Biacetal Photochemistry: Products in Solution

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BIACETYL photochemistry has been extensively studied in the gas phase from both mechanistic and product viewpoints.[1] Though biacetyl is now commonly used in solution studies in quencher-sensitizer roles,[2] little is known of the products of the photoreactions of this *β*-diketone in common organic solvents, partial product studies having been carried out only in isopropanol,[3] ethanol,[4] and cyclohexene.[5]

We report the products of irradiation of dilute, deoxygenated solutions of biacetyl in several solvents using light of wavelength >360 mμ

TABLE

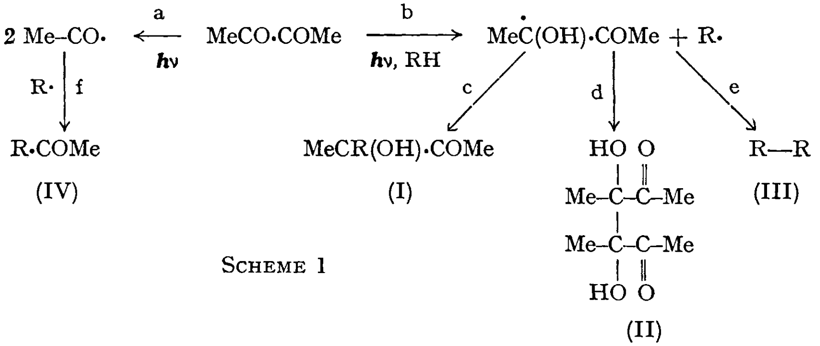
Yields of products from irradiation of biacetyl solutions

Solvent	Product				
	(I)[c]	(II)[e,f]	(III)[e,f]	(IV)[c]	$(MeCO)_2C(Me)OH$ (V)[c]
Cyclohexane[a]	10	36		24	7
Diethyl ether[a]	10[e]	36	4	16	5
Dioxan[b]	4[e]	18	*d*	39	13
Cyclohexane[a]	59[e]	37	50	*d*	
Ethylbenzene[a]	50[e]	50	41	*d*	
Isopropanol[a]		98			*d*

[a] 0·04M biacetyl, 100% conversion; [b] 0·08M biacetyl, *ca.* 10% conversion; [c] by v.p.c. analysis, corrected for sensitivity differences, calculated on the basis of one mole of product formed per mole of biacetyl consumed; [d] trace amounts may be present; [e] mixture of diastereoisomers; [f] based on assumed formation of half a mole of product per mole biacetyl consumed, corrected for sensitivities.

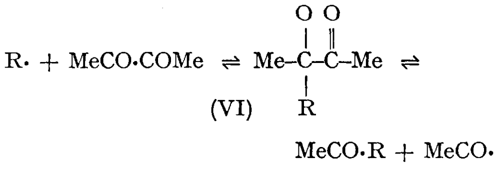
(see the Table). In solvents such as acetonitrile and benzene, which do not contain readily abstractable hydrogens, photoreaction occurs, but no volatile products are obtained. In contrast to the reported[3] formation of a single pinacol in isopropanol, we found approximately equal amounts of diastereomeric pinacols. Our results confirm the previous work in cyclohexene,[5] but most of the acetylcyclohexane found in the cyclohexene reaction is a secondary product from photoreaction of the hydroxyketone (I; R = cyclohexenyl).

On the basis of recent e.s.r. work,[6] it seems likely that the first step (b) in these reactions is hydrogen abstraction from solvent by electronically excited diketone to give the radical pair shown (Scheme 1)



SCHEME 1

We believe it unlikely that ketone (IV) arises *via* step f in Scheme 1, since those solvents which give the largest percentages of dimer (III) give little or no acetyl product. Further, we have shown[7] that (IV) can be formed from reaction of biacetyl with radicals generated non-photochemically from cyclohexane and dioxan, according to Scheme 2.



SCHEME 2

The yields of (IV) in the photoreactions are consistent with this mechanism. More stable radicals, *e.g.* those from toluene and ethylbenzene, were not acetylated. However, it has been proposed[8] that the formation of phenylacetone on irradiation of solutions of biacetyl and phenylacetic acid in aqueous acid is a result of Scheme 2 involving benzyl radicals.

The mechanism of formation of (I) is of considerable interest from the standpoint of the alternative radical processes which may be involved. In view of the acetylation sequence in Scheme 2 it is possible that (I) could be formed *via* a chain mechanism in which intermediate (VI), formed as in Scheme 2, is trapped in a chain transfer reaction with solvent to give (I) and regenerate R·. We have been unable, however, to initiate a radical addition of this type in ethyl benzene, dioxan, or cyclohexane. We suggest that (I) arises mostly from radical coupling, although it is possible that a concerted process gives (I). However, the evidence from e.s.r. studies and the large amounts of pinacol (II) and dimer (III) suggest a radical process.

The formation of product (V), not shown in Scheme 1 appears to involve acetyl radicals, as (V) is produced in appreciable yields when Scheme 2 is important. Also, product (V) is the major product on irradiation of solutions of acetaldehyde and biacetyl in cyclohexane. We were unable to detect acetaldehyde during irradiation of biacetyl in cyclohexane. The mechanism of formation of (V) requires further study.

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