Tetrahedron Vol. 47, No. 12/13, pp. 2211 2220, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

PHOTOADDITION OF BENZOPHENONE TO ALLENIC ESTERS

M.P.S. ISHAR and R.P. GANDHI*

Department of Chemistry
Indian Institute of Technology-Delhi
Hauz Khas, New Delhi - 110 016, INDIA

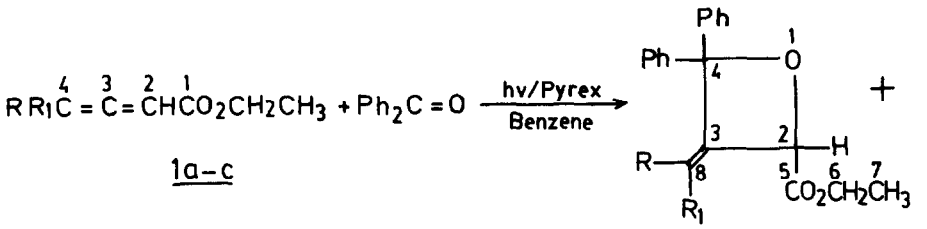
(*Received in UK 27 November* 1990)

ABSTRACT: Photochemical addition of benzophenone to ethyl-penta-2, 3-dienoate (1a), ethyl hexa-2,3-dienoate(1b) and ethyl 4-methylhexa-2,3-dienoate (1c) furnish various mono- and dioxetanes. Novel oxetanes (2a,b) result in the reactions of (1a,b) through addition of benzophenone to electron deficient C_2-C_3 π-bond of the respective esters. A rationalization of the obtained modes of photoaddition has been offered.

Although some aromatic aldehydes and ketones have been reported to photoadd to alkylallenes to produce mono-and dioxetanes[1], photoreactions of thiobenzophenone[2], xanthenethione[3], benzoquinones[4] and phenanthraquinone[5] with alkyl-, aryl-, alkoxy- and aryloxy-allenes furnish both 2+2 cycloadducts (thietanes, oxetanes, cyclobutanes) and 2+4 cycloadducts (dihydrodioxins, thiopyrans etc.). However, cyanoallene, which possesses electron deficient olefinic bond, fails to photoadd to phenanthraquinone[5a].

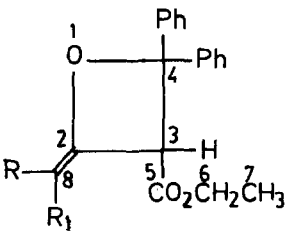
In this paper, we report on photoaddition of benzophenone to three allenic esters (1a-c) which possess both electron rich (alkyl bearing) and electron deficient (ester bearing) π-bonds. The reactions furnished various mono-and dioxetanes derived from addition of benzophenone to both C_3-C_4 and C_2-C_3 π-bonds of allenic esters; the latter mode of photoaddition, which involves allenic esters (1a,b), is unexpected[6]. A mechanistic rationale of the obtained results has been offered.

Irradiation of benzophenone in presence of allenic esters (1a-c, excess) in anhydrous sulfur-free benzene, with a 125 watt medium pressure mercury arc, for varying periods afforded, on chromatographic separation, monooxetanes (2a,b, 3a-c, 4a-c) and dioxetanes (5a-c),besides benzpinacol in varying amounts.



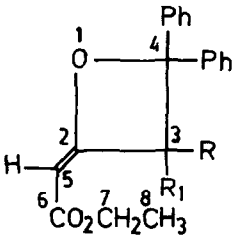
1a-c

2

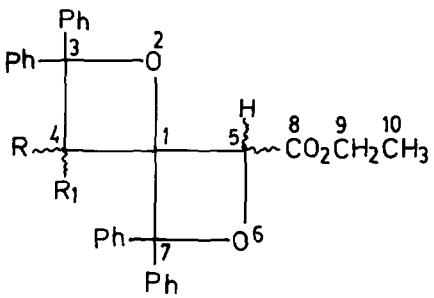


3

+



4



5

a. R = H ; R_1 = CH_3
b. R = H ; R_1 = CH_3CH_2
c. R = CH_3; R_1 = CH_3CH_2

The structure of the various products are based on their detailed spectral analyses (uv, ir, ^1H and ^{13}C NMR and Mass). The compound 2a was revealed to be a 1:1 adduct of benzophenone with 1a (M^+ at m/z 308). Its ir spectrum displayed bands due to ester carbonyl (1740 cm^{-1}) and oxetane (980 cm^{-1}). In its ^1H NMR spectrum, 2a revealed a 10H multiplet at δ 7.25 (aromatic Hs) and a quartet at δ5.66(J=5.60 Hz, C_8-H); the latter signal alluded

to the presence of $CH_3HC=$ moiety in 2a. The C_2-H appeared as a broad singlet at δ 4.22. The δ values of C_2-H and C_8-H were critical in structural assignment. Again, the presence of only one quartet in the olefinic region (due to C_8-H) confirmed the absence of geometric isomers involving the exocyclic double bond in 2a. However, the assigned geometry around the double bond is tentative and is based on the absence of any observable long-range-couplings involving C_2-H, C_8-H and C_9-Hs[cf.7]. The expression 2a is corroborated by ^{13}C NMR chemical shifts of C_2 (δ 88.2, d in SFORD) and C_4 (δ 93.4) revealing proximity of C_2 & C_4 to the oxygen atom. The structure of 2b was derived similarly; this again was found to be a single geometric isomer involving the exocyclic double bond (vide experimental). No oxetane (corresponding to structures 2a,b) was obtained in the reaction involving benzophenone and the ester 1c (Table 1).

The isomeric compounds 3a and 4a were obtained as a mixture (1:2, ^1H NMR). This revealed the highest peak in the mass spectrum at m/z 308 (1:1 adduct of benzophenone with 1a). The presence of oxetane moiety and other functional features were inferred from the ir spectrum [1725 b(ester C=O), 1600, 1540, 1500, 1450 (C=C), 1260, 1200 (C-O), 1035, 980 and 920 (oxetane) cm^{-1}]. The ^1H NMR of the mixture revealed, besides an aromatic protons multiplet at δ 7.27, a broad singlet at δ 5.32 and a quartet at δ 3.44 attributed to C_5-H and C_3-H, respectively, in the major component, 4a. A multiplet in the region, δ 4.50-3.91, was comprised of a quartet due to C_8-H of 3a (δ 4.40) and overlapping quartets at δ4.00 and 3.85 due to ester methylenes in 3a and 4a. The C_3-H in 3a appeared as a broad singlet at δ3.60. Here, the chemical shift of C_8-H (δ 4.40) was critical in assignment of expression 3a[cf.1]. The above ^1H NMR spectral assignments are based on homodecoupling experiments involving irradiation of resonances at δ 1.23 (split d, C_9-Hs in 3a), δ1.12 and 1.08 (triplets, ester methyls) and δ0.90(broad d, C_3-Me in 4a), and comparison with related systems[1-5]. However, the stereochemical assignments at C_8 in 3a and C_5 in 4a are tentative. It may be mentioned here that no isomers involving C_8 in 3a and C_5 in 4a were detected and the value of allylic coupling involving C_8-H and C_3-H in 3a (1Hz), and C_5-H and C_3-H(not determinable) in 4a was very low. The ^{13}C chemical shift data in support of expressions 3a and 4a are included in the experimental section. The structure of the isomeric compounds 3b and 4b (obtained in mixture) has been similarly brought out (vide experimental). In case of 3c, the presence of pairs of resonances due to alkyl hydrogens [δ 1.76 and 1.46 (b singlets, C_8-methyl), δ 0.88 and 0.80(triplets)] indicated isomeric arrangements at C_8. However, 4c was obtained as a single C_5 isomer.

The compound 5a was found to be a 1:2 adduct of 1a with benzophenone (M^+ at m/z 490). Its gross structural features were inferred from its ir spectrum (1740 cm^{-1}, ester C=O; 1000, 980, 960, 940 cm^{-1}, oxetane). Its ^1H NMR spectrum showed a 20H multiplet due to aromatic Hs at δ7.28 and singlets at δ 4.68 and 4.59 due to C_5-H (in isomeric arrangements). The spectrum further revealed two overlapping quartets at δ 3.87 and 3.84 attributed to isomeric C_9-Hs; from the δ values of C_9-Hs and C_5-H, it was inferred that the mode of addition of benzophenone to C_2-C_3 π-bond in 5a was similar to that in 2a (cf. ^1H NMR data for 2a). Further, the chemical shift of C_4-H in 5a (δ 3.49) is comparable to δ C_3-H(3.44) in 4a. These observations lead to expression (5a) for this compound, albeit, this was found to be a mixture of isomers involving C_4 and C_5. The expression 5b was arrived at in identical manner. However, the highest peak in its mass spectrum appeared at m/z 381 (M^+ - 123); the rest of mass spectral fragmentation pattern was similar to that of 5a. The compound 5c displayed similar spectral features (vide experimental).

In reactions involving 1a,b dimers (mass), in low yield, of 1a,b were obtained which could not be further examined.

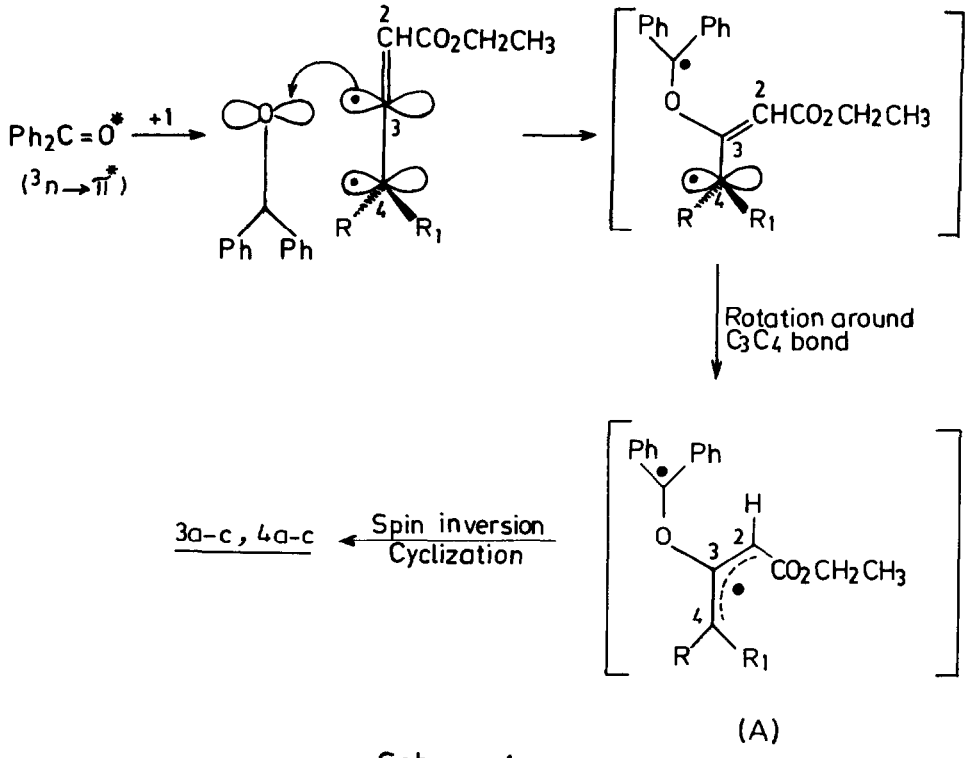
Table-1 [a] %yield of Various Photo-products

Allenic Ester	Product				
	2	3	4	5	Benzpinacol
1a	7	4.7	9.3	4.5	33
1b	6	5.7	11.3	5.5	36.5
1c	not isolated	3	12	6.5	42.6

a. Based on the amount of benzophenone taken.

The formation of oxetanes 3a-c and 4a-c is rationalised in terms of attack by the benzophenone molecule (n-π^*-triplet) on the central allenic carbon of the allenic esters to yield diradical (A). Since the attack through oxygen atom of benzophenone is characteristic of addition to electron rich π-bond[6], the C_3-C_4 π-bond of the respective esters must be involved in the initial step. The assigned geometries at the exocyclic double bond in 3a,b and 4a-c appear to be related to steric requirements of the bulky groups in the diradical (A). The loss of stereoselectivity in case of 3c, perhaps results

from the comparable size of the groups R_1 and R (Scheme 1).



Scheme-1

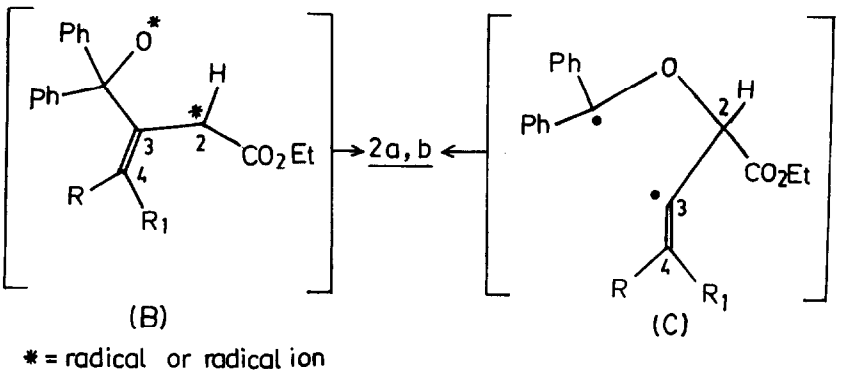
The formation of 2a,b, which involves addition of benzophenone to electron deficient C_2-C_3π-bond of the respective allenic esters (1a,b), appears to be of particular interest. Only aliphatic ketones are known to undergo such additions through a π* ketone- π* olefin type interaction[6,8]. A rationalization of the present observations requires consideration of the following routes to 2a,b:

i. involving π* benzophenone- π* olefin type interaction in which the C_2-C_3π-bond of allenic ester acts as an acceptor, leading to intermediate (B).

ii. involving π* benzophenone- π olefin type interaction leading to intermediate (C), albeit, this is deemed less likely.

iii. involving attack of sensitized allenic ester molecule on the benzophenone molecule [8,9]. This also explains the formation of dimeric products of allenic esters during some of the photoreactions. However, the formation of 2a,b is certainly an exclusive affair of the C_2-C_3π-bond of the respective allenic esters. Again, the reasons for nondetection of 2c (in the reaction involving 1c) may be a fast conversion of 2c into 5c (Scheme 3).

Alternately, steric hinderance, perhaps prevents approach of the benzophenone molecule to C_2-C_3 π-bond in 1c (which would have led to 2c) (Scheme 2).

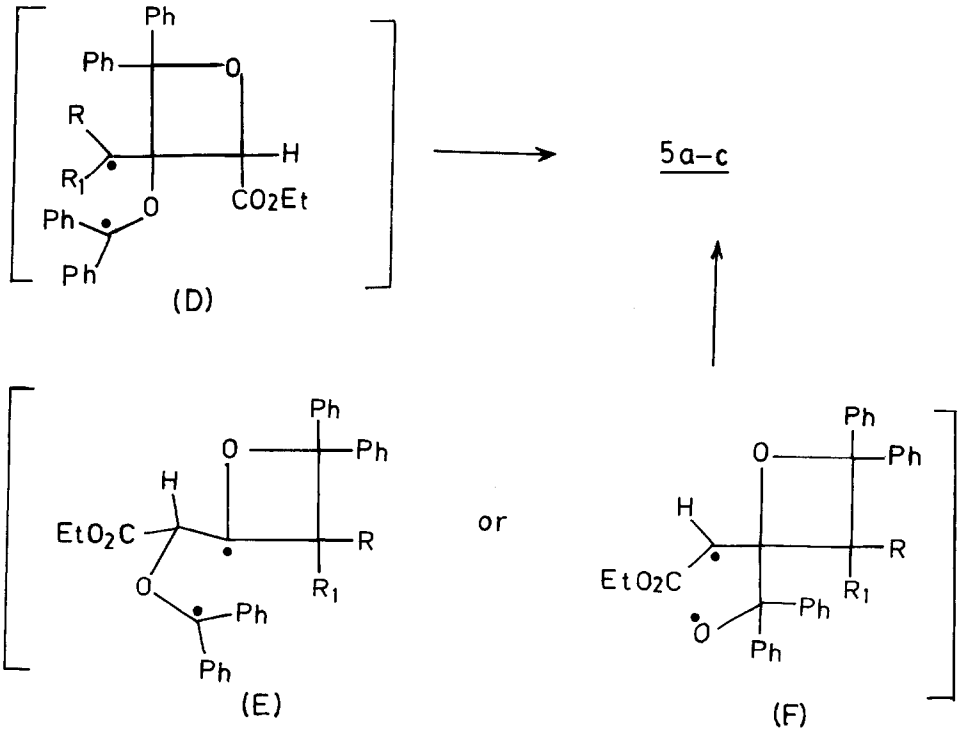


(B) (C)

* = radical or radical ion

Scheme-2

A priori, the formation of dioxetanes (5a, 5b and 5c) occurs through addition of excited benzophenone molecule, respectively, to mono-oxetanes 2a,b (2c) and/or 4a-c, and involves longlived triplet diradical intermediates (D,E,F) leading to observed loss of stereoselectivities.



(D) (E) (F)

Scheme-3

EXPERIMENTAL

General : Infrared spectra were recorded with a Unicam SP-1200 infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained on a Jeol-JNM-FX-100 FT NMR spectrometer (99.55 MHz for ^{1}H and 24.99 MHz for ^{13}C nuclei) using TMS as internal standard. Mass spectra were taken on a Jeol-JMS-D300 spectrometer. Allenic esters 1a-c were prepared by literature method[10]. Silica gel used for column chromatography was 60-120 mesh (E.Merck) and, unless otherwise specified, petroleum ether refers to 60-80°fraction.

Irradiation of benzophenone in presence of 1a in benzene

A solution of benzophenone (600 mg) and freshly distilled 1a (1.2 g) in anhydrous thiophene-free benzene (350 ml) was irradiated for 128 h in a water-cooled pyrex reactor, using medium pressure 125 Watt mercury lamp. N_2 was continuously bubbled through the solution during irradiation and the progress of the reaction was monitored through Tlc. The solvent was removed under vacuum and the resultant thick oil was chromatographed over silica gel(30 g, column packed in pet. ether). Elution of the column with pet. ether and pet.ether-ethyl acetate gradient yielded : unreacted 1a (100 mg, IR); a colourless thick oil (mixture of dimers of 1a), IR(CCl_4): 1720, 1640 1590, 1500, 1440, 1280, 1180 cm^{-1}, ^{1}H NMR($CDCl_3$): δ 5.40-4.80(m), 3.60(m), 3.56-3.24(m), 2.96-2.72(m), 2.25(m), 2.10(s), 1.88-0.60(br,m), mass: m/z 252, 196, 183, 181, 125, 115, 28(100); unreacted banzophenone (120 mg); 2a, a colourless thick oil (60 mg, 7%), IR(CCl_4): 1740, 1585, 1560, 1500, 1450, 1260, 1040, 980 cm^{-1}, ^{1}H NMR($CDCl_3$) : δ 7.25 (m, 10H, arom. Hs), 5.60(q, 1H J=6.50 Hz, C_8-H), 4.22(b s, 1H, C_2-H), 3.76 (q, J=7.10 Hz, C_6-Hs), 1.62 (b d, 3H, C_8-Me), 0.9(t, 3H, C_7-Hs), ^{13}C NMR($CDCl_3$): δ 167.6(C=O), 141.0, 138.5 (quaternary Cs), 128.6,127.4, 125.2, 93.4(C_4), 88.2(C_2), 60.7(C_6), 16.5 (C_8-Me), 13.7(C_7), mass:m/z 308(15,M^+), 253, 252, 235, 207, 206, 182, 77(100); a mixture (1:2) of 3a and 4a, colourless semisolid (120 mg, 14%), IR(CCl_4) : 1725(b), 1640, 1600, 1500, 1450, 1280, 1200, 1070, 1035, 980, 920 cm^{-1}, ^{1}H NMR ($CDCl_3$) : δ 7.27(m, arom.Hs), 5.32(b s, C_5-H in 4a), 4.50-3.91 [m, δ 4.40 (split q, J=6.8 Hz and 0.95 Hz, C_8-Hs in 3a), δ 4.00 and 3.85 (overlapping qs], 3.60 (b s, C_3-H in 3a), 3.44 (q, J=7.57 Hz, C_3-H in 4a), 1.30-1.05 [m,δ1.23 (split d, J=6.8 Hz and 1.05 Hz, C_8-Me in 3a), 1.12 and 1.08 (ts)], 0.90 (b d, J=7.57 Hz, C_3-Me in 4a), ^{13}C NMR($CDCl_3$): δ 168.2, 167.2, 154.1, 144.9, 141.3, 127.7, 127.5, 127.2, 126.9, 116.3, 105.4, 91.7 and 90.2(C_4), 61.2, 60.9, 54.2(C_3 in 3a), 42.6, 17.1, 14.4 and 13.8, mass: m/z 309(10, M^++1), 308(40, M^+), 279, 252, 194, 183, 77(100); benzpinacol(200 mg), m.p. 185-186° C(^{1}H NMR, IR); 5a, colourless semisolid, 38 mg (4.5%), IR(CCl_4): 1740, 1600, 1560, 1480, 1270, 1230, 1000, 980, 940 cm^{-1}, ^{1}H NMR($CDCl_3$): δ 7.28 (m,20H, arom.HS), 4.68 and 4.59 (b singlets, C_5-H), 3.87 and 3.84(overlapping qs, C_9-Hs), 3.49

(b q, C_4-H), 1.22 (b d, C_4-Me), 0.80 (b t, C_{10}- Hs), mass :m/z 490 (3,M^+), 461, 413, 367, 349, 262, 261, 258, 257, 222, 182(100).

Irradiation of benzophenone in presence of 1b in benzene

A solution of benzophenone (600 mg) and freshly distilled 1b (1.5 g) in anhydrous thiophene-free benzene (350 ml) was irradiated for 160 h under the above conditions. Chromatographic separation of the crude product over silica gel (30 g, column packed in pet. ether, pet. ether-ethyl acetate gradient as eluant) yielded: unreacted 1b (160 mg, IR); a mixture of dimers of 1b as a colourless thick oil (150 mg), ^{1}H NMR ($CDCl_3$): δ 6.24(d), 6.00-6.52(m), 4.50-3.94(m), 3.60-3.40(m), 2.98-2.60(m), 2.16(s), 1.90-0.65(b m), mass: m/z 280(5), 279, 210, 149(100), 113, 112, 97, 96, 72, 56, 55; unreacted benzophenone (110 mg); 2b, a colourless gummy material, 55 mg(6%), IR(CCl_4): 1730, 1630, 1590, 1580, 1500, 1450, 1270, 1190, 1040, 1000, 980 cm^{-1}, ^{1}H NMR ($CDCl_3$) : δ 7.26 (m, 10H, arom. Hs), 5.60(b t, 1H, J=6.96 Hz, C_8-H), 4.23(b s, 1H, C_2-H), 3.77(q, 2H, J=7.08 Hz, C_6-Hs), 1.98(b quintet, 2H,C_8-CH_2-) ,1.08 and 0.98 (overlapping ts, J=7.08 Hz and J=7.0 Hz), ^{13}C NMR ($CDCl_3$): δ 167.6, 141.2, 138.0, 128.4, 127.4, 126.8, 93.8(C_4), 86.2(C_2), 60.5, 23.8, 13.8 and 13.4, mass :m/z 322(20, M^+), 293, 279, 274, 252, 183, 182, 105, 85, 77(100); a mixture (1:2) of 3b and 4b, colourless semisolid, 150 mg(17%),IR(CCl_4): 1725, 1640, 1630, 1595, 1540, 1450, 1320, 1280, 1260, 1190, 1165, 1070, 1040, 980, 940 cm^{-1}, ^{1}H NMR($CDCl_3$): δ 7.27 (m, arom. Hs), 5.33(br s, C_5-H in 4b), 4.48 (split t, J=6.8 Hz and J=1.0 Hz, C_5-H in 3b), 4.00 and 3.9 (overlapping quartets), 3.61(b s, C_3-H in 3b), 3.50(split t, J=7.23 Hz and J=1.49 Hz,C_3-H in 4b), 2.10-1.60(b m, C_8-CH_2 - in 3b and C_3-CH_2-in 4b), 1.18, 1.06, 0.96 and 0.69(triplets), ^{13}C NMR($CDCl_3$): δ 169.4, 167.5, 153.8, 143.4, 142.2, 141.6, 127.4, 127.2, 126.9, 126.8, 119.9, 106.5, 92.8 and 89.8(C_4), 61.2, 60.8, 54.0 (C_3 in 3b), 49.6(C_3 in 4b), 24.6, 21.3, 14.4, 13.9, 12.2 and 11.6, mass; m/z 323(3, M^+ +1), 322(20,M^+),294, 293, 277, 276, 252, 194, 182, 165, 105, 77 (100); benzpinacol (220 mg); 5b, a colourless semisolid, 50mg(5.5%),IR(CCl_4): 1730(b), 1600, 1540, 1480, 1450, 1280, 1050, 980, 950, 910 cm^{-1}, ^{1}H NMR ($CDCl_3$): δ 7.28 (m, 20H, arom. Hs), 4.68 and 4.57 (singlets, C_5-H), 3.96 and 3.80 (overlapping quartets), 3.54 (b t, J=7.0 Hz, C_4-H), 1.69(m), 1.20, 1.18 and 0.76 (overlapping triplets), mass : m/z 381 (M^+-123), 348, 322, 276, 252 208, 193, 182, 181, 165, 154, 105, 77(100).

Irradiation of benzophenone in presence of 1c in benzene

A solution of benzophenone (700 mg) and freshly distilled 1c,(1.5 g) in anhydrous thiophene-free benzene was irradiated for 160 h, under the conditions as described above. The chromatographic separation of the photolysate (silica gel, 30 g, column packed in pet. ether and eluted with pet.

ether-ethyl acetate gradient) gave, [in addition to unreacted 1c (120 mg), unreacted benzophenone (60 mg), benzpinacol (300 mg)], 3c, a colourless thick oil, 34mg (3%), IR(CCl_4): 1730 (b s) 1650, 1590, 1540, 1490, 1450, 1340, 1280, 1200, 1075, 1060, 980, 930 cm^{-1}, ^1H NMR($CDCl_3$): δ7.28 (m, 10H, aromatic Hs), 4.02(q, 2H, J=7.08 Hz) 3.90(s, 1H, C_3-H), 2.24-1.66(m,C_8-CH_2-), 1.76 and 1.46 (singlets, C_8-methyls in isomeric structures), 1.24(t),0.88 and 0.80 (ts, J=7.08 Hz and J=7.50 Hz), ^{13}C NMR ($CDCl_3$): δ168.9, 141.1, 134.3, 133.8, 127.3, 127.0, 126.9, 93.8(C_4), 60.6, 55.8, 55.4, 24.4, 23.8, 16.7, 16.1, 13.5, 12.5 and 12.3, mass: m/z 366(10,M^+), 321, 292, 252, 222, 208, 207, 282, 153, 105 and 77(100); 4c, a colourless semisolid, 130 mg(12%), IR(CCl_4): 1730(b s), 1640, 1600, 1540 1450, 1270, 1060, 980, 940 cm^{-1}, 1H NMR ($CDCl_3$): δ 7.27 (m, 10H, arom. Hs), 5.44(s, 1H, C_5-H), 3.97(q, 2H, J=7.08 Hz), 1.80 (q, 2H, J=7.36 Hz), 1.37(b s, 3H), 1.20(t, 3H), 0.70(t, 3H), ^{13}C NMR($CDCl_3$); δ168.1, 146.1 (C_2), 142.8, 127.4, 127.1, 126.9, 112.3, 90.5(C_4), 60.2, 57.8, 21.4, 17.9, 13.9 and 10.6, mass: m/z 337(5, M^++1), 336(15,M^+), 292, 291, 263, 222, 182, 179, 105, 77(100), 57; 5c, a colourless gummy material, 70 mg(6.5%), IR(CCl_4): 1810(w), 1740(b s), 1620, 1600, 1500, 1480, 1450, 1280, 1240, 1050, 980, 960, 940 cm^{-1}, ^1H NMR($CDCl_3$): δ7.31(m, 20H, arom. Hs), 4.57 and 4.44 (singlets, C_5-H in isomeric structures), 3.84 and 3.58 (two overlapping qs, J=7.08 Hz), 1.80(m), 1.27 and 1.05(singlets), 0.87 and 0.86(overlapping triplets), 0.59, 0.44 (triplets, J=7.32 Hz), ^{13}C NMR($CDCl_3$): δ167.4, 143.4, 143.0, 127.5, 127.4, 127.1, 126.9, 90.7, 90.2, 88.8, 85.5., 83.4, 63.8, 63.4, 60.5, 25.7, 24.3, 18.9, 18.1, 14.5, 9.4 and 9.3, mass: m/z 473 (3, M^+-OC_2H_5). 472, 395, 367, 252, 182, 105, 77(100), 57.

REFERENCES AND NOTES

1. (a) Hogveen H.C. and Smit, P.J. Rec.Trav.Chim. (1966) 85, 1188-1190; (b) Gotthardt, H.; Steinmetz, R. and Hammond, G.S. J.Chem.Soc.Chem. Commun. (1967), 480-482; (c) Arnold, D.A. and Glick, A.H. J.Chem. Soc. Chem. Commun. (1966), 813-814; (d) Gotthardt, H.; Steinmetz, R. and Hammond, G.S. J.Org. Chem.(1968) 33, 2774-2780.

2. Gotthardt, H. Tetrahedron Lett. (1971), 2345-2348.

3. Kamphuis, J.; Hupkes, J.G.; Visser, R.G. and Bos, H.J.T. Rec. Trav. Chim. (1982) 101, 114-118.

4. (a) Ishibe, N. and Tanigushi, I.Tetrahedron(1971) 27, 4883-4887; (b) Ishibe, N.; Hashimoto, K. and Yamaguchi, T. J.Chem. Soc. Perkin I, (1975), 318-323; (c) Ogino, K.; Matsumoto, T.; Kawai, T. and Kozuka, S. J.Org. Chem. (1979) 44, 3352-3356.

5. (a) Boleij, J.S.M. and Bos, H.J.T. Rec. Trav. Chim. (1972) 91, 1212-1224; (b) Koster, R.J.C. and Bos, H.J.T. Rec. Trav. Chim. (1975) 94, 79-82; (c) Boleij, J.S.M. and Bos, H.J.T. Tetrahedron Lett. (1971), 3201-3202.

6. (a) Turro, N.J.Modern Molecular Photochemistry, Benzamin/Cummings, California, 1978, pp. 432-452; (b) Jones, G. II in Organic Photochemistry, edited by A. Padwa, Marcel Dekker, New York, 1981, Vol.5, Chapter 1, pp. 1-122; (c) Carless, H.A.J. in Synthetic Organic Photochemistry, edited by W.M. Horspool, Plenum Press, New York, 1984, Chapter 8, pp 425-487.

7. Gaudemer, A. in Stereochemistry, edited by H.B. Kagan, Georg Thieme Publishers, Stuttgart, 1977, Vol.1, pp. 44-59.

8. This is reminiscent of a mechanism proposed earlier for addition of ketones to some electron deficient olefins such as fumarates and maleates [Albone, E.S. J.Am. Chem. Soc. (1968) 90, 4663-4666].

9. A mechanism involving attack of a sensitized diene molecule on a benzophenone molecule in ground state was proposed by Saltiel et.al. [Saltiel, J.; Coates, R.M. and Dauben, W.G. J. Am. Chem. Soc. (1966) 88, 2745-2748]. However, kinetic measurements on the above reactions by Barltrop and Carless [Barltrop, J.A. and Carless, H.A.J. J.Am. Chem. Soc. (1971) 93, 4794-4801] do not support the above mechanism.

10. (a) Gandhi, R.P.; Ishar, M.P.S. and Wali, A. Tetrahedron Lett. (1987), 6679-6682; (b) Ishar, M.P.S.; Wali. A. and Gandhi,R.P. J. Chem. Soc. Perkin I (1990), 2185-2192.