5,5-Dihydro-2,5,5,5-tetraphenyl-Δ³-1,2,5-oxazaphospholine. Dependence of Ylide Structure on Solvent

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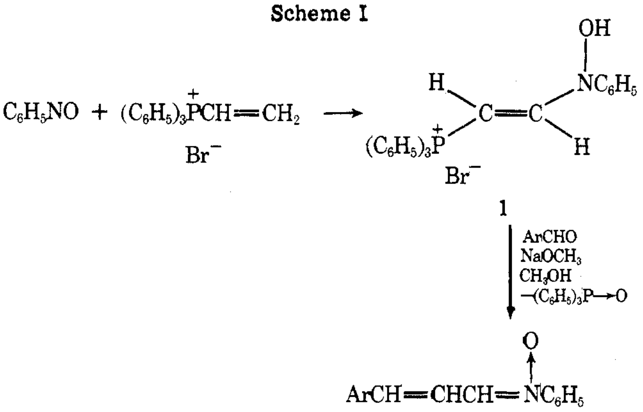
Wittig reactions of [(*E*)-2-(*N*-hydroxyanilino)vinyl]triphenylphosphonium bromide with aromatic aldehydes produced α-styryl-*N*-phenylnitrones **2a–d**. The intermediate ylide **3** was prepared and isolated as a yellow solid. ^{31}P and ^{1}H nmr spectra revealed that **3** exists solely in the cyclic form **3a** in carbon tetrachloride, benzene-d_6, and toluene. In chloroform-*d*, **3** exists as a mixture of **3a, 3b,** and **3c,** with **3a** and **3b** in an equilibrium that is rapid relative to the nmr time scale. Alcohol solvents favor the trans form **3c** over **3a** and **3b**; in methanol, the ylide exists predominantly as **3c.** The solvent effect results from a combination of polar solvent stabilization of polar forms **3b** and **3c,** with **3c** stabilized more than **3b,** and from hydrogen-bonding effects which stabilize **3c** more than **3b.**

Numerous studies of the structures of various phosphonium ylides have appeared in recent years.[1-15] Several of these have dealt with cis–trans isomerism in carbonyl-stabilized ylides and with various factors that can influence the cis–trans ratios.[2-14] This report deals with the preparation, Wittig reactions, and structure of the novel phosphonium ylide **3**, whose constitution is highly solvent dependent.

Nitrosobenzene and triphenylvinylphosphonium bromide react by a complex free-radical pathway to produce [(*E*)-2-(*N*-hydroxyanilino)vinyl]triphenylphosphonium bromide (1).[16] Treatment of methanol solutions of **1** and various aromatic aldehydes with sodium methoxide resulted in Wittig reactions that produced styrylnitrones **2a–d** (Scheme I). Apparently, these nitrones possess *E* stereochemistry about the carbon–carbon double bond, based on the ir spectra which show medium to strong absorption at ~10.2 μ (trans CH=CH[17]). Compounds **2a**[18] and **2d**[19] were reported previously.

Scheme I



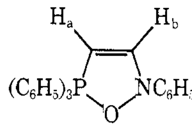
2a, Ar = p-$O_2NC_6H_4$ (88%)
b, Ar = p-ClC_6H_4 (71%)
c, Ar = 2,4-$Cl_2C_6H_3$ (56%)
d, Ar = 3,4-$(CH_2O_2)C_6H_3$ (39%)

The ylide **3** involved in these Wittig reactions was prepared and isolated as a yellow, moderately stable solid *via* treatment of a chloroform or methylene chloride solution of **1** at 0° with aqueous sodium hydroxide. Protonation of the

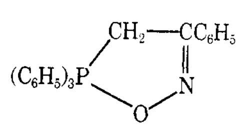
$$1 \underset{HBr}{\overset{NaOH}{\rightleftharpoons}} 3$$
(yellow ylide)

ylide with aqueous hydrogen bromide regenerated only **1**; no *Z* isomer of **1** was detected.

In nonpolar solvents such as carbon tetrachloride, benzene-d_6, and toluene, **3** evidently exists solely as 1,2,5-oxazaphospholine **3a,** based on ^{31}P and ^{1}H nmr spectra. The



3a



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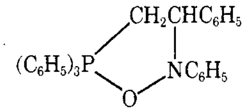

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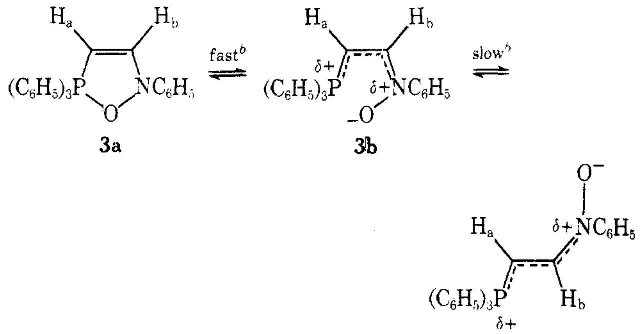
^{31}P resonance (decoupled from all the protons) of **3** appears as one sharp singlet at 20.3 ppm in CCl_4 and at 19.7 ppm in benzene-d_6 (relative to external 85% H_3PO_4 standard). Pentacovalent phosphorus compounds characteristically possess positive ^{31}P shifts,[20-23] while phosphonium salts and phosphonium ylides exhibit negative ^{31}P shifts.[2,12,14,20] Observed ^{31}P shifts for the related compounds **4** and **5** are 37.0 ppm ($CHCl_3$ solvent)[22] and 58.6 ppm ($CDCl_3$).[23] A variable temperature study of the ^{31}P resonance (decoupled from the protons) of **3** in toluene revealed a single sharp absorption at +20.7 ppm at −30°, 20.5 ppm at 25°, and 19.7 ppm at 90°. This shift with temperature is quite small and probably is due to normal temperature effects.[24] The proton nmr spectrum of **3** in CCl_4 at 25° shows resonances attributable only to **3a:** the phenyl protons appear as a multiplet at δ 6.5–7.75, proton H_b appears at δ 7.78 as a double doublet with J_{PH} = 39 Hz and J_{HH} = 4.8 Hz, and proton H_a appears at δ 3.47 as a double doublet with J_{PH} = 36.7 Hz and J_{HH} = 4.8 Hz. The proton spectrum of **3a** in benzene-d_6 at 25° exhibits the NC_6H_5 protons as a multiplet at δ 7.60, the PC_6H_5 protons as a multiplet centered at δ 7.05, proton H_b as a double doublet at δ 7.50 with J_{PH} = 38 Hz and J_{HH} = 5.2 Hz, and proton H_a as a double doublet at δ 3.62 with J_{PH} = 37.5 Hz and J_{HH} = 5.2 Hz. Spectral analyses were simplified through use of ^{31}P decoupling. The observed P–H_a coupling for **3a** is outside the normal range of 20–27 Hz for P–C–H couplings in open chain ylides,[3,4,6,8,10-12] evidently as a result of the cyclic structure of **3a.**

Nmr spectra of **3** in chloroform-*d* (Tables I and II, Chart I) indicate the presence of at least two species. The ^{31}P nmr spectrum displays resonances at −19.9 ppm and +9.5 ppm ($CDCl_3$ at 25°) in a 27:73 ratio. Two sets of signals for protons α to phosphorus appear in the ^{1}H nmr spectrum of **3** in a 22:78 ratio ($CDCl_3$ at 35°). The minor isomer gave a double doublet at δ 4.90 with J_{HH} = 12.3 Hz and J_{PH} =

Chart I
Ylide 3 in $CDCl_3$ at 35°[a]

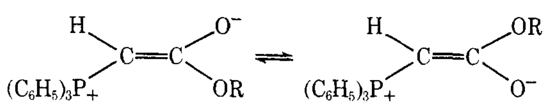


3a 3b 3c

3a ⇌ 3b		3c	
H_a	H_b	H_a	H_b
δ 3.45	δ 7.82	δ 4.90	obscured in
J_{HH} = 5.4	J_{HH} = 5.4	J_{HH} = 12.3	aromatic
J_{PH} = 34.3	J_{PH} = 43	J_{PH} = 18.9	region

[a] HA-100 spectrometer employed. [b] Relative to the nmr time scale.

18.9 Hz for H_a; the resonance due to H_b was obscured by the aromatic proton absorptions. Based on rather limited data for phosphonium ylides, in which trans H_a–H_b couplings of 11–14 Hz and cis H_a–H_b couplings of 3.5–9.5 Hz have been observed,[8,12] the H_a–H_b coupling of 12.3 Hz is consistent with a trans arrangement of these protons and thus suggests the structure **3c** for the minor isomer. The ^{31}P shift of this isomer, **3c**, is nearly temperature and solvent independent. The amount of **3c**, however, increases when either lithium chloride or alcohols are added to the $CDCl_3$ solvent, consistent with the results of Snyder[9] who found that lithium bromide and alcohols preferentially stabilize the trans form of ylide **6** in $CDCl_3$. The ^1H nmr spec-



trans-**6** *cis*-**6**

tra did reveal a 0.37-ppm downfield shift for H_a of **3c** when lithium chloride was added to the $CDCl_3$; the other H_a signal, a doublet of doublets at δ 3.45, did not shift. Similarly, H_a of **3c** shifted 0.13-ppm downfield when pure $CDCl_3$ solutions of **3** were diluted with alcohols to either 1.4:1 $CDCl_3$-*t*-BuOH or 12:1 $CDCl_3$–MeOH, and the H_a signal at δ 3.45 did not shift.

Contrary to the near independence of temperature of the ^{31}P shifts for **3c** in $CDCl_3$ and for **3a** in toluene, the ^{31}P shift for the "major" isomer in $CDCl_3$ (above −13°) is markedly temperature dependent, so much so that the data for this isomer seem consistent only with a time-averaged spectrum due to **3a** and **3b** in rapid (on the nmr time scale) equilibrium,[25] which is quite sensitive to the temperature. While the exact ^{31}P shifts for **3a** and **3b** in $CDCl_3$ are unknown, they can be estimated approximately as 20 ppm for **3a**, from the data in CCl_4, and −15 to −20 ppm for **3b**, based on the −20-ppm shift for **3c** in $CDCl_3$ and from the observed 5-ppm shielding[8,11] of the cis form relative to the trans form of formylmethylenetriphenylphosphorane. The time-averaged shift of 9.5 ppm in $CDCl_3$ at 25° thus appears to indicate that this **3a–3b** mixture consists of *ca.* 70–74% **3a** and 30–26% **3b**. As the temperature is lowered, the time-averaged shift decreases, evidently a result of a shift in the rapid equilibrium toward more of **3b**. At −51°, the time-averaged shift of 2.7 ppm indicates a **3a–3b** mixture of *ca.* 50–57% **3a** and 50–43% **3b**. The time-averaged ^1H nmr spectral data for **3a** plus **3b** are given in Chart I. The time-averaged H_a–H_b coupling constant of 5.4 Hz is in accord with the cis arrangement of these protons in **3a** and **3b**, and the 43-Hz P–H_b coupling is in agreement[8,12-14] with the trans configuration of H_b and the phosphorus atom.

Table I
^{31}P Spectra[a] of 3

Temp, °C	Solvent	3a, ^{31}P shift, ppm	3a ⇌ 3b ^{31}P shift, ppm[b]	3a ⇌ 3b %[c]	3c ^{31}P shift, ppm	3c %[c]
25	CCl_4	+20.3				
25	C_6D_6	+19.7				
−30	$CH_3C_6H_5$	+20.7				
25	$CH_3C_6H_5$	+20.5				
90	$CH_3C_6H_5$	+19.7				
−51	$CDCl_3$		+2.7	51	−20.4	49
−30	$CDCl_3$		+5.0	50	−20.4	50
−6	$CDCl_3$		+7.6	52	−19.9	48
10	$CDCl_3$		+8.5	63	−19.9	37
25	$CDCl_3$		+9.5	73	−19.9	27
40	$CDCl_3$		+10.3	81	−19.9	19
25	$CDCl_3$ (LiCl)		+9.5	38	−20.3	62
25	$CDCl_3$–*t*-BuOH (20:1)		+9.1		−20.3	
25	$CDCl_3$–*t*-BuOH (10:1)		+8.9	48	−20.3	52
25	$CDCl_3$–*t*-BuOH (5:1)		+8.9	41	−20.3	59
25	$CDCl_3$–*t*-BuOH (2.5:1)		+8.2	20	−20.3	80
25	$CDCl_3$–*t*-BuOH (1:1)		+7.9	13	−20.3	87
25	$CDCl_3$–MeOH (4:1)				−20.3	100
−30	MeOH				−20.4	100

[a] Protons noise decoupled. Shifts are relative to external 85% H_3PO_4 and are ±0.2 ppm. Positive shifts are upfield from the reference. [b] Time-averaged shift. [c] Percentages are *ca.* ±5% absolute.

Both ^{31}P and ^1H nmr spectra show that the amount of **3c** in $CDCl_3$ increases either with lowered temperature, addition of lithium chloride, or addition of alcohols. High concentrations of alcohol or pure methanol give **3c** as the predominant, if not sole, isomer of ylide **3**. Percentage values for isomer compositions derived from the ^1H nmr data (Table II) are more accurate than those derived from ^{31}P data (Table I); in the latter case, much higher noise levels and possible differential NOE effects[26] contribute to less accurate integrations. The ^{31}P shift data also show that alcohols tend to increase slightly the amount of **3b** relative to **3a**.

Since chloroform-*d* is more polar than carbon tetrachloride, benzene, and toluene, it is not surprising that ionic forms **3b** and **3c** exist in addition to **3a** in $CDCl_3$. However, the increase in the amounts of **3b** and **3c** relative to **3a** as the temperature is lowered seems strange at first, because **3a** is the major species (*ca.* 51–54%) at 25° and one would expect to get more of the major isomer by lowering the temperature. An explanation of our results based on self-aggregation effects[21] of ylide molecules seems implausible since the ratio of **3c** to **3a** plus **3b** in $CDCl_3$ was found by ^1H nmr studies to be invariant over a ylide concentration range of 0.055–0.8 *M* and since aggregation effects, which should be greater in nonpolar than polar solvents, were not

Table II
Temperature and Solvent Effects on Isomer Composition[a] as Determined by ^{1}H Nmr Studies

Temp, °C	Solvent	3a, %	3a ⇌ 3b, %	3c, %
25	CCl_4	100		
25	C_6D_6	100		
−60	$CDCl_3$		45	55
−52	$CDCl_3$		45	55
−41	$CDCl_3$		47	53
−32	$CDCl_3$		47	53
−23	$CDCl_3$		49	51
−13	$CDCl_3$		53	47
25	$CDCl_3$		75	25
28	$CDCl_3$		75	25
39	$CDCl_3$		78	22
35	$CDCl_3$ (LiCl)		33	67
25	$CDCl_3$–*t*-BuOH (11:1)		50	50
25	$CDCl_3$–*t*-BuOH (5.5:1)		38	62
25	$CDCl_3$–*t*-BuOH (2.75:1)		12	88
25	$CDCl_3$–*t*-BuOH (1.4:1)		2–5	95–98
25	$CDCl_3$–MeOH (12:1)		2–5	95–98

[a] Determined by integration of the PCH_a signals.

observed with toluene solvent. Snyder[9] has reported previously the importance of hydrogen bonding with chloroform-*d* and other solvents in discussion of factors that determine cis–trans ratios of ylide **6**. Chloroform-*d* stabilizes trans-**6** relative to *cis*-**6** due to preferential chlorocarbon association with the negative oxygen of *trans*-**6** by a hydrogen-bonding interaction; solvent association about the negative oxygen in *cis*-**6** is sterically hindered.[9] More effective hydrogen bonding and more polar solvents such as alcohols favor *trans*-6 over *cis*-6 to an even greater extent.[9] Hydrogen-bonding effects in addition to polar effects appear to explain several reports[9,11,13,14,21] of solvent effects on ylide structure.

The dependence of ylide **3** structure on solvent is explicable on the basis of solvent polarity and hydrogen-bonding effects. In nonpolar, non-hydrogen-bonding solvents, the nonpolar cyclic form **3a** is predominant. In polar solvents, ionization of the P–O bond occurs and polar forms **3b** and **3c** form. Hydrogen-bonding effects stabilize the polar forms **3b** and **3c** relative to **3a** through hydrogen-bonding interactions with the negative oxygen of the polar forms. As the temperature is lowered, hydrogen bonding becomes more important and forms **3b** and **3c** increase relative to **3a** in $CDCl_3$. Conversely, an increase in the temperature decreases the effectiveness of hydrogen bonding and increases the amount of **3a** in $CDCl_3$ (*cf.* results at 40 and 39°, Tables I and II). Because the negative oxygen of **3b** is sterically hindered and because there possibly may be some electrostatic interaction between positive phosphorus and negative oxygen in **3b**, hydrogen bonding of solvent with **3b** is considerably less effective than with the sterically unencumbered negative oxygen of **3c**. As the temperature is lowered in $CDCl_3$, the amounts of **3b** and **3c** both increase, but the latter increases to a greater extent. Addition of alcohols to **3** in $CDCl_3$ increases the polarity and hydrogen-bonding capabilities of the medium and increases the amounts of **3b** and **3c**, with **3c** favored more than **3b**. Lithium chloride forms an association complex (probably *via* lithium–oxygen interaction) with **3c** but not with **3b**, based on the data of Tables I and II and the observed 0.37-ppm downfield shift of H_a of **3c** and 0-ppm shift for the time-averaged H_a signal for **3a** plus **3b** in the ^{1}H nmr spectra. As expected, the differential steric requirements for association of lithium chloride with the polar forms **3b** and **3c** are greater than for hydrogen-bonding interactions with **3b** and **3c**. In a very polar, strongly hydrogen-bonding medium such as methanol, ylide **3** exists predominantly as **3c**.

The rapid equilibrium between **3a** and **3b** is similar to that observed[20,21] for certain cyclic 2,2-dihydro-1,3,2-dioxaphospholenes and their open chain forms and, in that it involves a reversible ionization, is similar to an equilibrium of covalent substrates with intimate ion pairs. The slow equilibration of **3b** with **3c** is analogous to slow (nmr time scale) equilibrium of a variety of cis–trans pairs of carbonyl-stabilized ylides.[2–14]

Experimental Section[27]

α-(*p*-Nitrostyryl)-*N*-phenylnitrone (2a). A solution of 9.52 g (0.02 mol) of [2-(*N*-hydroxyanilino)vinyl]triphenylphosphonium bromide,[16] 3.02 g (0.02 mol) of *p*-nitrobenzaldehyde, and 0.02 mol of sodium methoxide in 80 ml of methanol was stirred under N_2. After 24 hr, 4.7 g (88% yield) of light-sensitive yellow solid, mp 208° dec (lit.[18] mp 200–205°), was collected; ir (mineral oil mull) 9.35 (s, N→O), 10.2 μ (m, trans CH=CH).

Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.51. Found: C, 67.37; H, 4.53.

α-(*p*-Chlorostyryl)-*N*-phenylnitrone (2b). A solution of 4.76 g (0.010 mol) of [2-(*N*-hydroxyanilino)vinyl]triphenylphosphonium bromide, 1.40 g (0.010 mol) of *p*-chlorobenzaldehyde, and 0.010 mol of sodium methoxide in 40 ml of methanol was stirred under N_2 for 4 days. The resultant solid, 1.65 g, mp 186.5–188°, was pure product: ir ($CHCl_3$) 9.50 (s, N→O), 10.36 μ (s, trans CH=CH). Another 0.19 g of product, mp 185–186°, was recovered from the filtrate (total yield was 71%).

Anal. Calcd for $C_{15}H_{12}ClNO$: C, 69.91; H, 4.69. Found: C, 69.97; H, 4.78.

α-(2,4-Dichlorostyryl)-*N*-phenylnitrone (2c). By a procedure similar to that employed above, **2c** was obtained in 56% yield as a yellow solid: mp 127–128°; ir (mineral oil mull) 9.41 (s), 9.55 (m), 10.23 μ (s, trans CH=CH).

Anal. Calcd for $C_{15}H_{11}Cl_2NO$: C, 61.66; H, 3.80. Found: C, 61.45; H, 3.78.

α-(3,4-Methylenedioxystyryl)-*N*-phenylnitrone (2d). Compound **2d** was obtained in 39% yield as a yellow solid: mp 194–194.5° (lit.[19] mp 193°); ir (mineral oil mull) 9.55 (s), 9.64 (s), 10.16 (m), 10.24 μ (m).

5,5-Dihydro-2,5,5,5-tetraphenyl-Δ^3-1,2,5-oxazaphospholine (3). A solution of 9.52 g (0.020 mol) of [2-(*N*-hydroxyanilino)vinyl]triphenylphosphonium bromide in 80 ml of chloroform was extracted at 0° with 40 ml of ice water containing 0.80 g (0.020 mol) of sodium hydroxide and then with 20 ml of ice water containing 0.40 g (0.010 mol) of sodium hydroxide. The yellow-orange $CHCl_3$ layer was filtered through chloroform-wetted filter paper onto calcium sulfate in a flask at 0°. The dried $CHCl_3$ solution was filtered and concentrated under vacuum at ≤35°. The residual oil was dissolved in dry ethyl acetate; scratching resulted in rapid crystallization of 7.2 g of yellow solid, mp 181–183° dec. The solid was recrystallized from hot, dry ethyl acetate (minimum heating time possible) to give 3.9 g (49.4%) of yellow solid: mp 194–195° dec; ir ($CHCl_3$) 6.42 μ (vs).

Anal. Calcd $C_{26}H_{22}NOP$: C, 78.97; H, 5.61. Found: C, 78.71; H, 5.68.

Registry No.—**1**, 52810-32-9; **2a**, 52826-23-0; **2b**, 52826-24-1; **2c**, 52873-49-1; **2d**, 52826-25-2; **3a**, 52826-26-3; **3b**, 52826-27-4; **3c**, 52855-92-2; *p*-nitrobenzaldehyde, 555-16-8; *p*-chlorobenzaldehyde, 104-88-1; 2,4-dichlorobenzaldehyde, 874-42-0; 3,4-methylenedioxybenzaldehyde, 120-57-0.

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(24) The possibility cannot be excluded that a minute amount of **3b** is in rapid (on the nmr time scale) equilibrium with **3a** in toluene, and this equilibrium produces slightly larger (but still quite small) amounts of **3b** at higher temperatures. Since **3b** should have a negative ^{31}P shift, slightly larger amounts of **3b** would produce a lower time-averaged ^{31}P shift for **3a** plus **3b**.
(25) Equilibration between certain cyclic 2,2-dihydro-1,3,2-dioxaphospholenes and their open chain forms is rapid relative to the nmr scale; the observed ^{31}P shift is a time average of the positive shift for the cyclic form and the negative shift for the open chain form.[20,21] The value of the time-averaged ^{31}P shift is solvent dependent as a result of specific solvent effects on the position of the equilibrium.[20,21]
(26) Noise levels were too high to allow integrations without proton decoupling.
(27) Melting points were taken in open capillaries with a Mel-Temp apparatus and are corrected. Ir spectra were determined with Perkin-Elmer Model 137 and Beckman IR-10 spectrometers. Nmr spectral data reported in the text were determined with a JEOL JNM-C-60HL spectrometer and with Varian T-60 and HA-100 spectrometers. Temperatures for the variable temperature ^1H nmr spectra were calibrated by comparison of measured shifts between the OH and CH_3 protons of a methanol sample with a calibrated chart supplied by JEOL Co.; indicated temperatures are probably ±2. Temperatures for the variable temperature ^{31}P nmr spectra were calibrated by means of a thermocouple inserted into a methanol sample in the ^{31}P probe; indicated temperatures are probably ±2°. A variable temperature study of the 85% H_3PO_4 standard indicated that the shift was negligible (*ca.* 0.1 ppm downfield or upfield) as the temperature was varied from −60 to +90°. Positive ^{31}P shifts are upfield from 85% H_3PO_4.

Reaction of *p*-Toluenesulfonylhydrazones with *N*-Bromosuccinimmide in Methanol. Regeneration of Carbonyl Compounds[1]

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A number of aldehydes and ketones have been regenerated in high yields from the corresponding *p*-toluenesulfonylhydrazones by reaction with *N*-bromosuccinimmide in methanol. A mechanistic pathway of the reaction is proposed.

There has been considerable interest in the development of mild techniques for the conversion of oximes,[2,3] 2,4-dinitrophenylhydrazones,[4] and semicarbazones into aldehydes and ketones. A variety of procedures have been described but only one is concerned with the conversion of *p*-toluenesulfonylhydrazones into parent carbonyl compounds.[5]

Here we wish to describe a new method for the regeneration of aldehydes and ketones from their *p*-toluenesulfonylhydrazones by treatment with *N*-bromosuccinimmide (NBS).

The method involves additions of NBS (4 mol) to a methanolic acetone solution of *p*-toluenesulfonylhydrazone (1 mol). The reaction was rapid, evolution of nitrogen was observed, and the solution quickly turned red. Then sodium hydrogen sulfite was added and the mixture refluxed for 10 min, cooled, and worked up. Some representative conversions are summarized in Table I.

From an examination of the reactions of several *p*-toluenesulfonylhydrazones with NBS under a variety of conditions, the advantages and limitations of the present method can be summarized as follows. (1) Reaction proceeds virtually instantaneously at room temperature, and yields of pure products are uniformly high. (2) The addition of sodium hydrogen sulfite when nitrogen was evolved and the presence of acetone as a solvent are sufficient to almost completely suppress reactions of molecular bromine on the substrate such as α-bromination and oxidation of secondary alcohols to ketones. (3) Treatment of *p*-toluenesulfonylhydrazone derivatives of α,β-unsaturated ketones and aldehydes does not result in a consistent regeneration of the parent carbonyl compound but leads to mixtures of products.

Table I
Conversion of *p*-Toluenesulfonylhydrazones into Aldehydes and Ketones with NBS[a] in Methanol

Ketone or aldehyde	Registry no.	Yield, %[b]
Cyclohexanone	108-94-1	81.3
3,3,5,5-Tetramethylcyclohexanone	14376-79-5	85.2
Acetophenone	98-86-2	74.3
Deoxybenzoin	451-40-1	88.7
Benzoin	119-53-9	86.8
Cholestan-3-one	15600-08-5	89.0
Androstanolone	521-18-6	78.2
Cyclohexylphenyl ketone	712-50-5	84.5
Benzophenone	119-61-9	91.0
Fluoren-9-one	486-25-9	89.4
n-Heptaldehyde	111-71-7	75.3
Benzaldehyde	100-52-7	82.0
Anisaldehyde	123-11-5	84.2
p-Chlorobenzaldehyde	104-88-1	85.3

[a] Registry no. 128-08-5. [b] Calculated on pure chromatographed material.

Two moles of NBS are sufficient to regenerate aromatic ketones from the corresponding *p*-toluenesulfonylhydrazones. A nearly quantitative amount of nitrogen was evolved during such a reaction in methanol at room temperature; the solution turned red but slowly faded to yel-