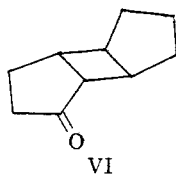


photolytic decomposition of the primary product.⁵



Light-induced cyclobutane formation has been observed to occur *intramolecularly* between an olefin and an α,β -unsaturated ketone: for example, the isomerization of carvone to carvone-camphor,⁶ and the conversions of various keto-dicyclopentadienes to the "cage" tautomers.⁷ The proximity of the π systems in these examples might have special significance in that orbital overlap may contribute to the ease of reaction. No *intermolecular* analog of this photochemical reaction has been fully demonstrated previously, although such a cyclo-addition has been proposed as an intermediate step in the photochemical synthesis of 1,5-diketones.⁸

Note can now be taken of the dichotomy between the Diels-Alder reaction⁹ and the observations made here. In the Diels-Alder reaction, the presence of an activating group such as carbonyl in the dienophile markedly influences the course of the reaction¹⁰; in addition, the *endo* stereochemistry of the major reaction product is, in most instances, predicted by the rule of maximum overlap.¹¹ Contrary to these specifications, a carbonyl group in the non-excited partner in the photo-addition reactions reported here is unimportant.¹² Further, the stereoselectivity of the photo-reaction is opposite to that of the Diels-Alder reaction. No products derived from the *endo* hydrocarbon *cis,cis,cis*-tricyclo[5.3.0.0^{2,6}]decane were formed in isolable amounts in either the photoreaction of cyclopentenone with itself or with cyclopentene.

Even in view of this divergence, many of the experimental approaches to elucidation of the mechanism of the Diels-Alder reaction are applicable to the study of photodimerization. Such experiments are in progress and will be reported subsequently.

(5) Cf. C. H. Bamford and D. G. Norrish, *J. Chem. Soc.*, 1531 (1938).

(6) G. Büchi and I. M. Goldman, *J. Am. Chem. Soc.*, **79**, 4741 (1957).

(7) P. Yates and P. Eaton, *Tetrahedron Letters*, **11**, 5 (1960); R. C. Cookson, J. Hudec and R. O. Williams, *ibid.*, **22**, 29 (1960).

(8) P. de Mayo, H. Takeshita and W. A. Mueller, *Proc. Chem. Soc.*, 119 (1962).

(9) See, for example, R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(10) E. Lehman and W. Paasche, *Ber.*, **68**, 1146 (1935); K. Alder and E. Rüden, *ibid.*, **74**, 920 (1941).

(11) The validity of this rule is now subject to some question: J. A. Berson, A. Hamlet and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962). Reference is made to it here only as a convenient label for the factors which control the stereochemistry of the Diels-Alder reaction.

(12) The possibility exists that the mechanism of addition of cyclopentenone to cyclopentene differs significantly from that applicable to the dimerization of the ketone. It is conceivable that the former reaction proceeds *via* triplet transfer from excited ketone to olefin, followed by attack of the excited olefin on a non-excited molecule of ketone. Although such a devious reaction path cannot be excluded rigorously, it is noted that the irradiation of the ketone-olefin mixture produced none of the dimers of cyclopentene which might be expected if the excited olefin were an important reactant.

Finally, attention is drawn to the potential synthetic utility of these photo-addition reactions. We have, for example, used cyclohexene and the butenes successfully as olefinic components. Presumably other α,β -unsaturated carbonyl compounds could replace cyclopentenone. The reaction therefore offers an excellent route to new ring systems.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

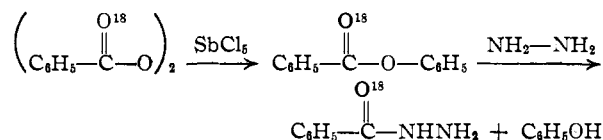
PHILIP E. EATON

RECEIVED APRIL 27, 1962

CONCERNING THE ANTIMONY PENTACHLORIDE
CATALYZED DECOMPOSITION OF BENZOYL
PEROXIDE AND SOME MIXED CARBONATES

Sir:

Reynhart¹ has shown that benzoyl peroxide in petroleum ether reacts at room temperature with molar amounts of antimony pentachloride to give a quantitative yield of phenyl benzoate and carbon dioxide. It has now been found that only catalytic quantities of antimony pentachloride are required to effect this conversion. The rate of the reaction is subject to profound solvent effects. For example, the reaction proceeds smoothly in petroleum ether (30–60°) at room temperature and is complete in *ca.* five hours. In toluene, under the same conditions, about three days are required. In diethyl ether very little, if any, reaction occurred after three days.



Benzoyl peroxide, labeled with oxygen-18 in the carbonyl groups, was converted to phenyl benzoate which was degraded by conversion to phenol and benzoic acid hydrazide. The analytical data are collected in Table I.

TABLE I

Compound ^a	Atom % excess oxygen-18 ^b	
	Run 1	Run 2
Benzoic acid ^c	1.56	0.76
Benzoyl peroxide	1.60	0.75
Phenyl benzoate	1.59	0.72
Benzoic acid hydrazide	1.47	0.71
Phenyl phenylurethan	0.07 ^d	0.00

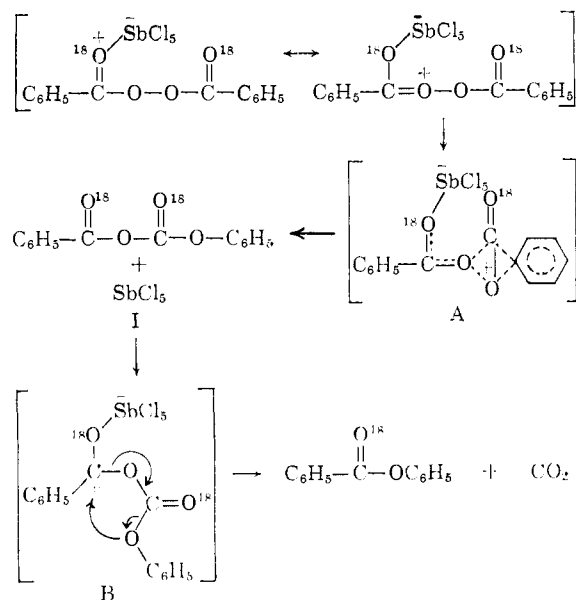
^a All compounds were characterized by m.p., mixed m.p., and infrared data. ^b Two runs using different samples of benzoyl peroxide were conducted. ^c Used in preparing the benzoyl peroxide. Oxygen-18 content per oxygen. ^d The analytical results in run 1 are inferior to those in run 2. The 0.07 atom % excess oxygen-18 found in the phenyl phenylurethan probably is due to a memory effect. An unlabeled sample combusted at the same time showed 0.04 atom %. The combustion apparatus was refurbished before the analyses for run 2 were conducted.

The results of this study demonstrate that the label remains in the carbonyl group during this transformation.² This finding eliminates from consideration a free benzyloxy anion, cation or radical as a product forming intermediate. The tracer results coupled with the Lewis acid character

(1) A. Reynhart, *Rec. trav. chim.*, **46**, 62 (1927).

(2) See footnote *d* of Table I for this interpretation.

of antimony pentachloride suggest the mechanism shown. The first step involves a Lewis acid



catalyzed carboxy inversion reaction which proceeds through transition state A to give the mixed carbonate, I.³ This hypothesis is supported by the report of Rasuwajew, *et al.*,^{3a} who have observed that antimony pentachloride catalyzed the rearrangement of acyl-sulfonyl peroxides to give mixed carbonates of an alkane sulfonic acid and phenol. The migration of phenyl to a peroxidic oxygen is in accord with a previous study of the carboxy inversion reaction.^{3c} The complete retention of the label in the migrating benzoyloxy group is unique^{3d} but accords with the postulate that antimony pentachloride is complexed with the carbonyl oxygen. The medium effects probably are due to interaction of the antimony pentachloride with the solvents.⁴ Such interaction will inhibit complex formation with the peroxide and therefore diminish the rate of the reaction.

The mechanism postulates the formation of I, or an antimony pentachloride complex of I, as an intermediate. A sample of I⁵ rapidly decomposed in petroleum ether in the presence of antimony pentachloride to give phenyl benzoate; no benzoic anhydride could be detected. Because of the inherent instability of I, ethyl benzoyl carbonate (II) was prepared. This material is stable at room temperature but decomposes at 150° to give ethyl benzoate, diethyl carbonate and benzoic anhydride.⁶

(3) (a) G. A. Rasuwajew, V. R. Likhterow and V. S. Etlis, *Tetrahedron Letters*, No. 15, 527 (1961); (b) J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 67 (1950); (c) D. B. Denney, *ibid.*, **78**, 590 (1956); (d) D. B. Denney and D. G. Denney, *ibid.*, **79**, 4806 (1957).

(4) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, *J. prakt. Chem.*, **154**, 112 (1940).

(5) The mixed carbonate was prepared from phenyl chloroformate and benzoic acid in the presence of triethylamine. It decomposes at room temperature to give phenyl benzoate, carbon dioxide, benzoic anhydride and presumably diphenyl carbonate. Freshly prepared material had m.p. 55–58° dec. The infrared spectrum had carbonyl bands at 5.45 and 5.65 μ .

(6) (a) E. T. Longosz and D. S. Tarbell, *J. Org. Chem.*, **26**, 2161 (1961). (b) D. S. Tarbell and E. T. Longosz, *ibid.*, **24**, 774 (1959); (c) T. Windholz, *ibid.*, **25**, 1703 (1960).

Treatment of II in petroleum ether, at room temperature, with antimony pentachloride led to fairly rapid decomposition, *ca.* five hours. Carbon dioxide was evolved. Ethyl benzoate, contaminated with *ca.* 5% of benzoyl chloride, was the only product detected. No diethyl carbonate or benzoic anhydride could be found. A mixture of diethyl carbonate, benzoic anhydride and antimony pentachloride in petroleum ether did not give carbon dioxide or ethyl benzoate.

These results demonstrate that antimony pentachloride is a remarkably efficient catalyst for the decomposition of these mixed carbonates. Two possibilities present themselves for explaining the catalytic effect. The first suggests that antimony pentachloride acts as a phenoxide or ethoxide carrier and directs it to attack at only the benzoyl carbonyl. Such a chain of events seems highly improbable. The second, and more attractive, mechanism suggests that antimony pentachloride complexes with the benzoyl carbonyl and promotes intramolecular decomposition to give the products directly. This transformation is represented by B. A similar mechanism has been proposed by Boschan⁷ to explain the decomposition of the mixed carbonate from trifluoroacetic acid and cholesterol. It should be noted that this postulate also explains the rate enhancing effect of boron trifluoride etherate on the decomposition of ethyl benzoyl carbonate.^{6c}

(7) R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959).

RUTGERS

THE STATE UNIVERSITY
NEW BRUNSWICK, N. J.

DONALD B. DENNEY
DOROTHY Z. DENNEY

RECEIVED APRIL 25, 1962

CATALYSIS BY SECONDARY VALENCE FORCES¹

Sir:

The second-order reaction of phenoxide ion with benzyldimethylsulfonium ion in water at 80° appears to be *accelerated* by ancillary molecular bonding of the π -complex or charge transfer type² at the transition state.

The rate constant for 0.12 *M* sodium phenoxide with 0.08 *M* benzyldimethylsulfonium *p*-toluenesulfonate is $2.7 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ in water at 79.8°. For the stronger base sodium hydroxide instead of sodium phenoxide, it is only $8.1 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$. Gas chromatography on ether extracts indicates that benzyl phenyl ether is formed in 89% yield from the first reaction under kinetic conditions, and benzyl alcohol in 93% from the second. On the other hand, hydroxide is 1.50 times as reactive as phenoxide with methyl bromide in water at 25°. With trimethylsulfonium perchlorate in water at 79.8°, another case where π -complexing is impossible, hydroxide ($3.6 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$)

(1) Supported in part by the Atomic Energy Commission and by NSF and NIH predoctoral fellowship to L. J. T.

(2) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949, pp. 18, 184; R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952); L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954); H. G. Smith and R. E. Rundle, *J. Am. Chem. Soc.*, **80**, 5075 (1958).

(3) J. J. Bloomfield, Ph. D. Thesis, M.I.T., September, 1958, pp. 14, 15.