Photochemistry of Acyclic βγ-Unsaturated Ketones. Determination of the Electronically Excited State responsible for α-Cleavage by Chemically Induced Dynamic Nuclear Polarisation

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The CIDNP effects during irradiation of six acyclic βγ-unsaturated ketones have been studied. The α-cleavage is mainly a reaction from the electronically excited singlet n–π^* state if the alkene part of the βγ-enone is substituted with a phenyl group at the γ-position. but the α-cleavage occurs mainly from the triplet excited state if the alkene system is substituted with methyl groups at that position. The difference in multiplicity is rationalized in terms of whether intramolecular quenching is possible or not.

THE photochemistry of βγ-unsaturated ketones has received considerable attention which is reflected by several recent reviews.[1] βγ-Unsaturated ketones can exhibit ketone (Norrish type I and II reactions) and alkene types of photochemistry (*E–Z*-isomerization and oxa-di-π-methane rearrangement). The multiplicity of the excited state from which the Norrish type I (α-cleavage) reaction occurs in βγ-unsaturated ketones is still a matter of debate. Theoretical calculations [2] on hex-4-en-2-one as a model βγ-unsaturated ketone predicted that the lowest excited singlet state is mainly of n–π^* character, whereas the lowest triplet state is mainly of π–π^* character. In accord with the knowledge that α-cleavage is a reaction typical of n–π^* excited carbonyl compounds [3] one would expect that for βγ-unsaturated ketones this reaction takes place from the singlet excited state. However, recent studies by Dalton [4] and Schuster [5] indicate that the α-cleavage may also be a triplet reaction.

In order to gain more insight into the problem of the multiplicity of the excited state exhibiting α-cleavage, the CIDNP effects observed during the photolysis of six βγ-unsaturated ketones have been studied. Only one CIDNP study of the photochemistry of an acyclic βγ-unsaturated ketone has been reported, that by DoMinh on the photochemistry of isomesityl oxide in CCl_4,[6] who concluded that α-cleavage occurs from the singlet excited state. However, for other carbonyl compounds it has been found that in CCl_4 a singlet reaction takes place, whereas for other solvents α-cleavage occurs from the triplet state.[7] Therefore the study of DoMinh may be not representative for the precursor multiplicity of α-cleavage.

CIDNP studies on the photochemistry of phenyl and *p*-methoxyphenyl 1,2,3-trimethylcyclopent-2-enyl ketone [8] revealed that for these compounds α-cleavage is a triplet reaction. With the related monocyclic βγ-unsaturated ketones in which the aryl group is replaced by a methyl substituent [9] it appears that α-cleavage leading to a radical pair intermediate is unimportant.

α-Phenyl aldehydes [10] and ketones [11] exhibit α-cleavage from the triplet excited state, as was concluded from CIDNP studies. α-1-Naphthyl aldehydes,[10] however, did not show any CIDNP effects upon irradiation. The absence of CIDNP effects with the naphthyl substrate was explained in terms of intramolecular quenching of the triplet excited carbonyl by the α-naphthyl group.

RESULTS AND DISCUSSION

Two types of acyclic βγ-unsaturated ketones have been investigated (Scheme), namely those in which the γ-carbon carries (i) two methyl groups [(1)—(3) [12]] and (ii) one phenyl group [(4)—(6)]. The electronically excited βγ-unsaturated ketones can undergo α-cleavage yielding an acyl and an allyl radical. These dissimilar radicals can recombine yielding the starting compound or the 1,3-acyl shift product, as observed with (1) and (4)—(6). Combination of two allyl radicals affords an octa-2,6-diene, as observed with substrates (1)—(3). In addition, decarbonylated products have been found, with (3), (5), and (6), for which the decarbonylation of the acyl radicals is relatively fast (for the isobutyryl and pivaloyl radicals the rate constants are 4×10^3 and 5×10^4 s^{-1} respectively [13]). *E–Z*-Isomerization cannot be

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[1] (*a*) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531; (*b*) W. G. Dauben, G. Lodder, and J. Ipaktschi, *Fortschr. Chem. Forschung*, 1975, **54**, 73; (*c*) K. N. Houk, *Chem. Rev.*, 1976, **76**, 1; (*d*) K. Schaffner, *Tetrahedron*, 1976, **32**, 641.

[2] K. N. Houk, D. J. Northington, and R. E. Duke, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 6233.

[3] P. J. Wagner, *Topics Current Chem.*, 1976, 1 and references cited therein.

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[5] D. I. Schuster, J. Erikson, P. S. Engel, and M. A. Schexnayder, *J. Amer. Chem. Soc.*, 1976, **98**, 5025.

[6] T. DoMinh, *Ind. Chim. belges*, 1971, **36**, 1080.

[7] (*a*) J. A. den Hollander, R. Kaptein, and P. A. T. M. Brand, *Chem. Phys. Letters*, 1971, **10**, 430; (*b*) B. Blank, A. Herne, and H. Fischer, *Helv. Chim. Acta*, 1974, **57**, 920; (*c*) N. A. Porter and P. M. Hoff, jun., *J. Amer. Chem. Soc.*, 1974, **96**, 6200.

[8] H.-U. Gonzenbach, K. Schaffner, B. Blank, and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 1741.

[9] H.-U. Gonzenbach, I.-M. Tegmo-Larson, J. P. Grosclaude, and K. Schaffner, *Helv. Chim. Acta*, 1977, **60**, 1091.

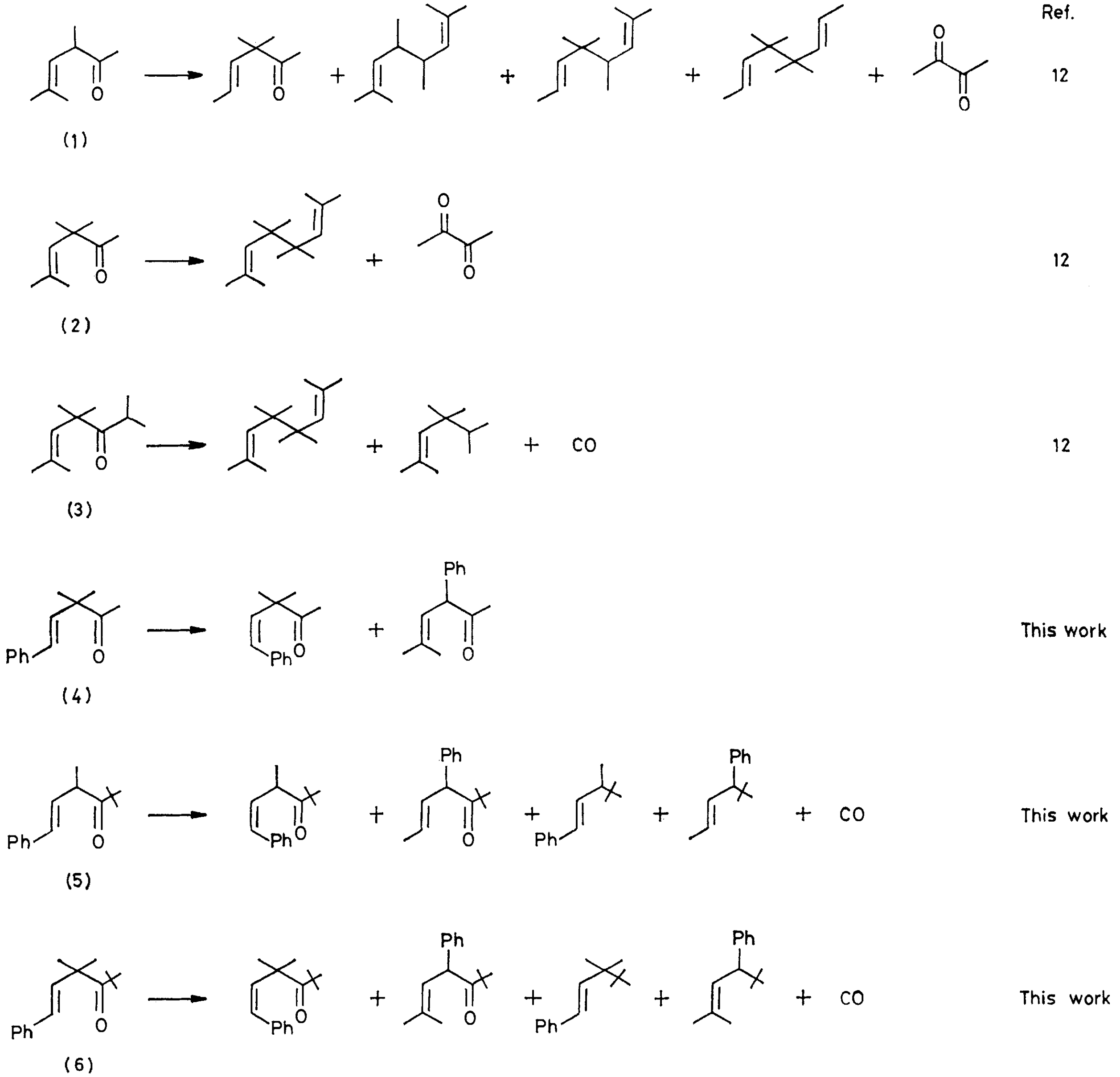
[10] K. Schaffner, H. Wolf, S. M. Rosenfeld, R. G. Lawler, and H. R. Ward, *J. Amer. Chem. Soc.*, 1972, **94**, 6553.

[11] K. Müller and G. L. Closs, *J. Amer. Chem. Soc.*, 1972, **94**, 1002.

[12] A. J. A. van der Weerdt and H. Cerfontain, *J. C.S.Perkin II*, 1977, 1357.

[13] M. J. Perkins and B. P. Roberts, *J.C.S. Perkin II*, 1974, 297.

detected with (1)—(3) for structural reasons, but has been observed with (4)—(6).



SCHEME Photoproduct formation of acyclic βγ-unsaturated ketones with λ 313 nm

U.v. irradiation of (1) and (2) leads to enhancement of the ^{1}H n.m.r. absorptions of the methyl groups at the α- and γ-positions of the starting material (see Figure 1). For (1) the acetyl group shows weak emission, whereas for (2) the initial absorption of that group is only reduced. For short irradiation times the starting material can be recovered almost quantitatively. The two methyl groups at the α-position in the 1,3-acyl shift product resulting from (1) show enhanced absorption. The other high field signals of this product overlap with those of the starting compound. The formation of the α-diketone and the octa-2,6-dienes for (1) and (2) which was established previously,[12] is not apparent from the ^{1}H n.m.r. spectrum of the reaction mixture. By application of Kaptein's rules[14] using *g*(acetyl radical) 2.000 5,[15] *g*(allyl radical) 2.002 5[16] and considering that the hyperfine coupling constant is positive for the methyls of the acetyl[15] and methyl substituted allyl radical,[16] the CIDNP effects may be explained in terms of (i) α-cleavage of (1) and (2) from mainly * the triplet excited state and/or (ii) re-formation of the starting compounds

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* With CIDNP only overall effects are observed. Accordingly it can only be concluded that a product results *mainly* from *e.g.* a singlet excited state.

[14] R. Kaptein, *Chem. Comm.*, 1971, 732.

[15] H. Paul and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 1575.

[16] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

from the encounter of free radicals. For the α-phenyl aldehydes[10] it was concluded that the observed CIDNP effects do not account for the major photochemical pathway of the product formation. The pronounced CIDNP effects of compounds (1) and (2), however, are in agreement with their photochemistry, which revealed that *ca.* 40% of the initially formed free radicals regenerate the starting compound.

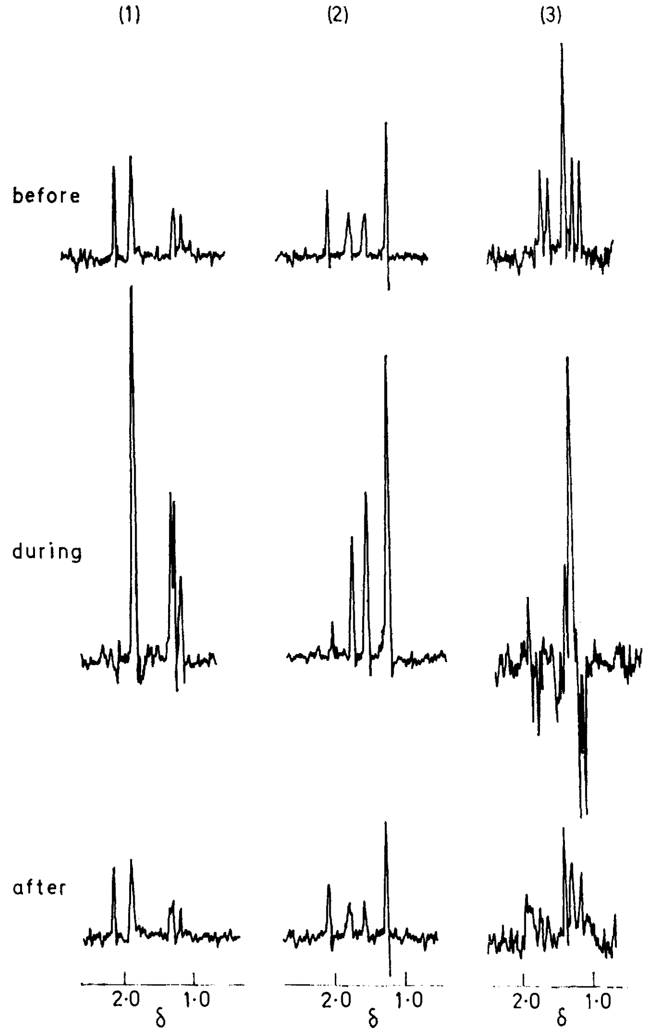

FIGURE 1 ^{1}H N.m.r. spectra of (1)—(3) before, during, and after u.v. irradiation

The high field part of the ^{1}H n.m.r. spectrum of (3) during irradiation (see Figure 1) is complicated. An accurate comparison of the spectra of (3) before, during, and after irradiation revealed that the intense CIDNP signals are not from the starting compound. The absorption and emission signals may be due to the formation of propane resulting from the reaction of the isopropyl radical, formed after decarbonylation of the acyl radical, with the allyl radical. At present it is not possible to assign the observed signals. It can, however, be seen from the ^{1}H n.m.r. spectrum of (3) during irradiation that the substrate itself, in contrast with (1) and (2), does not show a pronounced CIDNP effect. This is consistent with the conclusion drawn from the photolysis of (3) in the presence and absence of tri-n-butylstannane that none of the initially formed free radicals recombine to starting material.[12]

Irradiation of (4) leads to enhanced absorption at δ 4.55 and 2.10 and to emission at δ 1.79 and 1.68 (see Figure 2). All these signals come from the 1,3-acyl shift product, δ 4.55 (α-H); 2.10 (MeCO), and 1.79 and 1.68 (γ-CH_3). For the starting material the α-methyl groups show emission but the acetyl group shows hardly any effect. The *Z*-isomer product shows hardly any effect either. Assuming that the presence of a phenyl substituent does not significantly affect the *g* value of the allyl radical,* one can apply the same *g* values as used above in the case of (1) and (2). The coupling constant is positive for the methyl groups and negative for the methine hydrogen atom in the allyl radical.[16] The effects observed with (4) for the formation of starting compound and the 1,3-acyl shift product can only be explained if the α-cleavage reaction is coming mainly from the singlet excited state. The absence of any CIDNP effects for the signals of the *Z*-isomer product illustrates that this compound is not formed *via* a radical process.

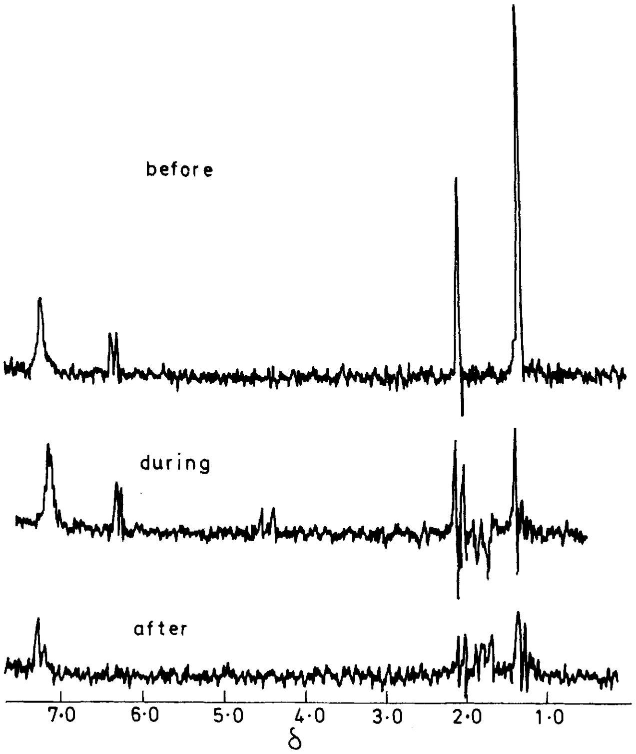

FIGURE 2 ^{1}H N.m.r. spectra of (4) before, during, and after u.v. irradiation

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* This assumption is based on the observation that even the *g* values of simple saturated alkyl radicals (2.002 6)[15] and allyl radicals (2.002 5)[16] are equal.

With (6) (see Figure 3) and (5), the high-field part of the n.m.r. spectrum is more complex than that obtained with (4). This may be due to the fact that, besides the pivaloyl radical, the t-butyl radical, formed from the former by decarbonylation, can react with the allyl radical [*cf.* (3)]. The 1,3-acyl shift products from both compounds show the same absorption and emission signals as the 1,3-acyl shift product of (4). For the α-methyl group(s) in the starting material a slight decrease in absorption is observed. The results for (5) and (6) indicate that α-cleavage, as with (4), originates mainly from the singlet excited state. Further, for both compounds an absorption–emission signal is observed at high field (δ 0.8) which can be caused by a CIDNP effect from the formation of isobutane. This product probably results from a disproportionation reaction of a random encounter (F) pair of t-butyl with allyl radicals.

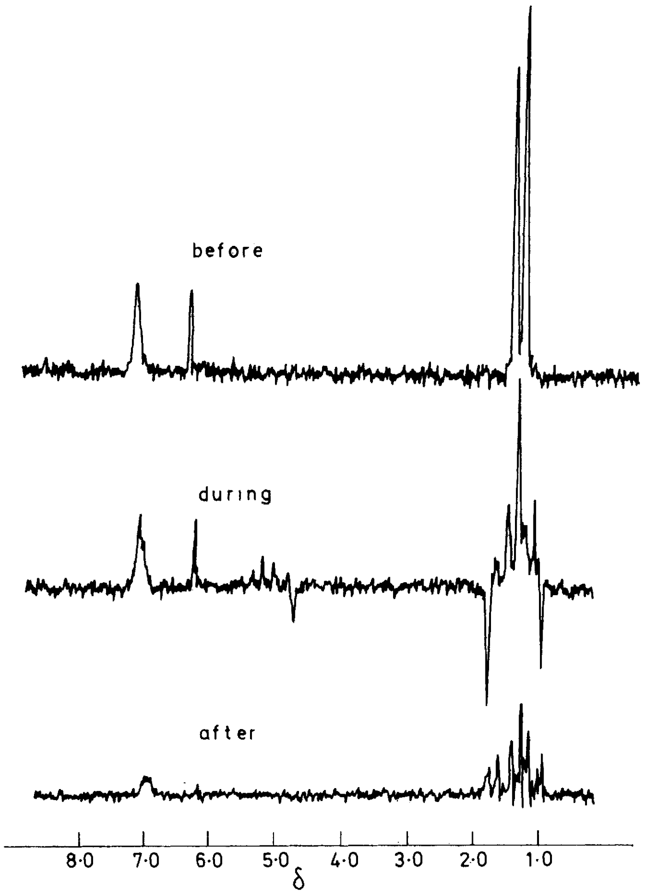

FIGURE 3 ^{1}H N.m.r. spectra of (6) before, during, and after u.v. irradiation

For (1) and (2) the CIDNP effects indicate a triplet precursor and/or a free radical encounter process. The possibility that the free radicals are formed from a singlet n–π^* excited state seems unlikely because in that case the same CIDNP effects are expected for (1) and (2) as for (4)—(6), which originate mainly from the singlet excited state (see before), since it seems unlikely that (1) and (2) are more willing to form free radicals from the excited singlet n–π^* than (4)—(6).

It thus appears that the α-cleavage in βγ-unsaturated ketones is mainly a singlet reaction if the alkene is substituted with a phenyl group at the γ-position [(4)—(6)], but mainly a triplet reaction if the alkene contains methyl substituents at that position [(1)—(3)]. For both types of compounds the electronically excited (singlet) state is probably n–π^* in character. The difference in the multiplicity of the reactive state of the two types of compounds can be explained by considering the two chromophores in the molecule (*i.e.* the carbonyl and the alkene systems) as isolated.[17] With (4)—(6) the triplet excited carbonyl (E_T *ca.* 80 kcal mol^{-1} [18]) can be efficiently quenched by the styrene part of the molecule (E_T *ca.* 60 kcal mol^{-1} [18]) and α-cleavage will be mainly a singlet reaction. With (1)—(3), however, the triplet excited state of the alkene has about the same energy content [18] as the triplet excited carbonyl. The quenching of the triplet excited carbonyl will thus not be an efficient process, and for the CIDNP effect the triplet reaction predominates. The mechanism now proposed will be subject to further study.

EXPERIMENTAL

Syntheses of βγ-Unsaturated Ketones.—(E)-5-*Phenylpent*-4-*en*-2-*one*. The βγ-unsaturated ketone was prepared by the reaction of methyl-lithium with 4-phenylbut-3-enoic acid [12, 15] in 42% yield, b.p. 134—136° at 8.5 mmHg (lit.,[19] 150° at 15 mmHg [19]). The spectral data were in accord with those already described.[20]

(E)-3,3-*Dimethyl*-5-*phenylpent*-4-*en*-2-*one* (4). This compound was synthesized by the reaction of the carbanion of 5-phenylpent-4-en-2-one with methyl iodide.[12] The crude product was purified by g.l.c. (5 m × ¼ in; 10% Carbowax 20 M; 160°). The product is a slightly yellow oil. δ (CCl_4) 7.3 (5 H, m), 6.44 (1 H, d, J 16 Hz), 6.26 (1 H, d, J 16 Hz), 2.13 (3 H, s), and 1.31 (6 H, s); $\nu_{max.}$ ($CHCl_3$) 3 050, 2 990, 2 930, 2 870, 1 705, 1 670, 1 600, 1 580, 1 500, 1 470, 1 450, 1 380, 1 350, 1 115, and 965 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 293 (ε 2 240), 284 (2 620), and 253 nm (18 000); m/e 188 (M^+), 145 (base) (Found: C, 82.9; H, 8.6. $C_{13}H_{16}O$ requires C, 82.95; H, 8.55%).

(E)-2,2-*Dimethyl*-6-*phenylhex*-5-*en*-3-*one*.—A solution of diethyl 3,3-dimethyl-2-oxobutylphosphonate [21] (42 mmol) in dry dimethoxyethane (DME) (30 ml) was added to a suspension of sodium hydride (42 mmol) in dry DME (80 ml) under nitrogen at 10—15°. After the addition a solid mass was formed which dissolved again after stirring at 40° for 0.5 h. The solution of the anion thus prepared was added slowly to a solution of phenylacetaldehyde (51 mmol; freshly distilled) in DME (50 ml) under nitrogen

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[17] I. M. Tegmo-Larson, H.-U. Gonzenbach, and K. Schaffner, *Helv. Chim. Acta*, 1976, **59**, 1376.

[18] S. L. Murov, 'Handbook of Photochemistry,' Marcel Dekker, New York, 1973, Table 1.

[19] R. Linstead and L. Williams, *J. Chem. Soc.*, 1926, 2735.

[20] D. Chambenois and G. Mousset, *Compt. rend.* 1972, **275**, 1287.

[21] G. Sturtz, *Bull. Soc. chim. France*, 1964, 2349.

at 0—3°. The mixture was stirred overnight at ambient temperature, and then poured onto ice. The mixture was extracted twice with ether. The combined organic layers were washed with brine till neutral and dried ($MgSO_4$). The solvent was removed and the residue was distilled *in vacuo*, b.p. 113—114° at 0.7 mmHg, yield 4 g (47%). The product is a slightly yellow oil, δ (CCl_4) 7.2 (5 H, m), 6.3 (2 H, m), 3.35 (2 H, m), and 1.12 (9 H, s); $\nu_{max.}$ (liquid capillary) 3 050, 2 980, 2 860, 1 700, 1 620, 1 600, 1 580, 1 500, 1 480, 1 470, 1 450, 1 395, 1 365, 1 280, 1 270, 1 160, 1 085, 1 060, 1 025, and 960 cm^{-1}.

(E)-2,2,4-*Trimethyl*-6-*phenylhex*-5-*en*-3-*one* (5). Compound (5) was synthesized by the reaction of the carbanion of 2,2-dimethyl-6-phenylhex-5-en-3-one, prepared by the reaction of this βγ-enone with potassium t-butoxide, with methyl iodide.[12] The crude product was distilled *in vacuo*, b.p. 95—98° at 0.05 mmHg, yield 55%. The distillate was further purified by g.l.c. (5 m × $\frac{3}{8}$ in; 15% SE-30; 200°). The product is an oil, δ (CCl_4) 7.22 (5H, m), 6.35 (1 H, d, *J* 15 Hz), 6.13 (1 H, dd, J_1 15, J_2 6 Hz), 3.78 (1 H, quintet, *J* 6 Hz), 1.22 (3 H, d, *J* 6 Hz), and 1.13 (9 H, s); $\nu_{max.}$ (liquid capillary) 3 080, 3 060, 3 020, 2 970, 2 930, 2 900, 2 870, 1 700, 1 600, 1 580, 1 480, 1 450, 1 395, 1 370, 1 320, 1 200, 1 075, 1 060, 1 040, 990, and 970 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 293 (ε 2 195), 285 (2 520), and 253 nm (17 350) (Found: C, 83.4; H, 9.3. $C_{15}H_{20}O$ requires C, 83.3; H, 9.3%).

(E)-2,2,4,4-*Tetramethyl*-6-*phenylhex*-5-*en*-3-*one* (6). Compound (6) was prepared by the reaction of the carbanion of 2,2,4-trimethyl-6-phenylhex-5-en-3-one with methyl iodide. The carbanion was prepared using sodium hydride, potassium t-butoxide being unreactive as base probably for steric reasons. A solution of 2,2,4-trimethyl-6-phenylhex-5-en-3-one (9.2 mmol) in dry tetrahydrofuran (THF) (5 ml) was added dropwise under nitrogen to a stirred suspension of sodium hydride (10.4 mmol) in dry THF (10 ml) at room temperature. After stirring overnight methyl iodide (2 ml) was added. The mixture was stirred for 4 h and then poured into ice–water. The aqueous mixture was extracted twice with ether. The combined organic layers were washed with brine till neutral. After drying ($MgSO_4$) and evaporating the solvent, the residue was purified by preparative g.l.c. (5 m × $\frac{3}{8}$ in; 15% SE-30; 200°), which revealed that the starting material and the product were present in a 1 : 1 ratio. The product is an oil, δ (CCl_4) 7.2 (5 H, m), 6.22 (2 H, s), 1.32 (6 H, s), and 1.22 (9 H, s); $\nu_{max.}$ (liquid capillary) 3 080, 3 055, 3 010, 2 965, 2 915, 2 870, 1 685, 1 640, 1 595, 1 575, 1 495, 1 480, 1 450, 1 390, 1 380, 1 365, 1 200, 1 075, 1 050, 1 020, 990, 975, 940, 750, and 700 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 294 (ε 3 220), 286 (3 610), and 254 nm (18 300); *m/e* 230 (M^+) and 145 (base) (Found: C, 83.4; H, 9.5. $C_{16}H_{22}O$ requires C, 83.45; H, 9.65%).

Irradiations.—The preparative scale irradiations (0.1—0.2 g) were carried out in a Rayonet RPR-208 photoreactor equipped with eight RUL-300 nm lamps at room temperature. The solutions of the ketones (0.05M) in benzene, contained in Pyrex tubes closed with a septum, were saturated with nitrogen before irradiation.

The CIDNP experiments were carried out in quartz glassware. As radiation source a Charles Goffin lamphouse equipped with a high pressure mercury lamp (Osram HBO-1000) was used. A nickel sulphate filter (80 g l^{-1}) with a pathlength of 70 mm was applied to limit the radiation to the wavelength region 250—350 nm. The (spinning) n.m.r. tube was irradiated directly in the probe.

Analysis, Product Isolation, and Identification.—The products were isolated by preparative g.l.c. using for the photoproducts of (4) a Carbowax 20 M column (5 m × $\frac{1}{4}$ in; 10% Carbowax 20 M; 150°) and for the photoproducts of (5) and (6) an SE-30 column (5 m × $\frac{1}{4}$ in; 10% SE-30; 190°). The ^1H n.m.r. spectra of the starting compounds and the isolated photoproducts were recorded with a Varian HA-100 spectrometer using tetramethylsilane as internal reference. The ^1H n.m.r. spectra with the CIDNP experiments were recorded with a Varian 60 MHz spectrometer, using Freon as solvent and an external H_2SO_4 lock. The assignment of the products was based on their spectroscopic data.

(Z)-3,3-Dimethyl-5-phenylpent-4-en-2-one had δ (CCl_4) 7.2 (5 H, m), 6.55 (1 H, d, *J* 12 Hz), 5.72 (1 H, d, *J* 12 Hz), 1.92 (3 H, s), and 1.25 (6 H, s); $\nu_{max.}$ (CCl_4) 3 080, 3 000, 2 950, 2 880, 1 705, 1 600, 1 500, 1 470, 1 450, 1 410, 1 380, 1 355, 1 225, 1 210, 1 160, 1 140, and 1 105 cm^{-1}; *m/e* 188 (M^+) and 145 (base).

5-Methyl-3-phenylhex-4-en-2-one had δ (CCl_4) 7.25 (5 H, m), 5.66 (1 H, d, *J* 10 Hz), 4.55 (1 H, d, *J* 10 Hz), 2.10 (3 H, s), 1.79 (3 H, s), and 1.68 (3 H, s); $\nu_{max.}$ (CCl_4) 3 050, 2 990, 2 920, 2 850, 1 710, 1 600, 1 500, 1 450, 1 420, 1 380, 1 350, 1 280, and 1 140 cm^{-1}; *m/e* 188 (M^+) and 145 (base).

(*Z*)-2,2,4-Trimethyl-6-phenylhex-5-en-3-one had δ (CCl_4) 7.2 (5 H, m), 6.36 (1 H, d, *J* 11 Hz), 5.61 (1 H, dd, J_1 11, J_2 10 Hz), 4.15 (1 H, dq, J_d 10, J_q 7 Hz), 1.20 (3 H, d, *J* 7 Hz), and 0.90 (9 H, s); $\nu_{max.}$ (CCl_4) 3 080, 3 060, 3 020, 2 960, 2 925, 2 900, 2 865, 1 700, 1 600, 1 500, 1 475, 1 450, 1 390, 1 370, 1 320, 1 300, 1 230, 1 200, and 1 185 cm^{-1}.

(*E*)-2,2-Dimethyl-4-phenylhept-5-en-3-one had δ (CCl_4) 7.2 (5 H, m), 5.70 (1 H, dd, J_1 15, J_2 7 Hz), 5.36 (1 H, dq, J_d 15, J_q 7 Hz), 4.67 (1 H, d, *J* 7 Hz), 1.63 (3 H, d, *J* 7 Hz), and 1.07 (9 H, s); $\nu_{max.}$ (CCl_4) 3 090, 3 080, 3 010, 2 960, 2 865, 1 700, 1 600, 1 500, 1 475, 1 460, 1 450, 1 390, 1 365, 1 330, 1 300, 1 275, 1 235, 1 200, and 1 180 cm^{-1}.

(*E*)-3,4,4-Trimethyl-1-phenylpent-1-ene had δ (CCl_4) 7.2 (5 H, m), 6.23 (1 H, d, *J* 15 Hz), 6.09 (1 H, dd, J_1 15, J_2 8 Hz), 2.04br (1 H, quintet, *J* 7 Hz), 1.03 (3 H, d, *J* 7 Hz), and 0.90 (9 H, s); $\nu_{max.}$ (CCl_4) 3 080, 3 060, 2 960, 2 900, 2 865, 1 600, 1 500, 1 490, 1 460, 1 450, 1 390, 1 365, 1 235, 1 180, and 1 140 cm^{-1}.

(*E*)-5,5-Dimethyl-4-phenylhex-2-ene[22] had δ (CCl_4) 7.3 (5 H, m), 5.96 (1 H, dd, J_1 15, J_2 9 Hz), 5.52 (1 H, dq, J_d 15, J_q 6 Hz), 3.08 (1 H, d, *J* 9 Hz), 1.76 (3 H, d, *J* 6 Hz), and 0.96 (9 H, s).

(*Z*)-2,2,4,4-Tetramethyl-6-phenylhex-5-en-3-one had δ (CCl_4) 7.15 (5 H, m), 6.31 (1 H, d, *J* 13 Hz), 5.74 (1 H, d, *J* 13 Hz), 1.22 (6 H, s), and 1.06 (9 H, s); $\nu_{max.}$ (CCl_4) 3 060, 2 970, 2 935, 2 905, 2 875, 1 690, 1 665, 1 600, 1 580, 1 500, 1 480, 1 470, 1 450, 1 400, 1 380, 1 370, 1 280, 1 235, 1 190, 1 075, and 1 045 cm^{-1}.

2,2,6-Trimethyl-4-phenylhept-5-en-3-one had δ (CCl_4) 7.15 (5H, m), 5.49 (1 H, d, *J* 10 Hz), 4.85 (1 H, d, *J* 10 Hz), 1.64 (6 H, s), and 1.03 (9 H, s); $\nu_{max.}$ (CCl_4) 3 090, 3 065, 3 030, 2 975, 2 935, 2 915, 2 870, 1 710, 1 600, 1 580, 1 500, 1 480, 1 465, 1 455, 1 395, 1 380, 1 370, 1 300, 1 230, 1 200, and 1 110 cm^{-1}.

(*E*)-3,3,4,4-Tetramethyl-1-phenylpent-1-ene had δ (CCl_4) 7.2 (5 H, m), 6.25 (1 H, d, *J* 16 Hz), 6.19 (1 H, d, *J*

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[22] C. M. Hill, D. E. Simmons, and M. E. Hill, *J. Amer. Chem. Soc.*, 1955, **77**, 3889.

16 Hz), 1.02 (6 H, s), and 0.87 (9 H, s); $\nu_{max.}$ (CCl_4) 3 085, 3 060, 3 030, 2 970, 2 915, 2 875, 1 645, 1 600, 1 580, 1 500, 1 480, 1 470, 1 450, 1 400, 1 380, 1 370, 1 320, 1 225, 1 185, 1 150, 1 130, 1 070, and 1 030 cm^{-1}.

2,5,5-Trimethyl-4-phenylhex-2-ene had δ (CCl_4) 7.05 (5 H, m), 5.55 (1 H, d, *J* 10 Hz), 3.11 (1 H, d, *J* 10 Hz), 1.67 (3 H, s), 1.49 (3 H, s), and 0.79 (9 H, s); $\nu_{max.}$ (CCl_4) 3 090, 3 065, 3 030, 2 970, 2 910, 2 870, 1 670, 1 600, 1 500, 1 480, 1 470, 1 455, 1 395, 1 380, 1 365, 1 225, 1 165, 1 120, 1 075, and 1 030 cm^{-1}.

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