ester was surprisingly close to that observed in the ketone–alcohol solvent whereas the reaction of the halide was still immeasurably rapid. Our kinetic results are presented in Table I.

TABLE I

SOLVOLYSIS OF TRIPHENYLMETHYL BENZOATE AT 54.5 ± 0.5°

Initial molarity of the ester was approximately 0.028 in each run. The solvent was 50% alcohol–methyl ethyl ketone in runs 1–6. The solvent was 50% benzene–alcohol in run 7.

Run	Initial concn. of solutes other than ester	$k \times 10^4$, sec.$^{-1}$	Probable error in $k \times 10^4$	% Ester reacted in last sample[a]
1	None	1.79	0.06	62
2	0.0437 *M* NaOEt	2.85	.28	85
3	.0437 *M* NaOEt	2.49	.27	79
4	.0875 *M* NaOEt	3.05	.25	90
5	.0875 *M* NaOEt	2.88	.25	89
6	.0437 *M* $NaClO_4$	5.04	.28	93
7	.0060 *M* $(C_6H_5)_3CCl$ .0066 *M* KOH	2.29	.21	78

[a] Disregarding infinite time samples taken to check concentrations.

The precision of our analyses was not high in the runs with added base. At the concentrations of sodium ethoxide employed the concentration of the ester is limited by the solubility of the sodium benzoate produced in the medium. Therefore, the decrease in the titer of the solution during the runs was small relative to the total titer.

Experimental

Triphenylmethyl benzoate was prepared by heating equivalent amounts of sodium benzoate and trityl chloride in refluxing dry acetone for seven hours. The sodium chloride was filtered from the mixture and the solution was concentrated until the ester began to separate from the hot solution. After cooling, solid melting about 145° was collected. Two recrystallizations from methyl ethyl ketone gave material melting in the range 166–169° cor. (highest 168–169°, lit.[5] 164°). The average yield of purified product was 40%. A weighed sample of the ester liberated 98.4% of the theoretical amount of acid when warmed with 95% ethanol.

The residual solution from one of the solvolysis runs was extracted with aqueous alkali, dried and evaporated until crystals began to separate and then cooled and filtered. The product was ethyl trityl ether, m. p. 78° (lit.[6] 82°).

Methyl ethyl ketone was dried by distillation from anhydrous potassium carbonate. Anhydrous alcohol was prepared by the method of Lund and Bjerrum.[7] A stock solution of sodium ethoxide was prepared by dissolving freshly cut sodium in anhydrous alcohol.

Sodium perchlorate, anhydrous reagent grade from the G. F. Smith Co., was used without further purification.

Procedure.—Weighed amounts of the ester and trityl chloride were dissolved and made up to the calculated volume in methyl ethyl ketone or benzene. This solution and either pure alcohol or an alcohol solution of the base or sodium perchlorate were brought to temperature in the thermostat. Fifty-ml. aliquots of each were taken, mixed rapidly by inversion, returned to the bath and sampled immediately. Subsequently, 2-ml. aliquots were removed at ten- or twenty-minute intervals and analyzed immediately. Solutions containing excess base were titrated with standard 0.1 *N* hydrochloric acid and the others with 0.1 *N* methanolic potassium hydroxide.

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(5) Wieland and Indest, *Ann.*, **532**, 166 (1937).

(6) Beilstein, "Handbuch der organischen Chemie," Fourth ed., Springer, Berlin, 1923, Vol. VI, 716.

(7) Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

Triboluminescence in *cis*-4-Octene[1]

BY MELVERN C. HOFF[2] AND CECIL E. BOORD

In the course of several cryoscopic determinations it was observed that *cis*-4-octene produced flashes of blue-white light when subjected to rapid cooling by immersing a test-tube containing this compound in liquid air. *trans*-4-Octene, *cis*-3-hexene and *trans*-3-hexene were carefully examined but did not produce flashes.

This phenomenon appears to be the same as that observed by Giauque and Ruehrwein[3] with hydrogen cyanide and which they interpreted as an electrical discharge generated by crystal fracture resulting from uneven heating or cooling. The flashes produced in *cis*-4-octene were shown to be electrical discharges by rapidly crystallizing a sample of the olefin under an atmosphere of neon[4] whereupon the flashes exhibited the characteristic red-orange color of an electrical discharge in neon. As was anticipated, no discharges were observed during slow crystallization under nearly equilibrium conditions.

The fact that, of the nearly two hundred hydrocarbons prepared under the auspices of the American Petroleum Institute Research Project 45, only *cis*-4-octene is known to exhibit this phenomenon, indicates either that the phenomenon has taken place unnoticed (it has not been reported by other workers who have crystallized *cis*-4-octene[5,6]) or that the particular crystal structure of this compound is conducive to the phenomenon. As a parallel, it was found to be very difficult to carry out cryoscopic determinations on *cis*-4-octene because of its unusual tendency to form relatively large, intermeshing crystals which cling to the stirrer and the walls of the dewar vessel used in determining freezing and melting points. Normally, under the conditions used in making these determinations, hydrocar-

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[1] This material was abstracted from a part of the dissertation submitted by Melvern C. Hoff in partial fulfillment of the degree of Doctor of Philosophy in Chemistry. The investigation was sponsored by the American Petroleum Institute (Research Project 45) in coöperation with The Ohio State University Research Foundation.

[2] Standard Oil Company of Indiana, Whiting, Indiana.

(3) Giauque and Ruehrwein, THIS JOURNAL, **61**, 2626 (1939).

(4) The authors wish to acknowledge their indebtedness to Dr. Thor R. Rubin, of this University, for suggesting the neon experiment. No evidence for an electrical discharge was observed when the flashes were produced in a tube containing a five ohm coil comprising two hundred turns of fine copper wire, connected through the high impedance transfer of an oscillograph.

(5) Henne and Greenlee, THIS JOURNAL, **65**, 2020 (1943).

(6) Campbell and Eby, *ibid.*, **63**, 216 (1941).

bons form fine microcrystals which produce an easily stirred slurry.

Several authors state that materials which show marked triboluminescence contain small amounts of impurities which serve as activators.[7] The role of impurities in the present case is not known. Samples ranging from 85–98 mole % purity exhibited the phenomenon; material of higher purity was not available. *cis*-4-Octene prepared either by quantitative inversion of the *trans* isomer[8] or by catalytic hydrogenation of 4-octyne exhibits the phenomenon equally well, and apparently neither of the most probable impurities, *trans*-4-octene and *n*-octane, respectively, in the *cis*-4-octene exhibits the phenomenon by itself. Thus, either *cis*-4-octene plus an impurity, or *cis*-4-octene alone is responsible for the triboluminescence.

The fact that *cis*-4-octene exhibits the phenomenon and that *trans*-4-octene does not, serves to emphasize the differences in crystallizing habits of *cis–trans* pairs.

(7) Dake and DeMent, "Fluorescent Light," Chemical Publishing Company, Inc., Brooklyn, N. Y., 1941.

(8) Presented in part at the 115th meeting of the American Chemical Society before the Organic Division and soon to be published in THIS JOURNAL.

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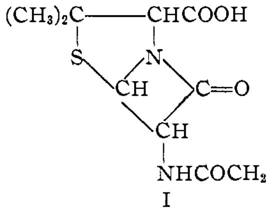
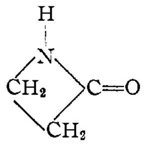
The Reactivity of Benzylpenicillin and Model β-Lactams toward Alkali

BY ANN D. HOLLEY AND ROBERT W. HOLLEY

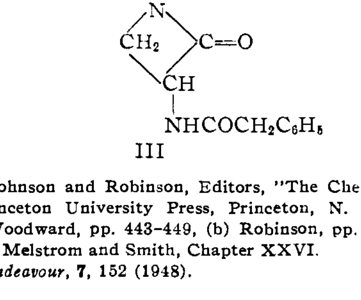
The chemical reactivity of the penicillins has been the subject of considerable discussion.[1,2] One difficulty with the thiazolidine-β-lactam structure (I for benzylpenicillin) has been that the reactivity of the penicillins toward alkali is much greater than that of the model β-lactams which have been studied.



I



II



III

The synthesis of 2-azetidinone (β-propiolactam) (II)[3] has provided a model to which hydrolysis rate studies may be referred. Accordingly, an investigation of the rates of alkaline hydrolysis of benzylpenicillin and desthiobenzylpenicillin (III) was undertaken, with the hope that the additional data would be of value in the comparison of the reactivities of benzylpenicillin and model β-lactams.

Hydrolyses were carried out in 85% ethanol using equimolar concentrations of compound and sodium hydroxide, as in previous studies of β-lactams.[3] As the alkaline hydrolysis of amides is known to be a bimolecular reaction,[4] apparent second order rate constants were calculated. The data are summarized in the table.

TABLE I

ALKALINE HYDROLYSES

Compound	Initial concn., moles/l.	T, °C.	Time, min.	Amount reacted, %	$k \times 10^2$, liter moles^{-1} min.$^{-1}$
Benzylpenicillin	0.10	0	7	20	36
			15	38	41
			25	48	37
				Av.	38
II		0	See ref. 3	Av.	0.12
		50 ± 1	See ref. 3	Av.	13
III	.45	50 ± 1	30	35	4.0
			60	52	4.0
				Av.	4.0
V	.49	0	3300	20	0.016
			6100	31	.015
			10000	43	.015
				Av.	0.015
VI	.39	50 ± 5	2340	24	0.035
			3120	32	.039
			3900	40	.044
				Av.	0.04
VII		50 ± 1	See ref. 3	Av.	1.0

Desthiobenzylpenicillin (III) was found to be somewhat less reactive than 2-azetidinone (II) toward alkali. Therefore, the combination of the effects of the carboxyalkyl group and the phenylacetamido group present in desthiobenzylpenicillin does not result in increased reactivity of the β-lactam ring for this reaction.[5] Presumably this would also be true in a compound having the thiazolidine-β-lactam structure (I).

Benzylpenicillin is much more reactive than 2-

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(1) Clarke, Johnson and Robinson, Editors, "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949; especially (a) Woodward, pp. 443–449, (b) Robinson, pp. 449–454, and (c) Ballard, Melstrom and Smith, Chapter XXVI.

(2) Chain, *Endeavour*, **7**, 152 (1948).

(3) Holley and Holley, THIS JOURNAL, **71**, 2124, 2129 (1949).

(4) (a) Crocker and Lowe, *J. Chem. Soc.*, **91**, 952 (1907); (b) Calvet, *Compt. rend.*, **192**, 1569 (1931); (c) Reitz, *Z. physik. Chem.*, **A183**, 371 (1939).

(5) It seems likely that the presence of the carboxyl group (carboxylate group in alkali) decreases the rate of alkaline hydrolysis. In a summary of relative rates of alkaline ester hydrolysis in water at 25°, Hammett ("Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, p. 212) gives the ratio of rates of hydrolysis of CH_3COOCH_3 and $^-OOCCH_2COOCH_3$ as 1:0.19. In the present study, the carboxylate group might be expected to influence the hydrolysis rate by increasing the basicity of the lactam nitrogen, thus retarding the reaction, as well as by simply repelling the attacking hydroxyl ion (approach of one anion to another). It also seems likely that the α-phenylacetamido group would increase the rate of alkaline hydrolysis.[10] Whatever the magnitudes of the effects of these two substituents, the combination does not result in an increased rate of alkaline hydrolysis.