α-Ketocarbene Formation on γ-Radiolysis of Phenylacetylenes in Liquid CO_2

By Akira Hori, Setsuo Takamuku, and Hiroshi Sakurai
(*The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka* 565, *Japan*)

Summary γ-Radiolysis of liquid CO_2 and $PhC{\equiv}CR$ (**1**) in the presence of methanol gives $PhCH(OMe)COR$ (**5**) and $PhRCHCO_2Me$ (**6**), indicating the formation of an α-ketocarbene (**2**) by the attack of $O(^3P)$, generated by γ-radiolysis of liquid CO_2, on the phenylacetylene.

It has been shown that γ-radiolysis of CO_2 in the liquid phase produces atomic oxygen.[1] We recently reported the radiolysis of alkenes in liquid CO_2, and obtained the corresponding oxiran and carbonyl compounds,[2] indicating that the most reasonable oxidizing species must be a ground-state oxygen atom. Furthermore, radiolysis of alkanes in liquid CO_2 produces isomers of alcohols with highly regioselective substitution of tertiary carbon atoms.[3] This result is consistent with that obtained in the reaction of alkanes with $O(^3P)$ atoms generated by visible light irradiation of ozone in the liquid phase.[4] Studies of the reaction of atomic oxygen with organic molecules in the liquid phase are thus possible by this technique. We now report the γ-radiolysis of alkynes in liquid CO_2; little is known about the reaction of alkynes with atomic oxygen.[5]

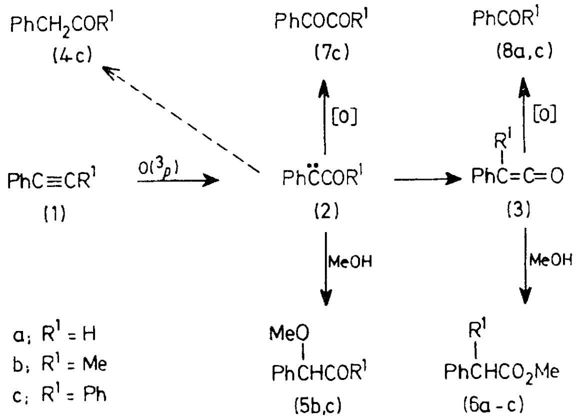
Diphenylacetylene (**1c**, 1 mmol) in liquid CO_2 (1·4 mol) was irradiated with a ^{60}Co (7000 Ci) source in a stainless steel autoclave at 0 °C for 6 h. The dose rate, measured by $FeSO_4$ dosimetry, was $1{\cdot}7 \times 10^{19}$ eV g^{-1} h^{-1}. G.l.c. analysis of the product showed the formation of benzophenone (**8c**, 3·7%), benzil (**7c**, 1·3%), and deoxybenzoin (**4c**, 2·5%). If methanol was added after the radiolysis, methyl diphenyl-

Table. γ-Radiolysis of phenylacetylenes in liquid CO_2 in the presence of alcohols[a]

$PhC{\equiv}CR^1$ (**1**) (amount /mmol)	R^2OH	Irradiation time/h	Conversion /%	Product yield/%[b] (**4**)	(**5**)	(**6**)	(**7**)	(**8**)
(**1a**) (3)	MeOH	24	56	c	d	17·6(97)	c	0·5(3)
(**1b**) (3)	MeOH	24	54	c	1·5(8)	16·4(92)	c	d
(**1c**) (3)	MeOH	24	42	0·7(2)	4·6(15)	20·3(66)	4·9(16)	0·2(1)
(**1c**) (1)	MeOH	1	6	2·5(7)	5·3(15)	15·5(45)	11·3(33)	d
(**1c**) (1)	MeOH	6	25	2·0(6)	4·6(13)	21·7(63)[e]	5·9(17)	0·1(0·3)
(**1c**) (1)	Pr^iOH	6	17	2·3(8)	0·1(0·4)	25·4(89)	0·2(0·7)	0·4(1)

[a] In liquid CO_2 (1·4 mol) with R^2OH (1 ml) at 0 °C. [b] All products were identified by comparison of retention times on g.l.c. and mass spectra with those of authentic samples. Product yields are based on the amount of phenylacetylenes (**1**) consumed; relative yields are shown in parentheses. [c] Amount not determined. [d] Not detected. [e] *G* value 0·68 (molecule/100 eV).

acetate (**6c**, 11·0%) was obtained, indicating the presence of diphenylketen. The radiolysis of phenylacetylenes (**1**) was carried out in the presence of an alcohol (1 ml) as a keten trap (see Table). The main products were the esters (**6**) in all cases (relative yields, 66—97%), showing the presence of considerable amounts of phenylketens (**3**). This observation, together with the formation of the ethers (**5**), suggests the generation of an α-ketocarbene (**2**). The relative ratios of the methyl ether (**5**) to the methyl ester (**6**) depended on the phenylacetylenes; (**5**) : (**6**) = *ca.* 0 : 1 for (**1a**), 0·087 : 1 for (**1b**), and 0·23 : 1 for (**1c**). Benzil (**7c**) and benzophenone (**8c**), which may be produced by further oxidation of (**2c**) and (**3c**), respectively, are also obtained in the case of (**1c**).[6] The formation of these products can be rationalized by the paths in the Scheme.



SCHEME

As shown in the Table, the use of Pr^{i}OH, a good hydrogen donor, instead of methanol does not increase the yield of (**4c**), indicating that the α-ketocarbene (**2**) produced in this reaction has a low ability for hydrogen abstraction.[7] The formation of (**4c**) may therefore not be interpreted in terms of hydrogen abstraction by the ketocarbene (**2**).

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