Triplet Participation in the Radiolytic Type II Cleavage of n-Butyrophenone

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IT was found by Coyle[1] that the predominant action of either γ-rays or ultraviolet light on n-butyrophenone was a degradation in the normal Type II pattern to acetophenone and ethylene. Evidence has been advanced by Pitts and his co-workers[2] that the photolysis proceeds *via* a triplet excited state and there is precedent, for example from recent studies on cyclopentanone,[3] and on steroidal ketones[4] for supposing that the same excited state may be involved in radiolysis. However, the photolytic Type II degradation is accompanied, as LaCount and Griffin[5] showed, by a Yang[6] reaction, also believed[7] to arise from triplet excitation, and the product of this reaction, 1-phenylcyclobutanol, was not observed in radiolysis by Coyle. Consequently, the radiolysis has been re-examined and it is found that upon γ-irradiation in benzene solution, 1-phenylcyclobutanol is in fact formed in about the same proportion as in photolysis. Additional evidence for triplet-state participation was noted in the suppression of product formation by anthracene and by naphthalene.

TABLE

Yields in γ-irradiation of n-butyrophenone in benzene solution

Concentration (M)	Dose $(\times 10^{-19})ev/g.$	Yield (*G*-value) Acetophenone	1-Phenylcyclobutanol
0·0111	0·95	0·82	0·094
	5·70	0·77	0·107
0·0205	0·95	0·91	0·082
	5·70	0·57	0·062
0·0505	5·70	1·07	0·12
	42·7	0·78	0·087
0·131	5·70	1·20	0·120
0·465	42·7	0·88	0·090
	41·8	1·38	0·084
0·0205 (plus anthracene at 0·0189 M)	4·70	0·037	——
	42·7	0·028	0·004
0·0505 (plus anthracene at 0·0101 M)	5·70	0·130	——
	42·7	0·122	——
0·0490 (plus naphthalene at 0·0488 M)	5·58	0·075	——

The identification and analysis of 1-phenylcyclobutanol in irradiated specimens was based on gas-chromatographic separation of the mixtures on an 18 foot Carbowax 20M column at 175°. In photolysis experiments on 0·007 M-solution of n-butyrophenone, exposed to a medium-pressure therapeutic-type mercury lamp under nitrogen and through a Pyrex filter to effect generally less than 10% conversion, the yield of 1-phenylcyclobutanol relative to acetophenone was found to be: in methanol, 0·10; in methylene chloride, 0·13; in benzene, 0·10. The irradiation of a pentane solution produced several other products in lesser amounts, among them the reduction product, 1-phenylbutan-1-ol. Traces of this alcohol were seen in the methanol experiments but none was detected in methylene chloride or in benzene. The indicated yields of 1-phenylcyclobutanol are concordant with the 7·7% yield, presumably in acetone and based on product isolated, that was reported by LaCount and Griffin.[5]

A persistent minor photolysis product in all solvents was identified, by isolation in a gram-scale experiment and comparison with authentic material as α-tetralone. It is formed in a yield, relative to acetophenone, approximately 0·01. Its formation is found to be suppressed by triplet scavengers to about the same degree as is the formation of acetophenone and phenylcyclobutanol. For example, equal exposures of 0·01 M-butyrophenone in benzene, alone and with added cyclo-octa-1,3-diene (0·01 M) produced acetophenone in 8·1 and 1·5% yield, respectively; 1-phenylcyclobutanol in 0·75 and 0·14% yield, and α-tetralone in 0·08 and *ca.* 0·01%. A common origin in the triplet state of butyrophenone is thus indicated for all three products. Details of the pathway to α-tetralone remain obscure. A possible precursor of α-tetralone might be the dihydrotetralone, in enolic form, that would be generated by (allylic) attack of the radical chain end at an *ortho*-position.

The irradiation of n-butyrophenone, in deaerated benzene (commercial zone-refined) solution, by γ-rays from a cobalt-60 source at a dose rate, of 4·75 × 10^{17} *ev*/g. min., produced acetophenone and 1-phenylcyclobutanol in the yields given as *G*-values in the Table. The decline in *G*-value with increasing dose, seen at each level of concentration, is a probable consequence of the known effectiveness[8] of olefinic materials in quenching benzene triplets since such materials will accumulate during the exposures. A more dramatic reduction in yield resulted from added anthracene or naphthalene. Measurement of the radiolytic yields of phenylcyclobutanol presented difficulty because this chromatographic peak was not fully resolved from that of biphenyl, the formation of which from benzene is not suppressed appreciably by triplet scavengers. Within the uncertainty thereby introduced, the production of acetophenone and of phenylcyclobutanol was equally lowered by these additives. The chromatograms of radiolysis products revealed peaks at the expected position for α-tetralone, identification not otherwise confirmed, at a level corresponding to *G*-values in the range 0·01—0·02 and these peaks were not seen in irradiations performed in the presence of anthracene or naphthalene.

The combined yields of products, derived from the triplet state of butyrophenone by way of energy-transfer from triplet benzene, indicate a minimum value for the yield of the latter in the neighbourhood of unity. This is in general agreement with triplet yields in benzene derived from other data by a number of workers.[9–11] Because of the trend toward higher values with increasing concentration the result is not necessarily in disagreement with the higher value, 4, derived by Cundall and Griffiths[12] from the butene isomerization where a plateau was reached at relatively low concentration.

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[1] D. J. Coyle, *J. Phys. Chem.*, 1963, **67**, 1800.

[2] E. J. Baum, J. K. S. Wan and J. N. Pitts, Jr., Abstracts 149th National Meeting, American Chemical Society, Detroit, Mich., April 1965, p. 75; J. K. S. Wan, R. N. McCormick, E. J. Baum, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, 1965, **87**, 4409.

[3] P. Dunion and C. N. Trumbore, *J. Amer. Chem. Soc.*, 1965, **87**, 4212.

[4] J. Hoigne, K. Schaffner, and R. Wenger, *Helv. Chim. Acta*, 1965, **48**, 527.

[5] R. B. LaCount and C. E. Griffin, *Tetrahedron Letters*, 1965, 1549.

[6] N. C. Yang and D. H. Yang, *J. Amer. Chem. Soc.*, 1958, **80**, 2913.

[7] N. C. Yang, A. Morduchowitz, and D. H. Yang, *J. Amer. Chem. Soc.*, 1963, **85**, 1017.

[8] R. B. Cundall and D. G. Milne, *J. Amer. Chem. Soc.*, 1961, **83**, 3902.

[9] J. Nosworthy, *Trans. Faraday Soc.*, 1965, **61**, 1138.

[10] H. P. Lehmann, G. Stein, and E. Fischer, *Chem. Comm.*, 1965, 583.

[11] E. A. Cherniak, E. Collinson, and F. S. Dainton, *Trans. Faraday Soc.*, 1964, **60**, 1408.

[12] R. B. Cundall and P. A. Griffiths, *J. Amer. Chem. Soc.*, 1963, **85**, 1211; *J. Phys. Chem.*, 1965, **69**, 1866.