

Photochemical Reactions of Benzoyl Cyanide and Benzoyl Halides with Alkenes

By THOMAS S. CANTRELL

(Chemistry Department, American University, Washington, D.C. 20016)

Summary Irradiation of benzoyl cyanide in the presence of electron-rich alkenes gives both oxetans and ketones such as (2) and (3), whereas benzoyl halides give ketones such as (2) *via* loss of HX from α -halogeno-oxetans, the primary photoadducts.

RECENTLY the first photochemical reaction at an excited cyano group, *viz.*, the cycloaddition of benzonitrile to electron-rich alkenes to give 1-azabutadienes was reported.¹ Now the first example of hydrogen abstraction by a photochemically excited cyano group, as well as an interesting example of competition between two different functional groups in the same molecule is also reported.

Irradiation[†] of benzoyl cyanide (1) with excess 2,3-di-

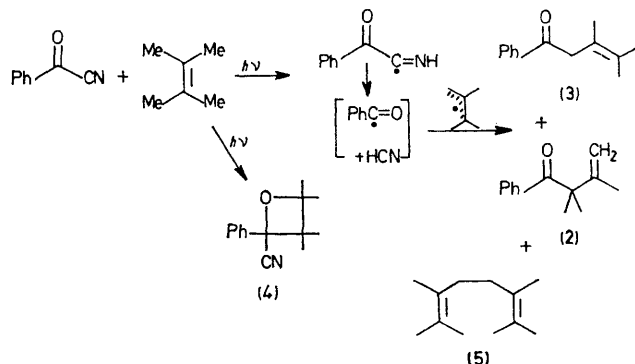
methyl-2-butene gave products (2)—(5) in yields of 20, 29, 22, and 48%, respectively. Products (2), (3), and (5) were identified by comparison with authentic samples.²

The structure of the oxetan (4), m.p. 99—100°, was assigned on the basis of its spectral properties.[‡] The mechanism shown for formation of (2) and (3) is supported by (a) the observation that the ratio of (2), (3), and (4) is essentially constant over the reaction course; (b) the isolation of both (2) and (3), rather than only (2), as with benzoyl halides (*vide infra*); and (c) the stability of the oxetan (4). Both (b) and (c) above rule out the possible intermediacy of the oxetan (4) in the formation of (2) and (3), as is the case with benzoyl halides. Hydrogen abstraction from the alkene by the cyano group of photoexcited (1) is followed by loss

[†] Medium pressure mercury arc, Pyrex filter, spectrograde hexane.

[‡] The i.r. n.m.r., and mass spectral data for this compound were consistent with the assigned structure.

of HCN to give the benzoyl radical, which combines with the β,γ,γ -trimethylallyl radical at either end to give (2) and (3). Irradiation of (1) in excess 2-methylbut-2-ene as substrate gave products entirely analogous to those above.



Irradiation§ of benzoyl bromide (6) or chloride with excess 2,3-dimethylbut-2-ene, followed by fractional distillation *in vacuo* gave the ketone (2) (41%) and the hydrocarbon (5) (51%). Irradiation in a similar manner, followed by evaporation of (5) and excess reactants, always keeping the temperature below 10°, gave a brown oil which evolved HBr and decomposed to (2) on attempted distillation.

§ Medium pressure mercury arc, Vycor filter, spectrograde hexane solvent.

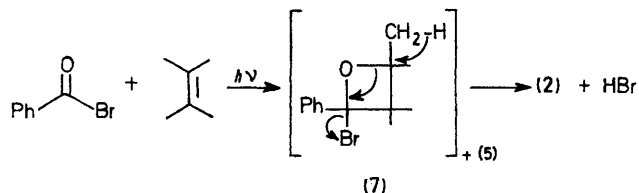
¹ T. S. Cantrell, *J. Amer. Chem. Soc.*, 1972, **94**, 5929.

² T. S. Cantrell, *J.C.S. Chem. Comm.*, 1973, 468; *J. Amer. Chem. Soc.*, 1973, **95**, 2714.

³ L. Brandsma and J. F. Arens, in 'The Chemistry of the Ether Linkage,' ed. S. Patai, Wiley-Interscience, New York, 1967, pp. 587—591.

⁴ U. Schmidt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 239.

The i.r. spectrum of the oil showed only a weak carbonyl band for (2), but strong C—O absorption at 1000—1160 cm^{-1} . The n.m.r. spectrum showed singlets at τ 8.68, 8.75, 8.87, and 8.97 and the mass spectrum showed weak parent peaks at m/e 268 and 270 and a base peak at 189 (parent—Br). This information strongly supports oxetan (7) as the major component of the crude oil. Although α -halogenoethers are noted for the great S_N1 reactivity of the halogen atom,³ a 2-step reaction involving initial ionization seems improbable in the solvent of low dielectric constant. More likely, the



loss of hydrogen halide with concomitant ring opening is a thermal process, concerted or nearly so, initiated as the carbon-halogen bond begins to break. The present results are in contrast to those of Schmidt, who observed only photolytic hydrogen abstraction by benzoyl bromide.⁴

(Received, 29th April 1975; Com. 490.)