it nor **5** can be an intermediate leading to products at that temperature. It is reasonable, therefore, to postulate that the observed photochemistry at 77°K proceeds from the short-lived singlet excited state of **1** and yields **3** and/or **6**.

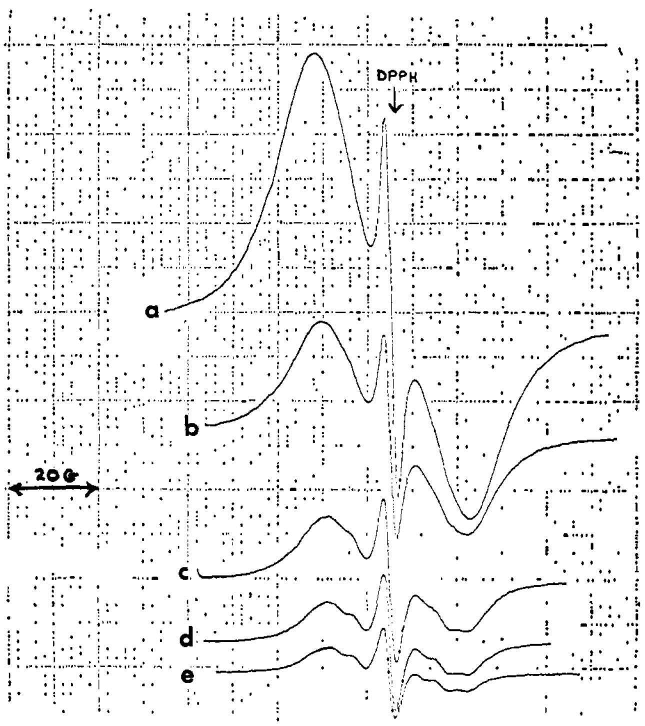


Figure 3. Warm-up of the *o*-phthalaldehyde radical (spectra a–e were recorded as the temperature increased).

The formation of **4** and the subsequent dark reactions would result from intersystem crossing of the initially formed singlet excited species followed by α cleavage of the C–H bond from the triplet.

Acknowledgment. We thank the National Science Foundation (GP 12379), the National Institutes of Health (GM 16759), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are indebted to M. Miskevitch for some technical assistance, and to Dr. M. G. Ettlinger for comments.

* Address correspondence to this author.

David A. Harrison, Robert N. Schwartz, Jacques Kagan*
Department of Chemistry, University of Illinois at Chicago Circle
Chicago, Illinois 60680

Received May 6, 1970

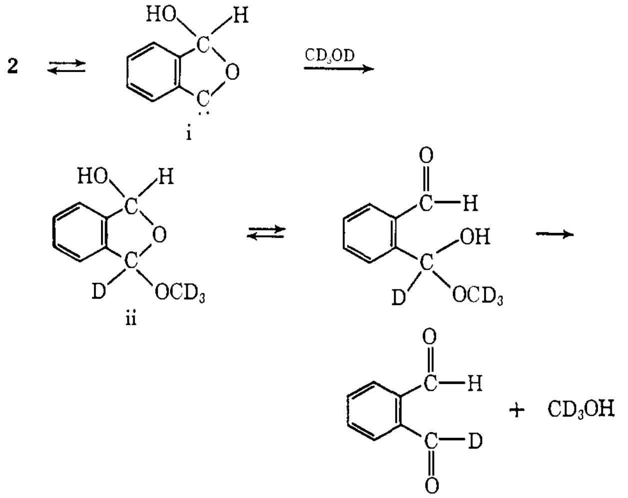
---

[10] M. Cocivera and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **92**, 1772 (1970).

[11] One referee objected to our postulating a free-radical *chain* mechanism. However, the H· formed upon irradiation of **1** was not detected and it is likely that much of it diffused rapidly and was deactivated, *e.g.*, by forming H_2. To the extent that H· is lost, the formation of the observed products derived from **5** requires another hydrogen radical source, and **1** is a reasonable candidate. However, because of the difficulty of getting absolute measurements on the number of free radicals, the average chain length is unknown. The similarity among the fingerprint regions in the spectra of **1**, **3**, and **6** precluded a direct product analysis by ir, and the ratio of **3** to **6** formed in the warm-up could not be compared to that formed at 77°K.

[12] The mass spectra of **1** and **3** are practically indistinguishable, suggesting that a rearrangement similar to that experienced by **1** in the photochemical–thermal process may also occur upon electron impact.

[13] Deuterium was also absent in **1** which was recovered in the experiment, ruling out the participation of the singlet carbene i (obtained by cyclization of **2**[3]) which would have been expected to react with solvent to yield ii, from which **3**-*d* would be generated *via* the hemiacetal.



[14] Irradiation of **1** in pure CH_3OH, contrary to most solvents, yields a dark mixture which contains several products in addition to **3** and dimers.

Photoinduced Oxidative Addition of 9,10-Phenanthrenequinone to $Ir(PPh_3)_2(CO)(Cl)$

Sir:

We report in this paper a study of the photoinduced oxidative addition of 9,10-phenanthrenequinone to $Ir(PPh_3)_2(CO)(Cl)$. This and similar reactions we have observed afford convenient syntheses of *o*-quinone