above for the ketone **8**. The ketone was obtained in 34% yield as a colorless oil: b.p. 70–74° (0.49 mm.); $n^{25.5}$D 1.4882; ν_{max}^{neat} 2920, 1693 and 1462 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{17}ClO$: C, 63.65; H, 9.08. Found: C, 63.60; H, 9.06.

10-Chloromethyl-10-methyl-9(10H)-phenanthrone (13).—To a stirred solution of 222 mg. (1 mmole) of the alcohol **12** in 4 ml. of alcohol-free chloroform, was added 0.16 ml. (1.3 mmoles) of freshly distilled *t*-butyl hypochlorite, and the solution was allowed to stir in the dark at 55° for 15 hr. Concentration of the solution afforded 275 mg. of an orange oil that solidified on standing. The material was recrystallized once from hexane (Norit) and then six times from aqueous ethanol. The ketone **13** was obtained as colorless crystals: m.p. 118–119°; $\nu_{max}^{CHCl_3}$ 2990, 1660, 1603, 1480, 1443, 1290, 1265, and 980 cm.$^{-1}$; n.m.r. singlet at δ 1.76 (3H), pair of doublets centered at 4.58 (2H), and complex aromatic pattern centered at 8.80 (8H).

Anal. Calcd. for $C_{16}H_{13}ClO$: C, 74.85; H, 5.10; Cl, 13.82. Found: C, 72.83 and 72.84; H, 4.83 and 5.02; Cl, 15.87.

2-Methylcyclohexanone Semicarbazone.—To a solution of 2.24 g. (20 mmoles) of the alcohol **14** in 7 ml. of alcohol-free chloroform, was added 2.8 ml. (23 mmoles) of *t*-butyl hypochlorite and the solution was allowed to stir in the dark at 58–60° for 4 hr. Concentration of the mixture afforded 3.92 g. of a colorless oil whose infrared spectrum (neat) exhibited a strong carbonyl peak at 1713 cm.$^{-1}$. The vapor phase chromatogram of the crude material on Carbowax was found to vary with the sample size. Injection of a small amount (2 μl.) showed the mixture to contain only one major component. Injection of amounts exceeding 25 μl. caused the appearance of a new compound, which eluted before the major peak. A portion of the new substance was collected and examination of its infrared spectrum revealed the presence of a new carbonyl peak at 1670 cm.$^{-1}$. The new material was presumed to be 2-methylenecyclohexanone. The crude oil from the ring expansion was dissolved in a mixture of 15 ml. of absolute ethanol, 3 g. of sodium acetate, and 600 mg. of 10% palladium on carbon. The resulting mixture was hydrogenated at 55 p.s.i.g. for *ca.* 24 hr. at room temperature. The mixture was filtered through Celite and concentrated *in vacuo* to *ca.* 10 ml. To a small portion, water was added and the mixture was extracted with ether. The ether extracts were combined, washed with water, dried, and concentrated to leave a small amount of a colorless oil. Vapor phase chromatographic analysis of the oil indicated the presence of three new compounds in addition to the starting ketone **15**. The major compound eluted first, and was not separated from authentic 2-methylcyclohexanone on analysis of a synthetic mixture. Water was added to the remainder of the crude hydrogenation mixture until a faint cloudiness persisted and 6 g. each of semicarbazide hydrochloride and sodium acetate were added. The mixture was refluxed on a steam bath for 15 min. and cooled in ice; the precipitated semicarbazone was filtered. One crystallization from aqueous methanol afforded 1.46 g. of colorless crystals, m.p. 190–195°. The melting point was not depressed on admixture with an authentic sample.

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Synthesis of Oximes[1]

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Alkyl-substituted heteroaromatic compounds and allyl-substituted benzenes were oximinated in liquid ammonia at −33° with sodamide and an alkyl nitrite. Oximes were obtained from 2-, 3-, and 4-picoline, 2,4- and 2,6-lutidine (monooximes), 4-ethylpyridine (ketoxime), 2-methylquinoline, 2-methylpyrazine, 2-methylbenzoxazole, 2-methylbenzothiazole, allylbenzene, and indene. The effects of other metalation agents and other solvents were determined. The oximes were assigned configurations on the basis of n.m.r. evidence.

Pyridinecarboxaldehyde oximes can be quaternized with alkyl halides to form compounds which are known to be antidotes for "nerve gas" poisons[2] and it was therefore of interest to develop a direct route to these intermediates. One such synthesis would result from the oximination of picoline, but numerous attempts in

TABLE I

PREPARATION OF 2-PYRIDINECARBOXALDEHYDE OXIME[a]

Expt.	NH_3, ml.	2-picoline, moles	Bu ONO, moles[b]	Yield, %[c]
1	1500	2.0	1.0	56
2	1000	2.0	1.0	61
3	1000	2.0	1.2	53
4	1000	3.0	1.0	68[d]
5	670	2.0	1.0	66
6	535	2.0	1.0	64
7	535	3.0	1.0	74
8	470	3.0	1.0[e]	71
9[f]	400	3.0	1.0	75
10	400	4.0	1.0	74
11	270	3.0	1.0	47

[a] Effect of variations in the proportions of reagents with 2.0 g.-atoms of sodium in liquid anhydrous ammonia. [b] Diluted with an equal volume of ethyl ether. [c] Two g.-atoms of sodium required theoretically to produce 1 mole of oxime. [d] Yield of 73.5% based on 2-picoline consumed. [e] Diluted with 500 ml. of ethyl ether. [f] Preferred conditions. See Experimental.

TABLE II

PREPARATION OF 2-PYRIDINECARBOXALDEHYDE OXIME[a]

Expt.	Solvent	Metalation agent	Nitrite[b]	Yield, %[c]
1	NH_3[d]	$NaNH_2$[d]	n-C_4H_9ONO[d]	75
2	NH_3	$NaNH_2$	N_2O_3	0
3	NH_3	$NaNH_2$	CH_3ONO	34
4	NH_3	$NaNH_2$	$C_8H_{17}ONO$[e]	49
5	NH_3[f]	KNH_2[f]	n-C_4H_9ONO[f]	70
6	T.H.F.[g]	KNH_2	n-C_4H_9ONO	7
7	NH_3	$LiNH_2$	n-C_4H_9ONO	0
8	T.H.F.[g]	$LiNH_2$	n-C_4H_9ONO	0
9	Et_2O[h]	C_6H_5Li	n-C_4H_9ONO	0
10	Et_2O[i] + NH_3[i]	C_6H_5Li	n-C_4H_9ONO	1
11	T.H.F.[g]	C_2H_5MgBr	n-C_4H_9ONO	0

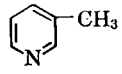
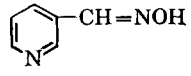
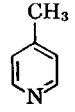
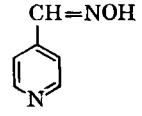
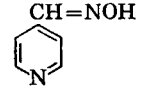
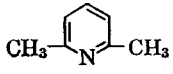
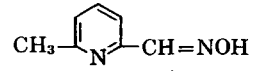
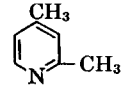
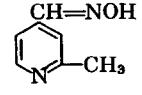
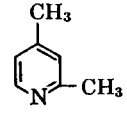
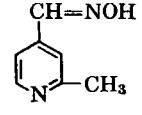
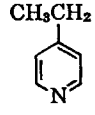
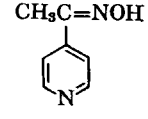
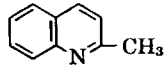
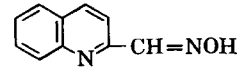
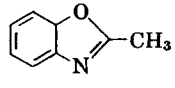
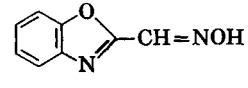
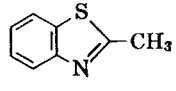
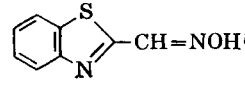
[a] Variations of the types of metalation agents and nitrite in runs of 0.1-mole quantities of each reactant with 50 ml. of solvent, except where noted. [b] Dissolved in 10 ml. of ethyl ether and added 1 hr. after addition of 2-picoline. [c] Two moles of metalation reagent required theoretically to produce 1 mole of oxime. [d] Method, quantities, and proportions for this run are the preferred conditions described in Experimental section. [e] 2-Ethylhexyl nitrite. [f] 500 ml. of NH_3, 1.0 mole of KNH_2, 0.6 mole of BuONO in 60 ml. of Et_2O, 1.0 mole of 2-picoline. [g] Tetrahydrofuran. Same solvent (10 ml.) used for the nitrite. [h] 100 ml. [i] 110 ml. of Et_2O; 150 ml. of liquid NH_3 added 1 hr. after addition of 2-picoline; butyl nitrite added 1 hr. after NH_3.

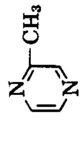
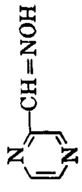
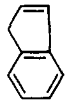
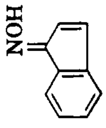
(1) Presented at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964.

(2) S. Ginsburg and I. B. Wilson, *J. Am. Chem. Soc.*, **79**, 481 (1957).

TABLE III

OXIMES PREPARED BY SCREENING PROCEDURE[a]

Expt.	Reactant[b]	Product	Yield, %[c]	M.p., °C. Crude	M.p., °C. Recryst.	M.p., °C. Lit.	Formula	Found, % C	Found, % H	Found, % N	Calcd., % C	Calcd., % N	Calcd., % N
1			1.5	80–145		150–151[d]		*e*	*e*	*e*			
2			29	118–132	132–133.5	132[d]	$C_6H_6N_2O$	58.8	5.0	22.6	59.0	5.0	22.9
3			30	115–134	130–133	132[d]							
4			50		165–168	170–171[d]	$C_7H_8N_2O$	61.7	6.2	20.5	61.7	5.9	20.6
5			41	105–155	157–159.5		$C_7H_8N_2O$	62.0	6.0	20.5	61.7	5.9	20.6
6			83.5		158.5–160								
7			44	110–155	147–161	142[i] 121–123[j] 157–159[j]	$C_7H_8N_2O$	62.0	6.0	20.8	61.7	5.9	20.6
8			28	180–185	187–190	189[k]	$C_{10}H_8N_2O$	69.7	4.5	16.2	69.7	4.7	16.3
9			55	100–150	168–170		$C_8H_6N_2O_2$	59.1	3.7	17.5	59.3	3.7	17.3
10			39	120–178	192–196[m] 167–173[o]	186–187[n]	$C_8H_6N_2OS$ $C_8H_6N_2OS$	54.0 54.0	3.7 3.1	15.4 15.7	53.9 53.9	3.4 3.4	15.7 15.7

11			39	88–96	90–97		$C_5H_5N_3O$	48.9	4.3	34.1	48.8	4.1	34.1
12			76[p]	74–100	109–112	Impure oil[q]	C_9H_7NO	74.6	4.9	9.7	74.5	4.9	9.7
13	$C_6H_5CH_2CH{=}CH_2$	$C_6H_5C({=}NOH){-}CH{=}CH_2$	19	sirup and crystals[r]		109–110[s]							

[a] From 0.10-mole quantities of sodium, reactant, and butyl nitrite in 10 ml. of ethyl ether, reacted in 50 ml. of anhydrous liquid ammonia. [b] Oximes were not obtained from 6-methylquinoline, 3-methylisoquinoline, 2-methylindole, 2-methylbenzimidazole, 2-methylfuran, toluene, 2-methylnaphthalene, tetrahydronaphthalene, bicyclo[2,2,1]hepta-2,5-diene, cyclohexene, 1-octene, or isoprene. [c] Two g.-atoms of Na required theoretically to produce 1 mole of oxime except in expt. 12. [d] See ref. 2. [e] Identified by infrared spectrum. Elemental analyses were not run. Not recrystallized because of small quantity. [f] Product from 1000 ml. of NH_3, 2.0 g.-atoms of Na, 2.0 moles of 4-picoline, and 1.0 mmole of BuONO in 110 ml. of Et_2O. [g] Position of oxime group based on n.m.r. data. [h] Product from 1000 ml. of NH_3, 2.0 g.-atoms of Na, 2.0 moles of 2,4-lutidine, and 1.0 mole of BuONO in 110 ml. of Et_2O. [i] F. K. Beilstein, "Handbuch der organischen Chemie," Vol. XXI, 4th Ed., 1919, p. 279. [j] Two isomers reported. See M. V. Rubtsov, E. S. Nikitakaya, and V. S. Usavskaya, *Zh. Obshch. Khim.*, **25**, 2453 (1955). [k] S. F. Mason, *J. Chem. Soc.*, 22 (1960). [l] Obtained in two forms, approximately in equal amounts. [m] S: calcd., 18.0; found, 19.2. [n] N. Borsche and W. Doeller, *Ann.*, **537**, 53 (1939). [o] S: calcd., 18.0; found, 19.2. [p] Yield calculated on basis of 1 mole of sodamide required for 1 mole of oxime. [q] See ref. 5. [r] Could not be purified by crystallization. Identified by infrared spectrum. See H. Levy and A. C. Cope [*J. Am. Chem. Soc.*, **66**, 1684 (1944)] for evidence of metalation of alkylbenzene on the allylic position. [s] Z.-Y. Kyi and W. Wilson, *J. Chem. Soc.*, 790 (1953).

this laboratory to treat 2-picoline with butyl nitrite and sodium butoxide, or with a nitrite and an acid catalyst did not succeed under conditions which have worked with many other compounds.[3] Although the oximination of ketones with alkyl nitrites and sodium or potassium amide has been reported,[3] previous work with these metal amides has been limited until recently to the reaction of 6-phenylcamphor or epicamphor in ethyl ether solution.

The author has found that sodio derivatives of many alkyl-substituted heteroaromatic compounds or of allyl-substituted benzenes can be oximinated with alkyl nitrites in refluxing anhydrous liquid ammonia at atmospheric pressure according to the following scheme.

$$RCH_2R' + NaNH_2 \xrightarrow{\text{liq. } NH_3} R\bar{C}H(\overset{+}{N}a)R' + NH_3$$

$$2R\bar{C}H(\overset{+}{N}a)R' + R''ONO \longrightarrow RC({=}NO^-\overset{+}{N}a)R' + RCH_2R' + R''\bar{O}\overset{+}{N}a$$

a, R = heteroaromatic
R′ = –H or $-CH_3$
R″ = lower alkyl
b, R = phenyl or benzo
$-CH_2R'$ = allyl or cyclopenteno
R″ = lower alkyl

After this work was complete, Kato and Goto[4] reported the synthesis of 2- and 4-pyridinecarboxaldehyde oxime from 2- and 4-picoline with potassium amide and amyl nitrite in liquid ammonia at −33°, although they failed to obtain either of these oximes when the reaction was carried out with sodamide in liquid ammonia at room temperature in a sealed tube.

Most of the present work concentrated on the conversion of 2-picoline with sodamide to 2-picolylsodium and the subsequent oximination with butyl nitrite to the sodium salt of 2-pyridinecarboxaldehyde oxime. The free oxime can be isolated in yields as high as 75%. Variations in experimental conditions (Table I) indicated that a concentrated solution, an excess of 2-picoline, and a stoichiometric amount of butyl nitrite, corresponding to 1 mole of nitrite per 2 moles of amide, were conducive to high yields. The excess picoline was recovered.

The effects of varying the types of reagents and solvent used in the oximation of 2-picoline are shown in Table II. Other alkyl nitrites can be used successfully in place of butyl nitrite; however, nitrogen trioxide gave none of the desired product. Potassium amide gave a good yield, but solvents other than liquid ammonia gave poor results. Only a trace of product was obtained in experiments involving lithium compounds. In the experiments tabulated here, attempts were not made to obtain optimum conditions.

The scope of this reaction was explored with a variety of related compounds following a procedure similar to one used with 2-pyridinecarboxaldehyde oxime (Table III). In only two cases (expt. 3 and 6) was any attempt made to improve conditions. In most cases equimolar amounts of alkyl nitrite and sodio compound were used in the hope that a mole-for-mole reaction might take place. However, since the sodium alkoxide produced is generally a weaker base than the sodioalkyl aromatic, the stoichiometry of one alkyl nitrite to two sodioalkyl aromatics (sodamide) was generally required. Indene

(3) O. Touster, *Org. Reactions*, **7**, 327 (1953).
(4) T. Kato and Y. Goto, *Chem. Pharm. Bull.* (Tokyo), **11**, 461 (1963).

TABLE IV

CONFIGURATION ASSIGNMENTS FROM N.M.R. SPECTRA

No.	Compd.	=N—O—H,[a] p.p.m.	—CH=N—O—, p.p.m.	Δ p.p.m.[b]	Configuration
1	2-Pyridinecarboxaldehyde oxime	11.23	8.38	2.85	*syn*
2	4-Pyridinecarboxaldehyde oxime	11.79	8.18	3.61	*anti*
3	6-Methyl-2-pyridinecarboxaldehyde oxime		8.15		*anti*
4	2-Methyl-4-pyridinecarboxaldehyde oxime		8.13		*anti*
5	2-Pyrazinecarboxaldehyde oxime, m.p. 90–97°	12.40	7.78	4.62	*anti*
6	2-Pyrazinecarboxaldehyde oxime[c]	11.30	8.33	2.97	*syn*
7	2-Benzothiazolecarboxaldehyde oxime, m.p. 192–196°	11.49	8.10	3.39	*anti*
8	2-Benzothiazolecarboxaldehyde oxime, m.p. 167–173°	10.89	8.50	2.39	*syn*
9	2-Benzoxazolecarboxaldehyde oxime	11.07	8.27	2.80	*syn*

[a] The positions of these peaks can be shifted by dilution until a constant value is obtained at high dilution. See ref. 6. [b] Δ p.p.m. equals the —CH=NO— value in p.p.m. subtracted from the =N—O—H value. [c] Present as a minor amount in **5**, evidenced by small peaks at positions noted in this table.

proved to be an exception, and the stoichiometry in this case is 1 mole of sodamide for 1 mole of oxime. However, sodium ethylate has been reported to be a sufficiently strong base to permit oximination of indene in alcoholic medium, although the previous worker could not obtain the resulting product in a pure state.[5]

Only one of the methyl groups in either 2,4- or 2,6-lutidine participated in the oximination reaction and an attempt to prepare a dioxime from the monooxime of 2,4-lutidine did not succeed. That the 4-methyl group of 2,4-lutidine reacted exclusively is indicated by the nuclear magnetic resonance spectrum of the product. The methyl peak in the spectrum of the oxime from 2,4-lutidine occurs at 2.55 p.p.m. similar to the methyl peak of 2-picoline which occurs at 2.53 p.p.m. and the methyl peak of 6-methyl-2-pyridinecarboxaldehyde oxime which occurs at 2.53 p.p.m. and differing from the methyl peak of 4-picoline which occurs at 2.40 p.p.m.

The configurations of the aldoximes were assigned on the basis of n.m.r. evidence[6] (Table IV). The peaks —CH=N—O— and =N—O—H of a *syn*-aldoxime are closer together than the corresponding peaks obtained with the *anti* configuration. Comparison of the n.m.r. spectra of similar compounds were made when pairs of isomers were not available. When it was necessary to use a solvent which did not allow the position of the =N—O—H peak to be determined, assignment was made on the basis of the position of the CH=N—O— peak alone by comparison with the position of this peak in the spectrum of an aldoxime compound of similar structure.

The first two compounds in Table IV are sufficiently similar in structure to expect both *syn* and *anti* forms to have nearly the same spread between the peaks of interest. Since the two samples which were available had different Δ p.p.m., the one with the smaller Δ p.p.m. value was assigned the *syn* configuration while the other was evidently the *anti* form. With compounds **3** and **4**, the =N—O—H peak was obscured, and both were assigned the *anti* configuration because the peak CH=N—O— was in nearly the same position as the similarly constituted *anti* form of compound **2**. Although only one sample of 2-pyrazinealdoxime was available, and this specimen was largely one isomer, the presence of a small amount of the other isomer was evidenced by two unequal peaks for each of the two hydrogens of interest. The isomer present in major quantity was assigned the *anti* configuration. The two 2-benzothiazolealdoximes were isolated and assigned configurations on the basis of the spread between the two peaks. The position of and spread between the peaks in the spectrum of 2-benzoxazolealdoxime more nearly approximates the *syn* isomers of **8** or **1** in the table.

Ginsburg and Wilson[2] have assigned configurations to three of these oximes, basing their choice on chemical evidence obtained with one isomer of each oxime. The assignment of *syn*-2-pyridinecarboxaldehyde oxime agrees with theirs, but the assignments of *anti*-4-pyridinecarboxaldehyde oxime and *anti*-6-methyl-2-pyridinecarboxaldehyde oxime differ from their previous assignments. Physical properties which can be related to the structure of a compound are probably more reliable than chemical methods for the establishment of structure, but in cases where only one isomer is available, some doubt about any assignment will exist until the other isomer is made available for comparison of properties.

Experimental

2-Pyridinecarboxaldehyde Oxime. A. Preferred Method.—Sodium (46 g., 2.0 g.-atoms) was added in small pieces to 400 ml. of anhydrous liquid ammonia containing 0.5 g. of $Fe(NO_3)_3 \cdot 9H_2O$, in a flask equipped with a stirrer and Dry Ice cooled reflux condenser. After the metal had dissolved, the blue color had vanished (about 20 min.), and the mixture had assumed a gray color, 279 g. (3.0 moles) of 2-picoline was added during 30 min. One hour later, a solution of 103 g. (1.0 mole) of butyl nitrite in 110 ml. of ethyl ether was added during 45 min. to the intensely red-colored mixture. The instantaneous reaction was accompanied by an exotherm, and a thick slurry of solids formed. After 1 hr., a solution of 198 g. (1.5 moles) of ammonium sulfate in 300 ml. of water was added as rapidly as possible. The red color, which had persisted, quickly disappeared and a thick precipitate of sodium sulfate replaced the previous solids. The ammonia was allowed to evaporate while 500 ml. of ethyl ether was added, and, when the temperature had risen to about 25°, the liquids were decanted and filtered from the solids which were washed with ether. The ethereal phase was separated from the aqueous phase which was also extracted with ethyl ether. The combined ether layers were distilled, first at atmospheric and then under reduced pressure, to remove solvent and recover butanol and unreacted 2-picoline, up to a pot temperature of 80° at 2 mm. The pot temperature was then increased and the product was distilled at 110° at 0.9 mm. The 2-pyridinecarboxaldehyde oxime was collected as a solid in a wide-diameter tube (91.5 g., 75% yield) based on the requirement of 2 g.-atoms of sodium per mole of product, m.p. 105–111°; recrystallized once from benzene, m.p. 113–113.5° (lit.[2] m.p. 114°).

Anal. Calcd. for $C_6H_6N_2O$; C, 59.0; H, 5.0; N, 22.9. Found: C, 59.1; H, 5.0; N, 23.0.

(5) W. Marckwald, *Ber.*, **28**, 1504 (1895).

(6) A. J. Durbetaki and C. M. Miles, presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964.

B. Other Methods.—Similar runs were made where the proportions of reagents were varied (Table I) and where the solvent, metalation reagent, and alkyl nitrite were varied (Table II). The product was isolated as in the preferred procedure.

Other Preparations of Oximes.—The procedures employed were similar to the ones described above. The oximes listed in Table III were usually prepared in 50 ml. of anhydrous liquid ammonia from 0.1-mole quantities of sodium, reactant, and butyl nitrite in 10 ml. of ethyl ether. Some of the products were sublimed at 0.005 mm. Other exceptions are noted in the table.

N.m.r. Spectra.—The spectra were determined with a Varian Model A-60 apparatus using deuteriochloroform or deuteriomethanol as solvent for the compounds and tetramethylsilane as the internal standard.

Infrared Spectra.—The spectra were determined on each compound in a potassium bromide pellet with a Baird Model 4–55 apparatus.

The Chemistry of Carbanions. VI. Stereochemistry of the Wittig Reaction with Stabilized Ylids[1a]

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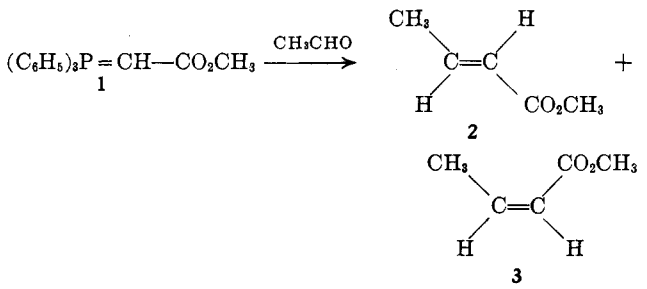
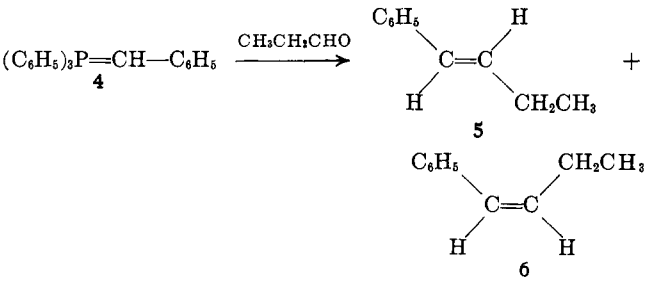
The effect of various reaction conditions on the proportions of *cis* and *trans* olefinic products obtained from the Wittig reaction of stabilized ylids **1** and **10** with acetaldehyde and chloroacetaldehyde has been studied. The highest proportion of *cis* isomer was obtained by the use of the protonic solvent, methanol. Solutions of lithium salts were less effective and suspensions of lithium salts were without effect in enhancing the proportion of *cis* olefin in these cases. Our study of the Wittig reaction of the benzylidene phosphorane **4** with propionaldehyde does not support the previous reports that the proportion of the *cis* isomer may be markedly enhanced by the presence of a suspension or a solution of lithium bromide or lithium iodide in the reaction mixture.

Earlier investigations[2] of the Wittig reactions of aldehydes with ylids stabilized by the presence of carbonyl substituents at the α-position (*e.g.*, **1**) have indicated that the predominant stereoisomer in the olefinic product is that isomer in which the carbonyl substituent is *trans* to the larger group at the β-carbon atom (*e.g.*, **2**).



Other studies of the stereochemistry of the Wittig reaction[3,4] have indicated that the degree of stereoselectivity observed is somewhat dependent on the substituents present and is markedly influenced by changes in the reaction medium. For example, the reaction of the benzylidene phosphorane **4** with propionaldehyde in benzene solution was found to yield a mixture of olefins **5** and **6** containing 26% of the *cis* isomer **6**. However, if the solution of the ylid **4** was treated successively with a *suspension* of lithium bromide or lithium iodide (obtained from *n*-butyllithium and hydrogen bromide or hydrogen iodide) and then with propionaldehyde, the proportion of the *cis* stereoisomer **6** in the product was reported to be increased to over 90%.[4]



These reports prompted us to explore the stereochemical changes which would result from changes in the medium employed for reactions of stabilized ylids with aldehydes since procedures allowing substantial change in the stereochemical composition of the product would have obvious synthetic utility. Also we hoped that working with stabilized ylids which could be isolated and purified prior to reaction might offer some advantage in studying the previously reported[4] medium effects. For this purpose we have studied the reaction of the ylid **1** with acetaldehyde and chloroacetaldehyde to form the esters **2**, **3**, **7**, and **8**. The stereochemical outcome in the presence of a small amount of benzoic acid, a reported catalyst for the Wittig reaction,[5] was also explored. The reaction of the phosphonate anion **10**[6] with acetaldehyde to form esters **2** and **3** was also examined as well as the reaction of the ylid **11** with chloroacetaldehyde to form the unsaturated ketone **12**. In the latter case, we were unsuccessful in efforts to determine the stereoselectivity of the reaction since only the *trans* isomer **12** was isolated. For all of the

(1) (a) This research has been supported by grants from the National Science Foundation (Grant No. G-25214) and the National Institutes of Health (Grant No. RG-8761); (b) National Institutes of Health Predoctoral Fellow, 1963–1964.

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