Bromination of α-Methylstyrene with *N*-Bromosuccinimide. Synthesis of 2-Phenyl-1,5-hexadiene

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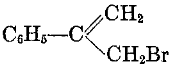
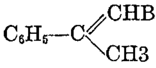
During the bromination of α-methylstyrene by means of *N*-bromosuccinimide[1] it was observed that the bromides obtained from this reaction consisted of a mixture of two compounds: the expected 2-phenylallyl bromide (I) and 1-methyl-1-phenylvinyl bromide (II).



$C_6H_5-C\begin{matrix}\diagup\!\!\diagup CH_2\\ \diagdown CH_2Br\end{matrix}$

(I)



$C_6H_5-C\begin{matrix}\diagup\!\!\diagup CHBr\\ \diagdown CH3\end{matrix}$

(II)

The presence of II was first suspected when the crude bromide failed to react quantitatively with an alkyl Grignard reagent.

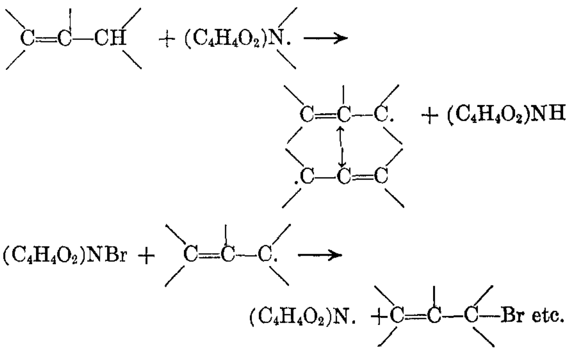
Bromides I and II were separated in pure form chromatographically at room temperature, using activated silica as adsorbent and absolute ethanol as desorbant. During chromatography the allylic isomer I underwent partial polymerization and attempts to carry out the separation at 3–5° did not result in any appreciable improvement. The two isomers have distinct different infrared and ultraviolet spectra.

The bromination of α-methylstyrene by means of *N*-bromosuccinimide yields on the average, according to infrared spectroscopy, 65–75% of isomer I and 25–35% of isomer II. The allylic bromide is a strong lachrymator, reacts readily with aqueous silver nitrate solution in the cold and it clouds on standing at room temperature. The vinylic bromide, II, does not possess the lachrymatory properties and is stable toward alcoholic silver nitrate solution even at reflux temperature.

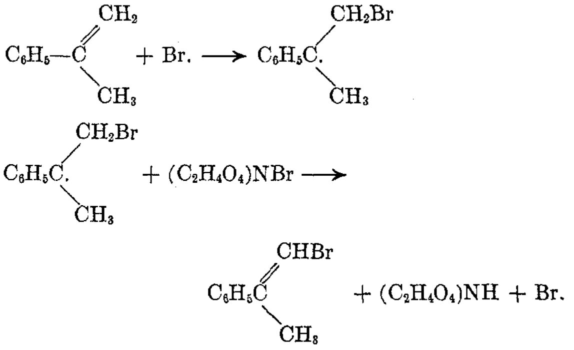
Ozonolysis of II yielded acetophenone while the ozonolysis of I formed a compound which was a very strong lachrymator, presumably bromoacetophenone. Compound I reacted with allyl magnesium bromide to form the expected 2-phenyl-1,5-hexadiene, which on ozonolysis yielded β-benzoylpropionic acid.

The bromination with *N*-bromosuccinimide and related compounds[2] is assumed to proceed *via* a free radical mechanism[3] which involves the homolytic dissociation of *N*-bromosuccinimide.

$(C_4H_4O_2)NBr \longrightarrow (C_4H_4O_2)N. + Br.$



In the case of α-methylstyrene however, owing to the resonance-stabilizing effect of the phenyl group, it appears to be possible for the bromine atom to add to the olefinic double bond, followed by the elimination of a hydrogen atom:



A similar type of abnormal bromination was observed by Roberts and coworkers in the case of camphene which formed 8-bromocamphene[4] and norbornylene which formed 3-bromonortricyclene.[5]

EXPERIMENTAL

Bromination of α-methylstyrene. One hundred grams of *N*-bromosuccinimide, 250 ml. of α-methylstyrene, and 40 ml. of carbon tetrachloride were heated just to boiling, and the flask was then quickly immersed in an ice bath. One hundred ml. of pentane was added to the flask and the solid succinimide was separated by filtration. The unreacted α-methylstyrene was then removed from the filtrate by means of vacuum distillation. An additional 100 ml. of pentane was added to the residue of the flask in order to precipitate the remaining succinimide, and the solid was then separate by filtration. The filtrate on distillation yielded 64 g. of bromides boiling at 105–110° at 15 mm.; yield 64%, based on *N*-bromosuccinimide.

Forty two grams of the bromides dissolved in 30 ml. of n-pentane were chromatographed using activated silica gel[6] as the adsorbent and absolute ethanol as the desorbant.

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[1] K. Ziegler, A. Spaeth, E. Schaaf, W. Schumann, and E. Winkelman [*Ann.*, **551**, 80 (1942)] reacted α-methylstyrene with *N*-bromosuccinimide and in connection with it they stated the following: "Die etwa 1 Stunde dauernde Reaktion soll in anderem Zusammenhang publiziert werden." According to our knowledge further report of this reaction was not published.

[2] For the general review of the Wohl-Ziegler reaction see C. Djerassi, *Chem. Revs.*, **43**, 271 (1948).

[3] G. F. Bloomfield, *J. Chem. Soc.*, **1944**, 114.

[4] J. D. Roberts and E. R. Trumbull, *J. Am. Chem. Soc.*, **71**, 1630 (1949).

[5] J. D. Roberts, E. R. Trumbull Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **73**, 3116 (1950).

[6] Davison Chemical Co., Baltimore, Md.

The first fractions were composed of pure 1-methyl-1-phenylvinyl bromide (II), while the end fractions were composed of 2-phenylallyl bromide (I); about 24% of I underwent polymerization during separation. From the infrared spectra of the pure I and II isomer it was calculated that the crude bromides were composed of 73% of I and 27% of II.

Compound I: b. p. 104–105° at 10 mm., n_D^{20} 1.5925, d_4^{20} 1.3729. MR$_D$: found 48.39; calcd. 47.46. $\lambda_{max.}$ 242 mμ.: ϵ 8,700 (in isooctane).

Anal. Calcd. for C_9H_9Br: C, 54.82; H, 4.57. Found: C, 54.90; H, 4.49.

Compound II: b.p. 98° at 10 mm., n_D^{20} 1.5891, d_4^{20} 1.3716. MR$_D$: found 48.39, calcd. 47.46. $\lambda_{max.}$ 247 mμ (in isooctane) ϵ 13,240 (in isooctane) Literature:[7] b.p. 105–106° at 9 mm., d_4° 1.366.

Anal. Calcd. for C_9H_9Br: C, 54.82; H, 4.57, Found: C, 54 78; H, 4.44.

Ozonolysis of II. Compound II, 2.35 g., dissolved in 25 ml. of methylene chloride was ozonized at −78°. The ozonide was decomposed by the usual method with hot water. Acetophenone, 1.23 g., (89%) was obtained which formed 2,4-dinitrophenylhydrazone, m.p. 246°. It did not depress the melting point of an authentic sample.

Synthesis of 2-phenyl-1,5-hexadiene. Phenylallyl bromide, I, 31 g. was reacted with 15% excess of allylmagnesium bromide. A 78% yield of 2-phenyl-1,5-hexadiene was obtained, which distilled at 104° at 10 mm, n_D^{20} 1.5314.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.75; H, 8.75.

Ozonolysis of 2-phenyl-1,5-hexadiene. Two grams of the hydrocarbon dissolved in 25 ml. of methylene chloride was ozonized at −78° and decomposed oxidatively,[8] except that no sulfuric acid was added. The benzoylpropionic acid which was obtained melted, after recrystallization from water, at 116–117° (literature[9]) m.p. 116.5°.

Anal. Calcd. for $C_{10}H_{10}O_9$: C, 67.41; H, 5.62. Found: C, 67.11; H, 5.95.

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Effect of Substituents on the Rates of Pyrophosphate Hydrolysis[1]

FRED H. BROCK

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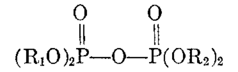
In a recent paper,[2] Heath has summarized (from earlier work of Ketelaar and Blaksma,[3] and of Toy[4,5]) the neutral hydrolysis rate constants of the pyrophosphates listed below. Since Heath has concluded that the transmission of electronic effects along the P-O-P bond is small,[6] the observed rate constant will be the sum of the rate constants for the groups attached to each phosphorus atom. Individual rate constants were obtained based upon the symmetrical pyrophosphates. Using these constants to calculate the expected rate for the unsymmetrical pyrophosphates, agreement was observed only in the cases when R_1 = Et, R_2 = Pr, and R_1 = Et, R_2 = *n*-Bu. Consequently, Heath concluded that steric effects are very much more important than inductive effects in this series.

TABLE I

Rate Constants for Hydrolysis of Pyrophosphates,



$$(R_1O)_2\overset{\overset{\displaystyle O}{\|}}{P}—O—\overset{\overset{\displaystyle O}{\|}}{P}(OR_2)_2$$

No.	R_1	R_2	$k \times 10^3$ min^{-1}	$\Sigma\sigma^*$
1	Me	Me	25	0.000
2	Me	Et	7.0	−0.200
3	Me	Pr	5.6	−0.230
4	Et	Et	1.6	−0.400
5	Me	iPr	1.1	−0.380
6	Et	nPr	1.0	−0.430
7	Et	nBu	0.95	−0.460
8	nPr	nPr	0.65	−0.460
9	Et	iPr	0.28	−0.580
10	nPr	iPr	0.20	−0.610
11	nBu	iPr	0.20	−0.640
12	iPr	iPr	0.09	−0.760

The hydrolysis data have been reexamined in an attempt to establish a quantitative correlation of these reaction rates with structure.

All of the above data are correlated successfully by means of Taft's linear free energy-polar energy equation.[7]

$$\log k/k_0 = \rho^*\Sigma\sigma^*$$

where ρ^* = reaction rate constant, $\Sigma\sigma^*$ = sum of polar substituent constants (aliphatic series), k = observed rate constant, k_0 = observed rate constant for tetramethyl pyrophosphate. The accompanying figure gives the plot of log k/k_0-vs. $\Sigma\sigma^*$, the line being that calculated using the method of least squares. The following constants were obtained: $\rho^* = 3.38 \pm 0.08$, intercept = 0.0561 ± 0.0376, correlation coefficient = 0.994.

Unfortunately, the range of σ^* values is small. Consequently, if the above correlation is confirmed for the reaction with groups of greater σ^* values, then the following conclusions, based on this limited data, will follow.

1. The fact that the total polar effect of all groups is operative, as given by $\Sigma\sigma^*$, indicates a

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(1) The work herein reported was carried out on Project NR055-328 between the Office of Naval Research and The Pennsylvania State University. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) D. F. Heath, *J. Chem. Soc.*, **1956**, 3804.

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