Rates and Products of Acetolysis of *p*-Nitroneophyl *p*-Bromobenzenesulfonate

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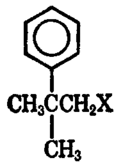
p-Nitro- and *p*-cyanoneophyl brosylates were synthesized and their acetolysis rates were determined. The acetolysis of the nitro brosylate proceeds with 72.2% phenyl rearrangement and 25.4% methyl rearrangement forming four kinds of olefins (β,β-dimethyl-*p*-nitrostyrene, α,β-dimethyl-*p*-nitrostyrene, α-ethyl-*p*-nitrostyrene, and 2-methyl-3-(*p*-nitrophenyl)prop-1-ene) and three kinds of acetates (*p*-nitroneophyl acetate, dimethyl-*p*-nitrobenzylcarbinyl acetate, and an acetate of unknown structure).

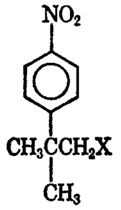
The high reactivity and the large effect of substituents on the solvolysis of neophyl derivatives have been suggested by Winstein to be primarily the result of aryl participation.[1] The ability of a neighboring phenyl to assist in ionization is greatly depressed by introduction of a nitro substituent. We observed that the *anti*-*syn* rate ratio in the solvolysis of 9-benzonorbornenyl derivatives, which has been attributed to participation of the benzene ring in the *anti* isomer and its absence in the *syn*, decreases from 1200 for the parent 9-benzonorbornenyl brosylate to 4.4 for the 6-nitro derivatives.[2b] However, we suggested a slightly persisting participation ability of the nitrobenzene ring by the *anti*-*syn* rate ratio of 4.4 and by the fact that 6-nitro-*anti*-9-benzonorbornenyl brosylate undergoes solvolysis 11 times faster than the saturated 7-norbornyl brosylate.[2] This work was undertaken to evaluate the effect of a *p*-nitro substituent on the rate and the migratory aptitude of the *p*-nitrophenyl group in the acetolysis of the neophyl derivatives. The effect of a *p*-cyano substituent on the rate was, in addition, determined.

Results and Discussion

Preparation of *p*-Nitro- and *p*-Cyanoneophyl Brosylates (2-OBs and 4-OBs).—Nitration of neophyl acetate (1-OAc) with fuming nitric acid in acetic anhydride yielded mainly the *p*-nitro derivative 2-OAc, with the minor formation of the *o*- and *m*-nitro isomers. Hydrolysis of the product mixture followed by careful recrystallization gave the main crop of 2-OH in the pure state. The remainder present in the mother liquor was converted into the corresponding *p*-nitrobenzoate ester. Recrystallization of the ester followed by hydrolysis afforded the second crop. The structure and purity of 2-OH was determined not only by its nmr spectrum but also by $NaBH_4$ reduction of the corresponding brosylate 2-OBs in the presence of aluminum chloride, which gave only *p*-nitro-*t*-butylbenzene (5) without contamination of *o*- and *m*-nitro-*t*-butylbenzenes. Catalytic reduction over platinum oxide converted 2-OH into *p*-aminoneophyl alcohol (3-OH). Diazotization of 3-OH followed by its decomposition in a cuprous cyanide solution led to *p*-cyanoneophyl alcohol (4-OH). The brosylates, 1-OBs, 2-OBs, and 4-OBs, were prepared by treatment with *p*-bromobenzenesulfonyl chloride in pyridine. Completion of this esterification was checked by elemental analyses and infrared spectra, as well as the absence of the alcohols in the products in the above borohydride reductions.

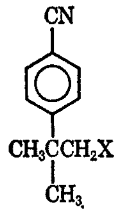


1-OH, X = OH
1-OAc, X = OAc
1-OBs, X = OBs



2-OH, X = OH
2-OAc, X = OAc
2-OBs, X = OBs

3-OH, X = OH



4-OH, X = OH
4-OAc, X = OAc
4-OBs, X = OBs

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Kinetics.—Rates were determined by standard procedure[3] in glacial acetic acid containing 1 equiv of sodium acetate. Good first-order kinetics were observed in the reactions of all the brosylates, and the infinity titers corresponded to theory. The solvolysis rates are summarized in Table I, together with the derived activation parameters and the data of relevant compounds. For comparison, the rate constants at 75° were calculated from Arrhenius plots.

The nitro and cyano substituents decelerate acetolysis by factors of 0.0011 and 0.0028, respectively.[4] However, the rate of 2-OBs is somewhat greater than one-fourth that of the neopentyl brosylate. If one considers the polar retarding effect of a β-nitrophenyl group on solvolysis,[5] the rate is significantly fast. The reason can be attributed to the slightly remaining participation effects of the *p*-nitrophenyl group and/or the relief of strain augmented by the introduction of a phenyl group. A combination of the present results and the data of Winstein and Heck[1] confirms the

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(1) (a) S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, **78**, 4801 (1956); (b) R. Heck and S. Winstein, *ibid.*, **79**, 3432 (1957).

(2) (a) H. Tanida, T. Tsuji, and H. Ishitobi, *ibid.*, **86**, 4904 (1964); (b) H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *ibid.*, **89**, 2928 (1967).

(3) *E.g.*, S. Winstein, C. Hanson, and E. Grunwald, *ibid.*, **70**, 812 (1948); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

(4) The rate-decelerating effect of the 6-nitro substituent in the acetolysis of *syn*-9-benzonorbornenyl brosylates is 0.037. Therefore, the nitro effect is 34 times more effective in the neophyl system.

(5) The rate-retarding effect of an unsubstituted β-phenyl group has been estimated by Winstein as a factor of 10. Refer to S. Winstein, *et al.*, *J. Amer. Chem., Soc.*, **72**, 5795 (1950), and A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N.Y., 1962, p 146.

TABLE I

ACETOLYSIS RATES OF *para*-SUBSTITUTED NEOPHYL BROSYLATES[a,b]

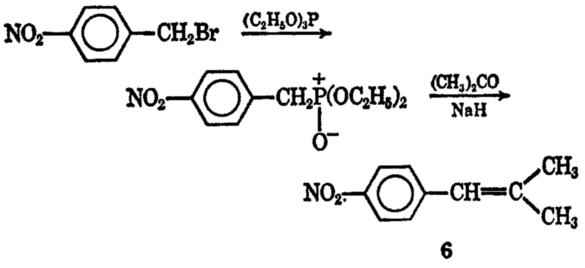
			Calculated at 75°		
Substituent	Temp, °C	k_1, sec^{-1}	Relative rate	$\Delta H‡$, kcal	$\Delta S‡$, cal/deg
NO_2	95.5	8.42×10^{-7}			
	126.1	1.82×10^{-5}			
	140.5	7.27×10^{-5}			
	156.0	2.57×10^{-4}			
	75.0[c]	7.60×10^{-8}	1.11×10^{-3}	29.1	−7.9
CN	114.8	1.38×10^{-5}			
	144.9	2.20×10^{-4}			
	75.0[c]	1.91×10^{-7}	2.79×10^{-3}	28.9	−6.5
H[d]	75.0	6.84×10^{-5}	1	25.5	−4.6
Neopentyl-OBs[e]	75.0		4.1×10^{-3}		

[a] The present runs were conducted in glacial acetic acid containing equivalent sodium acetate. [b] [ROBs] = 0.10 *M*. [c] Extrapolated value. [d] Reference 1b. We found $k_1(75.7°) = 6.91 \times 10^{-5}$ sec^{-1}. [e] Evaluated from the rate of tosylate reported by S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74,** 1113 (1952).

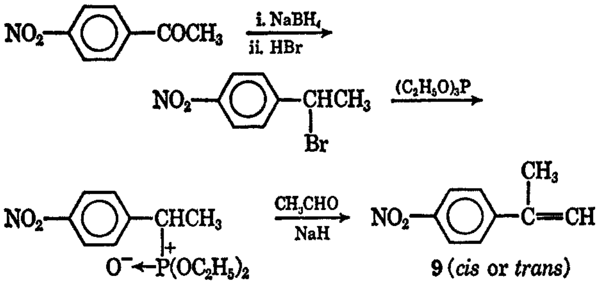
linearity attained by Yukawa and Tsuno using their equation,[6] $\log (k/k_0) = \rho[\sigma + \gamma(\sigma^+ - \sigma)]$, where $\gamma = 0.552$ and $\rho = -3.70$; the correlation coefficient is 0.936.

Products from *p*-Nitroneophyl Brosylate (2-OBs).—The solvolysis of 2-OBs at 137° for 40 hr in acetic acid buffered with the above amount of sodium acetate resulted in a mixture consisting of 94.1% of four kinds of olefins and 5.9% of three kinds of acetates. The per cent yields were determined by spearation of the olefinic and the acetate fractions using elution chromatography on Florisil and the composition of each fraction was revealed by vpc. The isolated yield was 97.4%.

Ozone oxidation of the olefin fraction gave, in order of decreasing yield, *p*-nitrobenzoic acid, *p*-nitroacetophenone, *p*-nitropropiophenone,[7] and 1-(*p*-nitrophenyl)-propan-2-one.[8] The first two products were isolated and identified by comparison with authentic samples. The structures of the other two products were assigned by retention time analysis on vpc with authentic samples. By these results, it is suggested that the olefin fraction is composed of β,β-dimethyl *p*-nitrostyrene (**6**), α,β-dimethyl-*p*-nitrostyrene (**9**), α-ethyl-*p*-nitrostyrene (**10**), and 2-methyl-3-(*p*-nitrophenyl)-prop-1-ene (**7**). An authentic sample of the most important product, **6**, was prepared by the modified Wittig reaction,[9] as shown in eq 1, and its presence in the acetolysis products was validated by vpc. A similar reaction with diethyl α-(*p*-nitrophenyl)ethylphosphonate and acetaldehyde (eq 2) yielded, in poor yields, two kinds of olefins in a ratio of 6:1 (by vpc). The main olefin was isolated by preparative vpc and its structure was established as **9** by nmr spectra, although the assignment of whether it is *cis* or *trans* has not been settled. This sample on vpc was superimposable with the second important olefin peak. We failed in independent syntheses of **10** and **7**. Accordingly, judging from the relative yields of the oxidation products, *p*-nitropropiophenone and 1-(*p*-nitrophenyl)-propan-2-one, the minor two olefinic peaks on vpc were assumed to be due to **10** and **7**. It is possible, however, that the other geometrical isomer of **9**, if it exists in the acetolysis products, is covered by these two peaks.

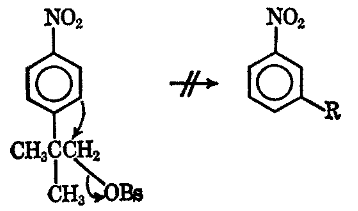


(1)



(2)

Retention time analysis on vpc indicated that the acetate fraction was composed of unrearranged 2-OAc, dimethyl-*p*-nitrobenzylcarbinyl acetate (**8**), and an acetate of unknown structure [presumably, ethylmethyl-*p*-nitrophenylcarbinyl acetate (**11**)]. An authentic sample of **8** was prepared by aromatic nitration of benzyldimethylcarbinyl acetate. Oxidation of the acetolysis mixture with sodium dichromate in sulfuric acid gave only *p*-nitrobenzoic acid, but not *m*-nitrobenzoic acid. This is additional support for the above structure proof, as well as evidence for the absence of such a rearrangement as shown in eq 3. Structures



(3)

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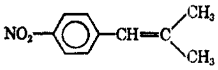
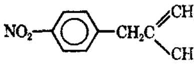
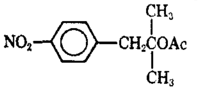
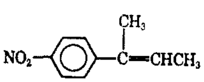
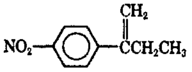
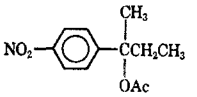
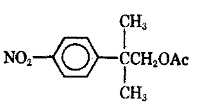
[6] (a) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jap.*, **32,** 965, 971 (1959); (b) also, refer to ref 1b.

[7] N. Sugimoto, J. Iwao, and H. Kakemi, *Yakugaku Zasshi*, **71,** 1151 (1951).

[8] C. G. Overberger and H. Biletch, *J. Amer. Chem. Soc.*, **73,** 4880 (1951).

[9] *Cf.* L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N.Y., 1967, p 1212.

Table II
Acetolysis Products

Formula		Yield, %	
	(6)	67.6	Phenyl rearrangement 72.2%
	(7)	2.2	
	(8)	2.4	
	(9)	19.1	Methyl rearrangement 25.4%
	(10)	5.2	
 (?)	(11)	1.1	
	(2-OAc)	2.4	Retention

and per cent yields, estimated by vpc, of the products are summarized in Table II. The errors in the product analyses are approximately ±2%. Thus it is shown that the acetolysis of **2**-OBs causes 72.2% of *p*-nitrophenyl rearrangement and 25.4% of methyl rearrangement, together with 2.4% of retention. After correction for the presence of two methyl groups, the migratory aptitude of the *p*-nitrophenyl substituent is demonstrated to be 5.7 times greater than that of the methyl substituent. In contrast, the study of Heck and Winstein,[1b] which was carried out without availability of vpc, reported that the acetolysis of **1**-OBs at 75° brought about 99.7% phenyl rearrangement and 0.3% retention with no detectable amount of methyl rearrangement. A more recent careful study of Saunders and Paine,[10] performed with the advantage of vpc, indicated 99.7% phenyl rearrangement and 0.3% methyl rearrangement in the acetolysis of **1**-OTs at reflux temperature of the solvent and, therefore, the phenyl/methyl migratory aptitude is 667.

The latter workers have observed a similarity of the partial rate factors for methyl migration, p_{CH_3}, in the acetolyses of **1**-OTs and neopentyl tosylate.[10] The p_{CH_3} obtained from **2**-Obs is 0.1 times smaller than the values in the above cases.[11,12] In the neophyl system, the introduction of such a deactivating group as *p*-nitro does not affect the ground-state energy, while it destabilizes the α-ethyl-α-methylbenzylcarbonium ion formed by the methyl migration. Thus, when compared with the case of **1**-OBs, the methyl migration step in **2**-OBs is more endothermic and the transition state will lie at a later point along the reaction coordinate. Consequently, p_{CH_3} in **2**-OBs becomes smaller.

Experimental Section

Melting points were taken by capillary and are corrected. Boiling points are uncorrected. Nmr spectra were determined at 60 Mc with a Varian A-60 spectrometer using tetramethylsilane as an internal standard.

Neophyl acetate (1-OAc) was prepared by treatment of **1**-OH with acetic anhydride and has bp 123–124° (23 mm), n^{26}D 1.4940.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.94; H, 8.43.

***p*-Nitroneophyl Alcohol (2-OH).**—To a solution of 21.6 g of **1**-OAc in 50 ml of acetic anhydride, a solution of 11.3 g of fuming nitric acid (*d* 1.50) in 15 ml of acetic anhydride was slowly added at 0–3°. After stirring for 4 hr at 3°, the reaction mixture was allowed to stand overnight at room temperature. The mixture was poured onto ice, extracted with ether, washed with aqueous sodium carbonate, and dried. After evaporation of the solvent, the residual oil was distilled to give 25.0 g of a mixture of mononitrated compounds at 120–121° (0.1 mm). Vpc of the mixture showed one large peak and two small peaks, which were assigned to the main *p*-nitro derivative and to the minor *o*- and *m*-nitro derivatives, respectively. Purification of the main *p*-nitro isomer was achieved in the following way. For hydrolysis, the above mixture was treated with a solution of 47.4 g of sodium bicarbonate in 500 ml of water and 250 ml of ethanol under reflux for 2 hr. The reaction mixture was concentrated under reduced pressure and extracted with ether. The ether solution was washed with water, dried, and concentrated. Addition of pentane to the concentrated ether solution separated 10.0 g of crystals. Evaporation of the mother liquor yielded 13.2 g of oily residue, which was converted into *p*-nitrobenzoates by treating with 15.0 g of *p*-nitrobenzoyl chloride in pyridine. The *p*-nitrobenzoates obtained were recrystallized from acetone to yield 6.3 g of pale yellow needles, mp 113–115°. Treatment of these needles in a refluxing solution of 4.6 g of sodium bicarbonate in 50 ml of water and 25 ml of ethanol for 6 hr afforded 3.2 g of the hydrolyzed crystalline alcohol, which was combined with 10.0 g of the above crystals. Recrystallization from a mixed solution of ether and pentane and then from aqueous methanol gave 5.0 g (22.8%) of **2**-OH as pale yellow needles, mp 64–64.5°. Nmr peaks of aromatic protons are typical A_2B_2 types.

Anal. Calcd for $C_{10}H_{13}O_3N$: C, 61.52; H, 6.71; N, 7.18. Found: C, 61.75; H, 6.92; N, 7.41.

The acetate had mp 58–59°.

Anal. Calcd for $C_{12}H_{15}O_4N$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.80; H, 6.60; N, 5.97.

The brosylate had mp 146.5–147.5°.

Anal. Calcd for $C_{16}H_{16}O_5NSBr$: C, 46.39; H, 3.89. Found: C, 46.52; H, 4.15.

***p*-Aminoneophyl alcohol (3-OH)** was prepared by catalytic reduction of **2**-OH over platium oxide, bp 129–131.5° (3 mm), n^{25}D 1.5586.

Anal. Calcd for $C_{10}H_{15}ON$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.61; H, 8.88; N, 8.37.

***p*-Cyanoneophyl alcohol (4-OH)** was prepared from **3**-OH by an application of the procedure described in ref 13, and was colorless prisms of mp 86.5–87.5°.

Anal. Calcd for $C_{11}H_{13}ON$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.49; H, 7.58; N, 8.18.

The brosylate had mp 87.5–88°.

Anal. Calcd for $C_{17}H_{16}SO_3NBr$: C, 51.79; H, 4.09. Found: C, 51.81; H, 4.14.

Sodium Borohydride Reduction of 2-OBs in the Presence of Aluminum Chloride.—To a solution of 244 mg of sodium borohydride in 5 ml of diglyme was added a solution of 670 mg of **2**-OBs in 10 ml of diglyme with stirring and then a solution of 265 mg of aluminum chloride in 5 ml of diglyme. The mixture

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(10) W. H. Saunders, Jr. and R. H. Paine, *J. Amer. Chem. Soc.*, **83**, 882 (1961).

(11) Our calculation involves the reasonable assumption that the migratory aptitudes are not significantly different at 137 (temperature for the product study) and 75° (temperature for rate comparison) and that methyl migration occurs in the rate-determining step of the acetolysis.

(12) For neopentyl tosylate, p_{CH_3} is 2.7×10^{-8} sec^{-1} (74.71°) (one-third of the over-all rate constant, 8.0×10^{-8} sec^{-1}, see the literature cited as footnote e in Table I). The acetolysis rate of neophyl tosylate at 75° is 2.00×10^{-5} sec^{-1}: A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763 (1956). Therefore, $p_{CH_3} = 2.00 \times 10^{-5} \times 0.003$ (fraction of methyl rearrangement) $\times 0.5$ (the correction factor due to the presence of the two methyl groups) $= 3.0 \times 10^{-8}$ sec^{-1}. By the use of the factor OBs/OTs = 3, the rate of **2**-OTs at 75° is obtained as 2.53×10^{-8} sec^{-1}. Therefore, calculation, $2.53 \times 10^{-8} \times 0.26$ (fraction of methyl rearrangement) $\times 0.5$, yields 3.29×10^{-9} sec^{-1} as p_{CH_3}.

(13) H. T. Clarke and R. R. Read, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1961, p 514.

was gradually warmed to 60° and stirred for 4 hr. The reaction mixture was cooled to room temperature, poured in a mixture of crushed ice and hydrochloric acid, and extracted with ether. The ether extract was washed with water and 10% aqueous sodium carbonate, and then dried. After removal of the solvent, distillation of the residue gave *p*-nitro-*t*-butylbenzene. Vpc showed absence of impurities in amounts greater than 0.4%.

Kinetic Measurements.—The acetolysis conditions and procedure were the same as reported.[2,3]

Acetolysis Products of 2-OBs.—The acetolysis solution of approximately 0.1 *M* in the brosylate was prepared by dissolving 828.8 mg of 2-OBs in 20 ml of 0.1 *N* sodium acetate–acetic acid solution. At 60°, 4 ml of the solution (containing 160.4 mg of 2-OBs) was pipeted into an ampoule. The sealed ampoule was allowed to remain in a constant temperature bath at 137° for 40 hr, cooled, concentrated, and poured in water. The products were extracted with ether, and the ether solution was washed with aqueous sodium bicarbonate and water, and then dried. Evaporation of the ether left 67.5 mg of the residue. Elution chromatography on Florisil indicated that the residue was composed of 92.3% (in weight) of an olefin mixture and 7.7% of an acetate mixture.

Identification and estimation of yields of the olefin mixture were conducted on a Hitachi Perkin-Elmer gas chromatograph, Model F-6, using hydrogen flame ionization detectors. A 2 m × 3 mm stainless steel column packed with 10% diethylene glycol succinate polyester on 60–80 mesh Chromosorb W was used. The column temperature was 175°. Helium was used as a carrier gas at a pressure of 0.7 kg/cm^2.

Identification and estimation of yields of the acetate mixture were conducted using helium as a carrier gas on a Shimazu gas chromatograph, Model GC-1B, equipped with a standard column of 2 m × 6 mm stainless steel tubing. The column was packed with 10% diethylene glycol succinate polyester on 30–60 mesh Chromosorb W. The column temperature was 190° and the flow rate of helium was 54 ml/min.

Ozone Oxidation of the Olefins from 2-OBs.—The olefin fraction (218 mg), separated from the acetolysis mixture by elution chromatography on Florisil as described above was dissolved in 10 ml of methanol and cooled to −40°. Oxygen containing ozone was passed into the methanol solution and, after passing through the reaction vessel, it was bubbled into a 1% potassium iodide solution. The flow of oxygen was adjusted at such a rate that no color was observed in the iodide solution. The oxygen was passed for some time after the test solution began to show a faint yellow. Nitrogen was introduced to remove the excess of ozone dissolved in the solution, and then the solution was concentrated under vacuum. In order to destroy the ozonide, 4 ml of 85% formic acid was slowly added to the concentrated solution, then 700 mg of 30% hydrogen peroxide was added portionwise, and the solution was warmed in a boiling water bath. After making basic with 10% aqueous sodium carbonate, the solution was extracted with ether. The ether solution was dried and evaporated. The residue was purified using a short alumina column and benzene solvent, and then analyzed by vpc. *p*-Nitroacetophenone crystallized when the benzene eluent was concentrated. The sodium carbonate solution was acidified and extracted with ether. Evaporation of the ether gave *p*-nitrobenzoic acid. Vpc analyses were carried out on the Hitachi Perkin-Elmer with the column specifications the same as described above. Helium was at a pressure of 0.7 kg/cm^2 and the column temperature was 195°.

β,β-Dimethyl-*p*-nitrostyrene (**6**).—Triethyl phosphite, 3.85 g, was placed in a distillation flask and warmed at 140° in a bath. Through a neck of the flask, 5 g of *p*-nitrobenzyl bromide was added to form *p*-nitrobenzyltriethylphosphonium bromide, which on refluxing lost ethyl bromide to form diethyl *p*-nitrobenzylphosphonate. To maintain gentle reflux, the bath temperature was gradually raised to 180°. After cooling, the phosphonate was dropwise added at 20° to a suspension of 1.36 g of 50% sodium hydride in 50 ml of 1,2-dimethoxyethane. The solution was stirred at room temperature for 1 hr until gas evolution had ceased. To the solution, maintained below 30°, was added dropwise 1.64 g of acetone. During the addition, a gummy precipitate appeared. After stirring for 1 hr, the reaction mixture was poured into water and extracted with ether. The ether solution was dried and concentrated. The residual oil was purified by alumina chromatography using benzene as a solvent and then distilled at 108–109° (2 mm). The oil (1.5 g) thus obtained was further purified by preparative vpc. A sample which was homogeneous on vpc had bp 77° (0.03 mm); $n^{24}\text{D}$ 1.6010; nmr (CCl_4) τ 1.9 and 2.7 (aromatic, A_2B_2 type), 3.7 (vinyl, 1 H, multiplet), and 8.07 and 8.13 (CH_3, 6 H, two doublets).

Anal. Calcd for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.97; H, 6.44; N, 8.04.

α,β-Dimethyl-*p*-nitrostyrene (**9**).—*p*-Nitroacetophenone was reduced to α-(*p*-nitrophenyl)ethanol by sodium borohydride in methanol and then the ethanol was converted into α-(*p*-nitrophenyl)ethyl bromide, bp 96–98° (0.03 mm), by treatment with 48% hydrobromic acid. Following the procedure used for **6**, the reaction of the bromide with triethyl phosphite and acetaldehyde was carried out. After working up, the pentane eluate from an alumina column displayed three peaks on vpc. The most important peak was separated by preparative vpc. A pure sample of **9** had bp 95° (0.14 mm); $n^{27}\text{D}$ 1.5915; nmr (CCl_4) at τ 1.9 and 2.6 (aromatic, A_2B_2 type), 4.03 (vinyl, 1 H, quartet), 7.94 (α-CH_3, singlet), and 8.13 (β-CH_3, doublet).

Anal. Calcd for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.26; N, 7.91. Found: C, 68.24; H, 6.69; N, 7.78.

Dimethyl-*p*-nitrobenzylcarbinyl Acetate (**8**).—Nitration of dimethylbenzylcarbinyl acetate with fuming nitric acid in acetic anhydride yielded three isomeric mononitro derivatives. The major two products were isolated by preparative gas chromatography. By the nmr pattern of aromtic protons, the most important product, mp 75–76.5°, was assigned as the *p*-nitro derivative **8** and the second one, mp 119–120°, as the *o*-nitro derivative.

Anal. Calcd for $C_{12}H_{15}O_4N$: C, 60.75; H, 6.37. Found for **8**: C, 60.92; H, 6.67. Found for the *ortho* isomer: C, 60.80; H, 6.63.

Registry No.—**1**-OAc, 18755-52-7; **2**-OH, 18755-53-8; **2**-OAc, 18755-54-9; **2**-OBs, 18755-55-0; **3**-OH, 18755-56-1; **4**-OH, 18755-57-2; **4**-OBs, 18755-58-3; **6**, 1012-18-6; **7**, 18755-60-7; **8**, 18755-61-8; **9**, 18755-62-9; **10**, 18755-63-0; dimethyl-O-nitrobenzylcarbinyl acetate, 18755-64-1.