

Reactivity ratio determinations. Polymerization was carried out in bulk at 60° using 1.0% benzoyl peroxide initiator. The polymer was precipitated in methanol and unreacted monomer was extracted by low-boiling petroleum ether in a Soxhlet extractor for 6 hr. For further purification the polymer was twice reprecipitated from benzene or trifluoromethylbenzene. The conversion in these reactivity ratio studies were of the order of 5–10% and never more than 10%. The experimental data are summarized in Tables II and III.

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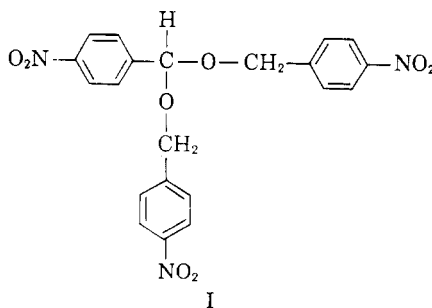
para-Nitrobenzyl Nitrite¹

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In the course of another study it became necessary to know something of the chemical properties of *p*-nitrobenzyl nitrite, a compound first prepared in 1955.²

p-Nitrobenzyl nitrite is a yellow liquid which has previously been reported² to decompose to a light yellow solid (uncharacterized) on standing overnight exposed to the atmosphere, in the dark, at room temperature. In the present study, the nitrite ester was protected from the atmosphere and allowed to decompose at room temperature in the dark; four days were required for complete solidification. During this time a colorless gas, which turned brown on contact with the air, and which attacked mercury, was evolved. The resulting light yellow solid was easily separated into two components: *p*-nitrobenzaldehyde (24% yield), and the acetal (I) of *p*-nitrobenzaldehyde with *p*-nitrobenzyl alcohol (72% yield). The colorless gas is presumably nitric oxide.



The formation of an acetal in the thermal decomposition of a nitrite ester is, to our knowledge,

(1) This work was supported by a grant from the Explosives Department of E. I. du Pont de Nemours and Co., Inc.

(2) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

unprecedented. Another interesting feature is the relatively great instability of *p*-nitrobenzyl nitrite. While it is not difficult to imagine why *p*-nitrobenzaldehyde should go over to the acetal rather readily, it is less than obvious why *p*-nitrobenzyl nitrite is so unstable.

EXPERIMENTAL³

Decomposition of *p*-nitrobenzyl nitrite. *p*-Nitrobenzyl nitrite was prepared by the previously reported method² except that purification was accomplished by molecular distillation at *ca.* 10⁻³ mm. and room temperature; the distillate was kept at Dry Ice temperature as it was being collected. A 6.4-g. (0.035 mole) sample, n_D^{20} 1.5498; m.p. 12.5°, was protected from the atmosphere by a mercury valve and allowed to stand in the dark at room temperature. Sometime during the first 12 hr. the evolution of a colorless gas, which attacks mercury and which turns brown on contact with air, commenced. After 4 days all the liquid had disappeared and in its place a pale yellow solid, 5.2 g., m.p. 105–155° remained.

Digestion of this solid with refluxing acetone gave, upon cooling, the acetal (I), 3.9 g. (0.088 mole), m.p. 209–210° (72% yield). Evaporation of the acetone left 1.3 g. (0.009 mole, 24% yield) of *p*-nitrobenzaldehyde, m.p. 102–104°; recrystallization gave m.p. 105–106°, mixed m.p. with an authentic sample of m.p. 105–106°, was undepressed.

The dinitrophenylhydrazone prepared from the aldehyde had m.p. 318° (dec.); a mixed m.p. determination with the dinitrophenylhydrazone of authentic *p*-nitrobenzaldehyde, m.p. 318° (dec.), showed no depression.

Characterization of acetal (I). This chalk white solid, m.p. 209–210°, was insoluble in water, ethyl ether, and benzene and was slightly soluble in acetone, dioxane, and ethyl acetate. Recrystallization from acetone raised the m.p. of I to 210–211°. I does not react with aqueous potassium permanganate or dinitrophenylhydrazine reagent. It dissolves in cold concentrated sulfuric acid to give a colorless solution which, when poured on to ice gave straw yellow crystals, m.p. 100–102°. Recrystallization from water raised the m.p. to 105–106°; a mixed m.p. with authentic *p*-nitrobenzaldehyde, m.p. 105–106°, was undepressed. The dinitrophenylhydrazone had m.p. 318° (dec.), and a mixed m.p. with authentic dinitrophenyl hydrazone m.p. 318°, was undepressed.

Hydrolysis of 0.3 g. of the acetal (I) was also accomplished by heating under reflux for 4 hr. in 35 ml. of 43% aqueous dioxane containing 5 drops of concentrated hydrochloric acid. The resulting solution was cooled to room temperature and treated with benzoyl chloride and 10% aqueous sodium hydroxide; this gave *p*-nitrobenzyl benzoate m.p. 89–92°. Recrystallization from ethanol raised the m.p. to 92–93°. A mixed m.p. with an authentic sample of *p*-nitrobenzyl benzoate (m.p. 91–93°) gave m.p. 91–93°.

Anal. Calcd. for C₂₁H₁₇N₃O₈: C, 57.6; H, 3.90; N, 9.56. Found: C, 57.6; H, 3.77; N, 9.76.

Synthesis of the acetal of *p*-nitrobenzaldehyde and *p*-nitrobenzyl alcohol (I). *p*-Nitrobenzyl alcohol, 1.0 g. (0.0065 mole), and *p*-nitrobenzaldehyde, 0.5 g. (0.0033 mole), were dissolved in 50 ml. of dry benzene. One drop of 85% phosphoric acid was added and the benzene-water azeotrope was slowly distilled out; from time to time dry benzene was added to maintain the volume between 15 and 50 ml. The distillation was conducted for 16 hr. during which time 85 ml. of benzene distilled.

The precipitate which formed, even in the hot solution, was isolated by cooling the mixture to room temperature and filtering; 1.14 g. (80% yield), m.p. 204–210°. Recrystal-

(3) Microanalyses by Dr. C. S. Yeh and Mrs. S. Margerum of this department.

lization of 0.26 g. from acetone gave 0.22 g., m.p. 210-211°. A mixed melting point with the acetal obtained from the decomposition of *p*-nitrobenzyl nitrite gave no depression.

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Allylic Chlorides. XXV. The Reaction of 1,1,3-Trichloro-1-propene and 1,1-Dibromo-3-chloro-1-propene with Potassium Iodide in Acetone¹

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The preparation and properties of 1,1,3-trichloro-1-propene and 1,1-dibromo-3-chloro-1-propene have been reported recently.¹ It was noted that the reaction of the 1,1-dihalo-3-chloro-1-propenes with potassium iodide, while giving the expected 1,1-dihalo-3-iodo-1-propenes, did not yield kinetic data of value at 20°.

Kinetic data have now been obtained for this reaction with 1,1,3-trichloro-1-propene at 0°, 5°, and 10° (Table I). From these data the energy of activation for the reaction was calculated by use of the Arrhenius equation to be 12 kcal./mole. The straight line relationship between $\ln k$ and $1/T$ indicated that k at 20° would be *ca.* 49. This figure represents a relative reactivity for 1,1,3-trichloro-1-propene of *ca.* 98 (allyl chloride as 1.00 with $k =$

TABLE I

REACTION OF 1,1,3-TRICHLORO-1-PROPENE WITH POTASSIUM IODIDE IN ACETONE

Temperature	Time, hr.	% Reacted	k	
			hr. ⁻¹ mole ⁻¹ l.	Average
0.0°	0.50	59.2	9.64	9.42 ± 0.17
	0.63	67.2	9.56	
	0.78	74.0	9.50	
	0.87	76.8	9.36	
	1.08	82.7	9.07	
5.0°	0.25	51.5	15.6	15.3 ± 0.2
	0.37	65.2	15.6	
	0.47	73.3	15.4	
	0.57	79.1	15.3	
	0.62	80.9	14.8	
10.0°	0.16	48.5	21.3	21.2 ± 0.2
	0.28	67.1	21.3	
	0.35	74.2	21.5	
	0.44	81.4	21.3	
	0.50	83.8	20.4	

(1) Number XXIV of this series: L. F. Hatch and S. D. Zimmerman, *J. Am. Chem. Soc.*, **79**, 3091 (1957).

(2) L. F. Hatch and L. S. Gerhardt, *J. Am. Chem. Soc.*, **71**, 1679 (1949).

0.502). When both 1,1-substituents are CH₃, the relative reactivity is 28.²

An attempt was made to obtain similar data for 1,1-dibromo-3-chloro-1-propene but the reaction was too fast at -10° to give acceptable kinetic data. Three points were obtained which gave an average k value of 151 ± 3.

The marked increase in reactivity in going from chlorine to bromine in the number 1 position has been noted previously³ and ascribed to steric effects related to the size of the bromine atom. Apparently steric, inductive, and resonance effects all influence the reactivity of the allylic chlorine atom and this makes it difficult to relate cause and effect.⁴

EXPERIMENTAL

1,1,3-Trichloro-1-propene. 1,1,3-Trichloro-1-propane was prepared from 1,1-dichloro-1-propene by bromination using *N*-bromosuccinimide, hydrolysis of the 3-bromo-1,1-dichloro-1-propene to 3,3-dichloro-2-propen-1-ol and conversion of the alcohol to the trichloride using phosphorus trichloride in dry pyridine in a manner similar to that described previously.¹ B.p. 59° (50 mm.); n_D^{25} 1.4931 [lit.¹ b.p. 59.5° (50 mm.); n_D^{25} 1.4930].

1,1-Dibromo-3-chloro-1-propene. This compound was prepared from 1,1-dibromo-1-propene (0.25 mole) by reaction with *N*-chlorosuccinimide (0.25 mole) at 70° for 8 hr. in the presence of benzoyl peroxide (10 g.), using carbon tetrachloride as the solvent. A 47% yield of 1,1-dibromo-3-chloro-1-propene was obtained and it had the following physical constants: b.p. 37-38° (1.0 mm.); n_D^{25} 1.5620 [lit.¹ b.p. 35.5-36° (0.6 mm.); n_D^{25} 1.5634].

Reaction of 1,1,3-trichloro-1-propene with potassium iodide in acetone at 0°, 5° and 10°. The procedure used was similar to that described previously.⁵ With the usual modified second-order rate equation, the plot of $\log 5-Z/(5)(1-Z)$ vs. time where Z is the fraction of potassium iodide having reacted in time t , gave a straight line between *ca.* 50 and 80% reacted at 0°, 5° and 10°. The rates at 0° and 5° showed some drift. The data are presented in Table I.

Reaction of 1,1-dibromo-3-chloro-1-propene with potassium iodide in acetone at -10°. Experimental difficulties prevented the obtaining of reliable kinetic data for this reaction. The following data are approximate.

Time, hr.	0.067	0.083	0.100
Reacted, %	85.	88.	93.
k , hr. ⁻¹ mole ⁻¹ l.	159	146	149
Av. k	151 ± 3		

It is assumed that the vinyl bromine atoms have not reacted.³

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(3) L. F. Hatch and K. E. Harwell, *J. Am. Chem. Soc.*, **75**, 6002 (1953).

(4) L. F. Hatch and P. R. Noyes, *J. Am. Chem. Soc.*, **79**, 345 (1957).

(5) L. F. Hatch, L. B. Gordon, and J. J. Russ, *J. Am. Chem. Soc.*, **70**, 1093 (1948).