This mixture was dissolved in 3 mL of methanol. Diazomethane in ether was added until a persistent yellow color showed an excess. The reaction was allowed to stand for 10 min, and then N_2 was bubbled through to dispel excess diazomethane. A stream of N_2 was directed at the surface while warming in an air stream at 40 °C to remove the solvent. The esterified mixture of alcohols was separated from minor impurities by repetitive two-dimensional TLC (eluent, system B) as described earlier. The ^1H NMR spectrum of the mixture of alcohols clearly showed them to be compounds **16d** and **20** in a ratio of 2:3, respectively: **16d** ^1H NMR ($CDCl_3$) (partial) δ 2.72 (d, 1 H), 2.91 (d, 1 H); **20** ^1H NMR ($CDCl_3$) (partial) δ 0.93 (m, 1 H), 2.68 (d, 1 H), 3.20 (d, 1 H).

Acknowledgment. We thank A. G. Zacchei for the crude mixture of chimpanzee metabolites, Y. C. Lee, A. Angenblick (deceased), J. L. Smith, and K. B. Streeter for technical assistance, and R. F. Hirschmann for unrelenting encouragement.

Registry No. **2**, 57296-70-5; **3a**, 97522-88-8; **3b**, 97550-78-2; **8**, 53107-38-3; **9**, 97522-89-9; **10**, 97522-90-2; **11a**, 97522-91-3; **11b**, 97522-92-4; **12a**, 97522-93-5; **12b**, 97522-94-6; **12c**, 97589-60-1; **13a**, 97522-95-7; **13c**, 97589-61-2; **13d**, 97522-96-8; **14a**, 97522-97-9; **14b**, 97522-98-0; **15a**, 97590-49-3; **15b**, 97589-62-3; **15c**, 97589-63-4; **16a**, 97589-64-5; **16c**, 97589-65-6; **16d**, 97590-50-6; **17**, 97522-99-1; **18**, 97523-00-7; **19**, 97589-66-7; **20**, 97589-67-8; **A**, 97523-01-8; **B**, 97589-68-9; 2-cyclopentenone, 930-30-3; 3-chlorocyclopentene, 96-40-2.

Supplementary Material Available: Table of chemical shifts of 1 and metabolite methyl esters (1 page). Ordering information is given on any current masthead page.

Low Temperature Free-Radical Reactions Initiated with *tert*-Butyl *p*-Benzoylperbenzoate. Selective Acyl Radical Additions to Substituted Olefins

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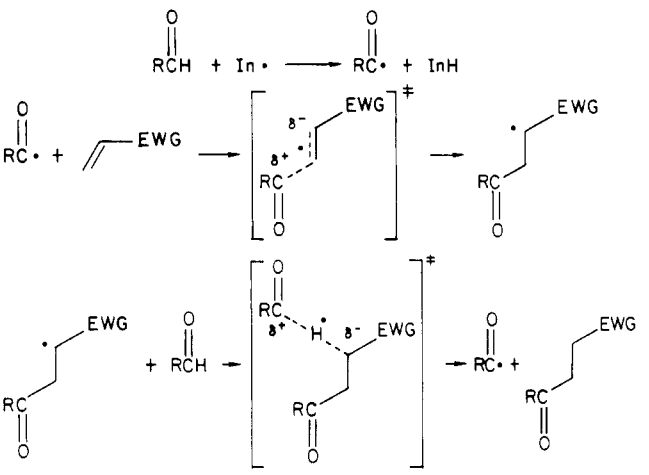
Competition experiments involving acyl radical additions to simple and electron-deficient olefins showed a definite preference for acylation of the latter olefin. This selectivity was significantly enhanced by using low temperature initiation with *tert*-butyl *p*-benzoylperbenzoate (1), which allows selective initiation of free-radical cyclization reactions that have synthetic importance.

In recent years free-radical cyclizations, originally elaborated by Julia,[1] Beckwith,[2] and others,[3] have been applied by Hart[4] and Stork[5] and their co-workers in a variety of total syntheses. Virtually all applications of radical cyclizations use a common strategy—a free-radical center is generated in proximity to a double bond such that addition of the radical to the double bond gives a five- or six-membered ring. These radical processes invariably employ thermal initiators as radical sources, such as AIBN or dibenzoyl peroxide. The reaction temperatures thus required are typically in excess of 50 °C simply because the initiators are stable at lower temperatures. Consequently, use of thermal initiators may impair the ability to prepare or employ thermally unstable reactants or intermediates, use volatile reactants, or enhance stereo- and regioselectivity.

tert-Butyl *p*-benzoylperbenzoate (1),[6] a photoinitiator, circumvents the potential disadvantages of a thermal initiation step. Radical centers, essentially identical with those produced from either benzoyl peroxide or *tert*-butyl perbenzoate, are formed via a singularly efficient photochemical dissociation process over a wide temperature range[7] and should prove useful in low temperature free-radical initiation. The quantum yield of homolysis of the peroxy linkage in (1) at 360 nm is 0.92 in benzene. In addition, this photochemical dissociation process utilizes long wavelength UV (360 nm) absorption, thus avoiding possible photochemical side reactions arising from excitation of chromophoric reactants such as α,β-unsaturated carbonyl compounds ($\lambda_{max} \leq 300$ nm). This photochemical

Scheme I



(1) Julia, M. *Acc. Chem. Res.* **1971**, *4* (11), 386.

(2) (a) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; Mayo, P. de, Ed.; Acacemic Press: New York, 1980; Vol. 1, pp 161-310. (b) Beckwith, A. L. J.; Easton, D. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482.

(3) Surzur, J. M. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982; Vol. II, Chapter 3.

(4) For recent examples, see: Hart, D. J.; Choi, J. K., Tsai, Y.-M. *Tetrahedron Lett.* **1982**, 4765. Hart, D. J.; Chuang, C. P. *J. Org. Chem.* **1983**, *48*, 1782.

(5) For recent examples, see: Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 3720. Stork, G.; Mook, R., Jr.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 3741. Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 3741. Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6765.

(6) Thijs, L.; Gupta, S. N.; Neckers, D. C. *J. Org. Chem.* **1979**, *44*, 4123.

(7) *tert*-Butyl *p*-benzoylperbenzoate is essentially a benzophenone combined with a *tert*-butyl perbenzoate moiety. When irradiated at 366 nm, one produces a benzophenone triplet which is quenchable, but marginally so, by typical triplet quenchers. An intersting mechanistic question is just how does the energy absorbed by the benzophenone component find its way to the weak -0-0- bond. We are studying this question at the present time.

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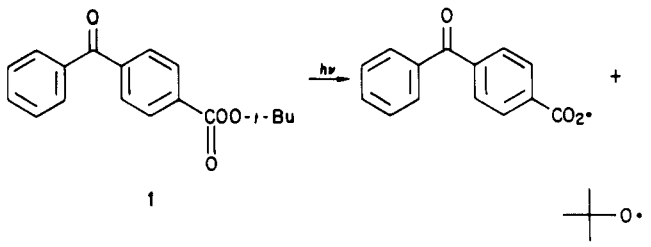


1

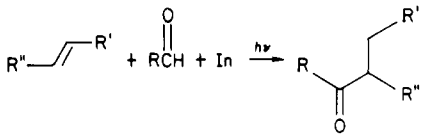
process also does not suffer from quenching effects in dilute solution. In studies using 1 as a photoinitiator of vinyl polymerization,[8] for example, quenching by styrene was not serious below 2 M monomer, and the $k_q\tau$ with naphthalene as a quencher is only 15.0. This perester is a thermally stable, white crystalline solid ($t_{1/2}$ = 2 h at 115 °C) making it convenient to use.

To probe the utility of low temperature photoinitiation with perester 1 we examined the selectivity of Kharasch additions of acyl radicals to simple and electron-deficient olefins as a function of temperature. Patrick demonstrated that the addition of acyl radicals produced from aldehydes via hydrogen abstraction to electron-deficient olefins generally proceeded more efficiently than did their addition to simple olefins.[9] Later workers attributed the acyl radical's nucleophilic nature to favorable polar contributions in the transition state, which decreased the activation energy of addition as well as of hydrogen abstraction in the propogation step[10] (Scheme I). Such a lowered activation barrier should manifest itself in a competition between simple olefins and electron-deficient olefins for acyl radical addition. Temperature dependence should be exhibited with an increasing percentage of product being derived from the lower energy pathway with decreasing reaction temperature. A systematic study of competitive acyl radical additions has not been previously reported, presumably because such experiments required a source of initiating radicals that could be efficiently formed independent of temperature.[11] A high degree of selectivity arising from low temperature initiation would have definite synthetic application allowing either selective functionalization of olefins or selective initiation of free-radical cyclization processes.

Results and Discussion

Competition Studies. The olefins chosen for competition studies were 1-hexene and methyl crotonate. The experiments were carried out with a solution of 10.0 mmol of aldehyde, 1.0 mmol each of the olefins, and 0.1 mmol of perester 1 in 1.0 mL of benzene. As predicted from Kharasch's work, relatively large quantities of aldehyde and initiator were required, owing to the small chain transfer constants (k_{ct}) for acyl radical additions. Solutions were degassed via several freeze/pump/thaw cycles, then irradiated in a Rayonet reactor fitted with 350-nm lamps. The yields of acylated products derived from individual olefins under noncompetitive conditions are given in Table I. A moderate preference for acyl radical additions to methyl crotonate was observed. Results for competition experiments at various temperatures are listed in Table

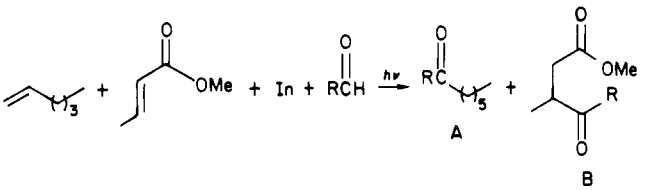
Table I. Noncompetitive Acyl Radical Additions to Olefins[a]



entry	R″	R′	R	% yield[c]
1a	H	$(CH_2)_3CH_3$	CH_3	13.4
b			CH_3CH_2	9.0
c			$CH_3(CH_2)_3$	22.0
d			$(CH_3)_2CH$	12.2
2a	CH_3	$CH_3OC(=O)$	CH_3	22.0
b			CH_3CH_2	24.4
c			$CH_3(CH_2)_3$	60.8
d			$(CH_3)_2CH$	27.0

[a] Relative stoichiometry of reactants is 1 equiv of olefin, 10 equiv of aldehyde, and 0.1 equiv of initiator. [b] In = perester 1. [c] Yields here and in subsequent tables were determined by VPC analysis (15 m capillary column containing J & W DB-1 nonextractable bonded phase) with acetophenone as an internal standard.

Table II. Competition Reactions between Substituted Olefins at Various Temperatures



entry	R	T, °C	%A	%B	A:B
1a	CH_3	4	1.9	20.0	1:10.4
b		ambient	3.1	20.0	1:6.3
c		78	12.7	26.6	1:2.1
2a	CH_3CH_2	4	0.72	14.9	1:20.8
b		ambient	1.5	17.0	1:11.0
c		78	5.0	32.3	1:6.4
3a	$CH_3(CH_2)_3$	4	2.4	45.0	1:17.5
b		ambient	4.8	49.4	1:10.2
c		78	18.2	68.6	1:3.8
4a	$(CH_3)_2CH$	4	0.50	12.0	1:23.2
b		ambient	0.78	11.8	1:15.2
c		78[b]		8.8	

[a] In = compound 1. [b] The VPC trace of this reaction mixture exhibited numerous products from which it was impossible to ascertain the presence of the small amount of product from the addition to 1-hexene.

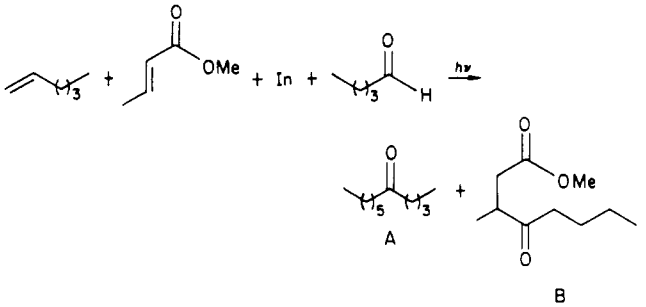
II. A substantial preference for acyl radical addition to methyl crotonate is clearly illustrated, which, as predicted, increased as the reaction temperature decreased.

Besides enhanced selectivity, these experiments illustrate other advantages of low temperature initiation. Initiation with perester (1) conveniently allowed the use of volatile acetaldehyde without requiring sealed tubes, except when a reaction temperature of 78 °C was used. Acyl radicals highly substituted at the α-carbon decompose at higher temperatures with loss of carbon monoxide.[12] This accounts for the low yield and complex product mixture obtained in the case of isobutyraldehyde (Table I, entry 2d; Table II, entry 4c) with a reaction temperature of 78 °C.

Cyclization Studies. Yield and selectivity as a function of time at room temperature were next examined (Table III). Individual samples were removed at various times of irradiation, and a small amount of hydroquinone was added to stop any continuing free-radical chains. Ap-

(8) Gupta, S. N.; Thijs, L.; Neckers, D. C. *J. Poly. Sci.* **1981**, *19*, 855.
(9) Patrick, T. M., Jr. *J. Org. Chem.* **1952**, *17*, 1009.
(10) (a) Walling, C. "Free Radicals in Solution"; John Wiley and Sons, Inc.: New York, 1954; pp 153–154. (b) Huyser, E. S. "Free Radical Chain Reactions"; Wiley Interscience: New York, 1970; p 152. (c) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *11*, 753.
(11) Low temperature addition of RC(=O) to olefins can be carried out by direct photolysis (253.7 mm) of RCHO, but the reaction is slow. See: Kharasch, M. S.; Urry, W. H.; Kuderna, B. M. *J. Org. Chem.* **1949**, *3*, 248.
(12) Reference 10b, pp 153–154.

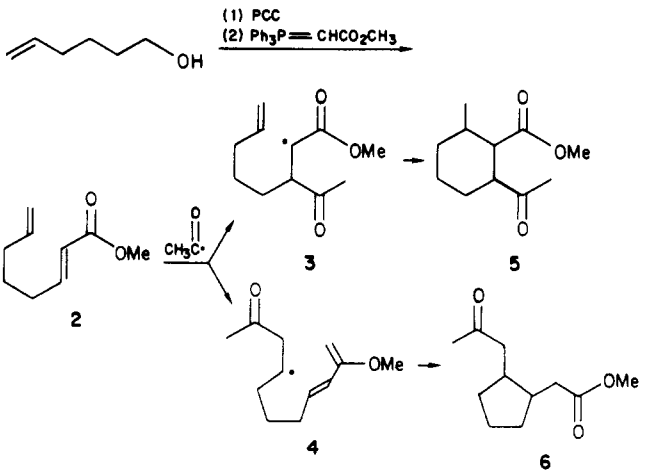
Table III. Yield and Selectivity as a Function of Time at Ambient Temperature



time, h	%A	%B	A:B
1.5	1.3	25.8	1:19.9
3.0	3.0	38.7	1:13.1
4.5	4.7	52.2	1:11.0
6.0	5.2	50.8	1:9.8

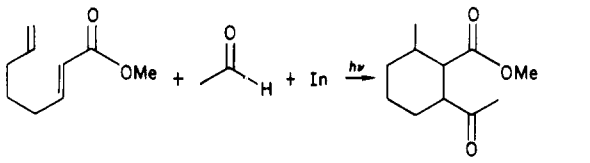
[a] In = compound 1.

Scheme II



proximately 4 h were needed for complete reaction. Selectivity decreased with time, presumably owing to the increasing relative concentration of 1-hexene as the amount of methyl crotonate was reduced via chemical reaction. This result has synthetic implications in that an enhanced degree of selectivity should be realized if the concentrations of both olefins were diminished at the same rate such as in a cyclization process. To ascertain the effectiveness of such a process, methyl octa-2,7-dienoate (**2**) was synthesized and subjected to acyl radical addition with acetaldehyde under conditions analogous to those used for the competition experiments (Scheme II). The acyl radical should add initially at either the 3- or 8-position of dienoate **2** to give intermediates **3** and **4**, respectively, followed by rapid cyclization and subsequent hydrogen abstraction to continue the chain. Intermediate **3** is expected to give only six-membered ring adduct **5** and none of the seven-membered ring product. Intermediate **4** should give only the five-membered ring adduct **6** and no six-membered ring. After reaction at various temperatures (Table IV), VPC analysis of the product mixture showed two products with no starting dienoate present. Silica gel chromatography (12:1, hexane–ethyl acetate) provided pure samples of each product. NMR analysis of each product showed them to be diastereomers of six-membered ring adduct **5** indicating the addition–cyclization sequence was very regioselective. Doublets (200 MHz NMR) at 0.86 (major isomer) and 0.92 ppm (minor isomer) were consistent with a cyclohexane ring bearing respectively an axial and

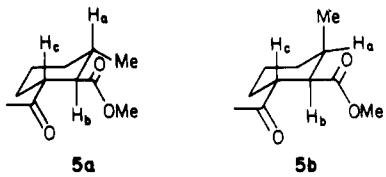
Table IV. Cyclization Results



T, °C	% yield	(ratio of minor:major product, 5b:5a)
−25[b]	45	(1:1.42)
4	57	(1:1.35)
ambient	41	(1:1.24)
78	43	(1:1.27)

[a] In = compound 1. [b] The reaction was carried out in a test tube immersed in a CCl_4/dry ice bath contained in a nonmirrored Dewar. The sample was irradiated for 9 h with 16 350-nm lamps. Methylene chloride was used as a solvent.

equatorial methyl group. The acyl and carbomethoxy groups were assumed to be trans since attempted epimerization under basic (DBU in refluxing CH_2Cl_2 or benzene) or acidic (5% HCl or *p*-TSA) conditions failed to change the existing product ratio. This was verified with decoupling studies (200 MHz NMR) giving results consistent with the assignment of structures **5a** and **5b**.



5a **5b**

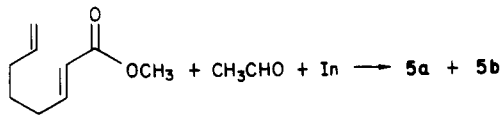
Protons H_b and H_c in **5a** showed first-order coupling, making structural assignment relatively easy with decoupling methods. H_b appeared as a triplet at 2.21 ppm. Irradiation at H_a (1.55 ppm) caused collapse of H_b to a simple doublet (J = 11.0 Hz). Likewise, irradiation at H_c (2.78 ppm) caused collapse of H_b to a doublet (J = 11.0 Hz). The large coupling constants indicated H_a, H_b, and H_c were all axial. H_c appeared as a ddd at 2.78 ppm (J = 3.4 Hz, 11.0 Hz, 11.7 Hz). Irradiation at H_b caused collapse of H_c to a dd (J = 3.4 Hz, 11.7 Hz) indicative of axial–axial and axial–equatorial coupling with the adjacent methylene protons.

The second-order coupling of H_b–H_c in **5b** made structure determination more difficult by NMR analysis. H_b and H_c appeared as a multiplet at 2.90 ppm making direct decoupling of H_b from H_c (and vice versa) impossible. H_a in **5b** was shifted downfield from H_a in **5a** by 0.87 ppm. The doublet for the methyl substituent in **5b** was shifted upfield from **5a** by 0.06 ppm. These chemical shifts indicate an inversion in the stereochemistry with **5b** having an axial methyl substituent and H_a equatorial. Irradiation at H_a caused what appeared to be a dd in the H_b–H_c multiplet to collapse to a doublet (J = 10.8 Hz), indicating axial–axial coupling for H_b–H_c and hence assignment of **5b**.

The adducts **5a** and **5b** were the only products obtained regardless of reaction temperature. VPC as well as isolated yields of **5a** and **5b** were on the order of 50%. No starting dienoate **2** was detected (VPC) in the product mixture suggesting telomerization, a known side reaction in acyl radical additions to olefins, may be occurring. No cyclopentane adduct corresponding to **3** was detected.

To compare the effectiveness of perester **2** as an initiator in this case, the cyclization (Scheme II) was performed through thermal initiation with benzoyl peroxide (sealed tube, 95 °C) and alternate photoinitiation with benzo-

Table V. Cyclization Results with Alternate Free-Radical Initiators[a]



In	T, °C	t, h	% cyclized products	5b:5a
benzoyl peroxide	95	16	15	1:1.36
benzophenone (*hν*)	4	5	30	1:1.34

[a] Relative stoichiometry of reactants is the same as stated in Table I.

phenone[13] (350 nm, 4 °C). Both methods gave lower yields of the same cyclized products (Table V) with the major component in the product mixture being unreacted dienoate **2**. Reasons for the less efficient reaction through thermal initiation are not apparent. The triplet state of benzophenone, though, is relatively inefficient as a free-radical initiator suffering from quenching effects, contrary to the behavior of perester **2**.

Conclusion

tert-Butyl *p*-benzoylperbenzoate (**1**) was shown to be a convenient variable temperature initiator for acyl radical reactions. Use of low temperatures enhanced the selective addition of acyl radicals to electron-deficient olefins, and this selectivity was utilized synthetically to initiate the cyclization of dienoate **2** (Scheme II) to give **5a** and **5b**. Use of thermal initiation with benzoyl peroxide or photoinitiation with benzophenone proved less efficient at promoting this addition–cyclization process than with perester **2**. This reaction's selectivity was based on a polar bias and complements the existing synthetic free-radical cyclization methodologies based on a steric bias or site selective free-radical formation by tin(IV) hydride reductions of organohalides.[3,14]

Experimental Section

Infrared spectra were recorded as neat films with a Perkin-Elmer 337 infrared spectrophotometer. NMR spectra were recorded on a Varian EM-360 or Varian XL-200 spectrometer with deuteriochloroform as the solvent and tetramethylsilane as the internal reference. Mass spectra were obtained with a Hewlett-Packard 5987A GC/MS system equipped with a 15-m methylsilicone OV101 capillary column. Product ratios and yields were determined by using a Hewlett-Packard 5880A FID gas chromatograph equipped with a 15-m J&W DB-1 capillary column using acetophenone as an internal standard. Photolyses were carried out using a "merry-go-round" attachment in a Rayonet RPR-100 reactor fitted with 350-nm fluorescent lamps.

All aldehydes (obtained from Aldrich) used in the competition studies were distilled and stored under nitrogen. Methyl crotonate and 1-hexene (from Aldrich) were used directly without further purification. The perester **1** was synthesized by a previously published method.[6]

General Procedure for Noncompetitive Addition of Acyl Radicals to 1-Hexene or Methyl Crotonate. To a small screw-top Pyrex test tube was added 1 mL of benzene, 10.0 mmol of aldehyde, 1.0 mmol of either 1-hexene or methyl crotonate, and 0.10 mmol of **1**. Oxygen was removed from the samples by several freeze/pump/thaw cycles during which the atmosphere of the test tube was replaced with argon. The caps were screwed on the test tubes and sealed with parafilm. The tubes were then placed in a Rayonet reactor which contained eight 350-nm lamps and was fitted with a "merry-go-round" type adapter. The samples were irradiated for 5 h at room temperature. The samples were then transferred to a 25-mL round-bottom flask, and the solvent reduced to half its volume in vacuo. Hexane was added until a white precipitate began to form *p*-benzoylbenzoic acid. The mixture was passed through a small plug of silica gel to remove this byproduct. The resultant solution was concentrated in vacuo and the subjected to VPC analysis. Complete removal of solvent in vacuo gave the products listed in Table I.

Entry 1a: IR (film) 2950, 1730 cm^{-1}; NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.22 (m, 8 H), 2.03 (s, 3 H), 2.32 (t, 2 H); low resolution mass spectrum for $C_8H_{16}O$ requires *m/e* 128, found *m/e* 128.

Entry 1b: IR (film) 2970, 1725 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.5 (m, 16 H), 2.2–2.6 (m, 4 H); low resolution mass spectrum for $C_9H_{18}O$ requires *m/e* 142, found *m/e* 142.

Entry 1c: IR (film) 2950, 1725 cm^{-1}; NMR ($CDCl_3$) δ 0.9 (bt, 6 H), 1.2–2.0 (m, 12 H), 2.34 (bt, 4 H); low resolution mass spectrum for $C_{11}H_{22}O$ requires *m/e* 186, found *m/e* 186.

Entry 1d: IR (film) 2980, 1715 cm^{-1}; NMR ($CDCl_3$) δ 0.90 (bt, 3 H), 1.05 (d, 6 H), 1.10–1.90 (m, 8 H), 2.20–2.60 (m, 3 H); low resolution mass spectrum for $C_{10}H_{20}O$ requires *m/e* 156, found *m/e* 156.

Entry 2a: IR (film) 2970, 1730, 1740 cm^{-1}; NMR ($CDCl_3$) δ 1.0 (d, 3 H), 2.08 (s, 3 H), 2.50 (d, 2 H), 2.81 (m, 1 H); low resolution mass spectrum for $C_7H_{12}O_3$ requires *m/e* 144, found *m/e* 144.

Entry 2b: IR (film) 2980, 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.10 (m, 6 H), 2.10–3.10 (m, 5 H), 3.63 (s, 3 H); low resolution for $C_8H_{14}O_3$ requires *m/e* 158, found *m/e* 158.

Entry 2c: IR (film) 2970, 1730 cm^{-1}; NMR ($CDCl_3$) δ 0.98 (bt, 3 H), 1.13 (d, 3 H), 1.2–1.7 (m, 4 H), 2.10–2.73 (m, 4 H), 2.90 (m, 1 H); low resolution mass spectrum for $C_{10}H_{18}O_3$ requires *m/e* 186, found *m/e* 186.

Entry 2d: IR (film) 2975, 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.13 (d, 6 H), 1.20 (d, 3 H), 2.70 (d, 2 H), 3.0 (m, 2 H); low resolution mass spectrum for $C_9H_{16}O_3$ requires *m/e* 172, found *m/e* 172.

General Procedure for Competition Experiments. The same general procedure and workup was used as outlined previously except that 1.0 mmol each of 1-hexene and methyl crotonate was added in the reaction test tube. The samples were irradiated in a Rayonet reactor with eight 350-nm lamps at three different external temperatures. Reaction at ambient temperature was performed in a laboratory hood. Reaction at 4 °C was performed in a cold room. Reaction at 78 °C was performed by irradiating the sample in a sealed tube which was suspended over a solution of refluxing ethyl acetate. VPC analysis gave the results shown in Table II.

Methyl Octa-2,7-dienoate[15] (2). 5-Hexen-1-ol (from Aldrich) was oxidized with pyridinium chlorochromate according to the method of Corey and Suggs[16] to give 5-hexenal in 61% yield after distillation (50–52 °C (60 torr)): NMR ($CDCl_3$) δ 1.50–2.20 (m, 4 H), 2.47 (t, 3 H), 4.85 (m, 1 H), 5.10 (m, 1 H), 5.40–6.00 (bm, 1 H), 9.72 (t, 1 H). The aldehyde was subsequently reacted with (carbomethoxymethylene)triphenylphosphorane[17] in refluxing benzene overnight. The reaction mixture was cooled, diluted with hexane, and filtered to remove the triphenylphosphine oxide. The filtrate was concentrated in vacuo. The resultant oil was distilled to give the product as a clear liquid (64–65 °C (1 torr)) in 74% yield: IR (film) 3100, 2950, 1740, 910 cm^{-1}; NMR ($CDCl_3$) δ 1.60 (m, 2 H), 2.14 (m, 4 H), 3.70 (s, 3 H), 4.82 (m, 1 H), 5.02 (m, 1 H), 5.45–6.00 (m, 3 H), 6.92 (dt, 1 H).

Methyl 2-Acetyl-6-methylcyclohexanecarboxylate (5a and 5b). (a) Using Perester (1) for Initiation. To 1.0 mL benzene was added 1.0 mmol of **2**, 10.0 mmol of acetaldehyde, and 0.10 mmol of initiator **1** in a small Pyrex test tube. The sample was degassed and irradiated at various temperatures according to the previous procedure. A temperature of −25 °C was maintained by immersing the reaction tube in a nonmirrored Dewar flask containing a dry ice/CCl_4 bath. In this instance deoxygenated CH_2Cl_2 (obtained by bubbling N_2 through the solvent for 45 min) was used as the solvent and sixteen 350-nm lamps were used to insure light penetration through the slightly turbid cold bath. After the standard workup, the resultant oil was chromatographed

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on silica gel (12 g, eluent = hexane–ethyl acetate, 12:1). The desired product was obtained as a mixture of two compounds by VPC analysis in the yields and ratios given in Table IV. A few fractions of the chromatographed material contained sufficiently pure material (ca. 97% by VPC) to allow spectral analysis of each compound. Minor isomer (**5b**): IR (film) 2950, 1750, 1725, 1050 cm^{-1}; 200 MHz NMR ($CDCl_3$) δ 0.86 (d, 3 H), 1.12 (m, 1 H), 1.58 (m, 4 H), 1.98 (bd, 1 H), 2.24 (s, 3 H), 2.42 (m, 1 H), 2.8–3.1 (m, 2 H), 3.65 (s, 3 H); low resolution mass spectrum for $C_{11}H_{18}O_3$ requires m/e 198, found m/e 198. Major isomer (**5a**): IR (film) 2930, 1740, 1720, 1370 cm^{-1}; 200 MHz NMR ($CDCl_3$) δ 0.92 (d, 3 H), 1.0–2.0 (m, 7 H), 2.14 (s, 3 H), 2.21 (t, 1 H), 2.78 (ddd, 1 H (J = 3.4, 11.0, 11.7 Hz)), 3.66 (s, 3 H); low resolution mass spectrum for $C_{11}H_{18}O_3$ requires m/e 198, found m/e 198.

(b) Using Benzophenone for Initiation. The reaction was carried out at 4 °C as in the previous experiment except that 0.10 mmol of benzophenone was used in place of perester 1. After the standard workup, VPC analysis gave the results listed in Table V.

(c) Using Benzoyl Peroxide for Initiation. To 1.0 mL benzene was added 1.0 mmol of **2**, 10.0 mmol of acetaldehyde, and 0.10 mmol benzoyl peroxide. After degassing with several freeze/pump/thaw cycles, the reaction tube was sealed under an Ar atmosphere and placed in an oil bath at 95 °C for 16 h. After the standard workup, VPC analysis gave the results listed in Table V.

Attempted Epimerization of Methyl 2-Acetyl-6-methylcyclohexanecarboxylate (5a and 5b). (a) Basic Conditions. The product mixture of **5a** and **5b** (100 mg, 0.5 mmol) obtained from initiation with perester (1) was dissolved in either benzene (2 mL) or CH_2Cl_2 (2 mL). One equivalent of DBU was added and each solution was refluxed for 24 h. VPC analysis of either reaction mixture indicated no change in the ratio of **5a** to **5b**.

(b) Acidic Conditions. The product mixture of **5a** and **5b** (100 mg, 0.5 mmol) obtained from initiation with perester 1 was dissolved in CH_2Cl_2 (2 mL) followed by addition of 0.1 equiv of *p*-TSA. The reaction was stirred at room temperature and monitored by VPC. After 24 h no change in the product ratio had occurred. Use of two drops of 5% HCl under the same conditions gave the same result.

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Evidence for an Unusual Charge-Transfer Complex in (Nitrophenacyl)anilines

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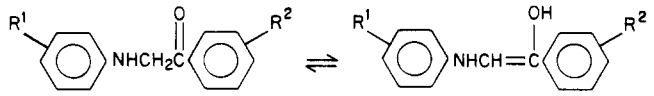
The color of (nitrophenacyl)anilines can be explained from an X-ray crystallographic study that indicates that one such compound is planar and stacked in the crystal in an alternating "head-to-tail" arrangement. This arrangement permits an unusual charge transfer between two molecules of the same compound, with the aniline end being the donor and the nitrophenacyl end being the acceptor. The possibility of charge transfer is supported by MNDO, MINDO/3, and extended Hückel molecular orbital calculations.

The (nitrophenacyl)anilines have been known for many years. Over 100 years ago, Möhlau[2] noted that these compounds formed deeply colored crystals. However, the origin of their color has not been explained. We[3-7] and others[8,9] have observed that, depending on the substituents on the *N*-aryl group and on the phenacyl ring of **1**, com-



1 **2**

pounds show transmitted and reflected crystal color ranging from scarlet to orange to yellow. The compounds that are the most intensely colored are those which have electron sources on the aniline ring and are concomitantly substituted with strong electron sinks on the phenacyl nucleus (Table I).

Table I. Effect of Ring Substituents on the Color of the Phenacylanilines

1	R^1	R^2	color
a	H	4′-NO_2	scarlet[a]
b	4-CH_3O	3′-NO_2	orange[b]
c	2-CH_3	4′-NO_2	orange-red[a]
d	4-CH_3CO	4′-NO_2	yellow[a,c]
e	4-C_2H_5OCO	4′-NO_2	yellow[b,c]

[a] Reference 3. [b] Reference 4. [c] Reference 9.

Though the reactions of the phenacylanilines and those of the phenacyl chloroacetanilides often proceed in solution via an enolate form of the respective substrates,[7-9] such a process, resulting in **2**, cannot be invoked in an explanation of the color of the crystalline state for two reasons. First the UV spectra in chloroform solution of numerous compounds 1 exhibit absorption maxima in the range of 350–425 nm,[9] while the crystalline forms show maxima in the range of 400–700 nm.[10] This suggests that the light absorption phenomenon in solution is electronically dis-

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