[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY]

The Acid-Catalyzed Reaction of Triarylmethyl Azides with Triphenylphosphine[1]

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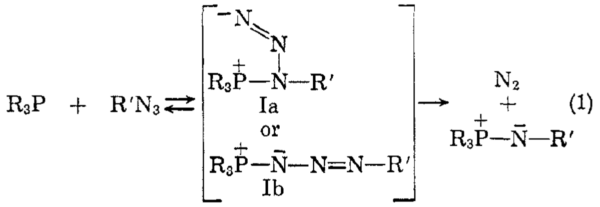
The complexes between triarylmethyl azides and triphenylphosphine are unusually stable as crystals or in neutral solvents, and do not give the radical decomposition typical of triarylmethyl azo compounds. In polar solvents there is an acid-catalyzed decomposition to nitrogen, carbonium ion, and triphenylphosphineimine. There is a rapid heterogeneous decomposition of the solid complexes in contact with organic solvents containing small amounts of acid or iodine. In acetic acid at 25° the reaction rate is given by the expression $k[(C_6H_5)_3P][(C_6H_5)_3CN_3] + k'[(C_6H_5)_3P][(C_6H_5)_3CN_3]^2$. There is a positive salt effect and catalysis by added hydrazoic acid.

Tertiary phosphines react with a wide variety of covalent azides to give nitrogen and phosphine imines. In a few instances the intermediate complexes have been isolated, but most such complexes decompose spontaneously to the phosphineimine at room temperature or below.[2,3]



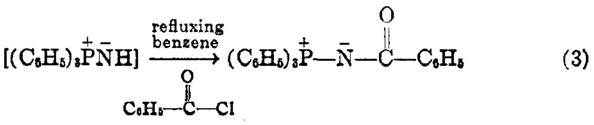
$$R_3P + R'N_3 \rightleftarrows \left[\begin{array}{c} \ulcorner\!-N{=}N \\ R_3\overset{+}{P}-\overset{|}{N}-R' \\ \text{Ia} \\ \text{or} \\ R_3\overset{+}{P}-\overset{-}{N}-N{=}N-R' \\ \text{Ib} \end{array}\right] \longrightarrow \begin{array}{c} N_2 \\ + \\ R_3\overset{+}{P}-\overset{-}{N}-R' \end{array} \quad (1)$$

The crystalline complexes formed from triphenylphosphine and triphenylmethyl azide[4] or 9-phenyl-9-fluorenyl azide (this paper), however, are remarkably stable. They melt at 104–105° and 73–74°, respectively, and appear to be dissociated in solution. We attribute the unusual stability of the triphenylphosphine–triarylmethyl azide system to steric hindrance to the formation of transition states resembling structure Ia. In conformity with a structure like Ib, the crystalline complexes contain neither covalent nor ionic azide groups as the azide band near 2100 cm.$^{-1}$, although strong in their solution spectra, is absent from the spectra of the solids. The decomposition of the triphenylmethyl azide in *neutral* solvents in the presence of triphenylphosphine, which begins only at elevated temperatures, appears to conform in rate and products (benzophenone anil) to the decomposition of triphenylmethyl azide in the absence of triphenylphosphine.[5,6]

The acid-catalyzed reaction. Although triarylmethyl azides are stable in the presence of triphenylphosphine in neutral solvents, the same system will evolve nitrogen at low temperatures in acidic media.

The products of the *acid-catalyzed* reaction are compounds derivable from Equation 2. *No* products corresponding to the usual decomposition and rearrangement of triarylmethyl azides are formed under these conditions.

$$(C_6H_5)_3P + Ar_3CN_3 \xrightarrow{H^+} \left[\begin{array}{l}\text{conjugate acid of the} \\ \text{complex}\end{array}\right] \longrightarrow [(C_6H_5)_3\overset{+}{P}-\overset{-}{N}-H + Ar_3C^+] + N_2 \quad (2)$$



$$[(C_6H_5)_3\overset{+}{P}\overset{-}{N}H] \xrightarrow[C_6H_5-\overset{O}{\overset{\|}{C}}-Cl]{\text{refluxing benzene}} (C_6H_5)_3\overset{+}{P}-\overset{-}{N}-\overset{O}{\overset{\|}{C}}-C_6H_5 \quad (3)$$

$$[Ar_3C^+] \xrightarrow{\text{acetic acid}} Ar_3COAc \quad (4)$$

$$[Ar_3C^+] + [(C_6H_5)_3\overset{+}{P}\overset{-}{N}H] \longrightarrow (C_6H_5)_3\overset{+}{P}-\overset{-}{N}-CAr_3 + H^+ \quad (5)$$

$$[Ar_3C^+] \xrightarrow[HOAc]{NaN_3} Ar_3CN_3 \quad (6)$$

The acid-catalyzed reaction consumes azide and phosphine in 1:1 mole ratio; if the azide is present in excess, the evolved nitrogen is equivalent or slightly less than equivalent to the triphenylphosphine (Table I).

Kinetics. When the solid complex is dropped into an organic solvent containing a low concentration of an acid (or even iodine) at room temperature, there is a rapid evolution of nitrogen. A similar experiment in which the complex is first dissolved in chloroform and then added to the solution gives no nitrogen evolution at room temperature.

To obtain a decomposition rate conveniently measurable by nitrogen evolution or by the azide band at 2100 cm.$^{-1}$ when the system is homogene-

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[1] This investigation was supported by the Office of Naval Research.

[2] (a) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, 4, 861 (1921). (b) H. Staudinger and I. Meyer, *Helv. Chim. Acta*, 2, 635 (1919).

[3] L. Horner and A. Gross, *Ann.*, 591, 117 (1955).

[4] E. Bergmann and H. A. Wolff, *Ber.*, 63B, 1176 (1930).

[5] W. H. Saunders, Jr., and J. C. Ware, *J. Am. Chem. Soc.*, 80, 3328 (1958).

[6] The lack of any major reaction corresponding to $(C_6H_5)_3P + (C_6H_5)_3CN_3 \rightleftarrows (C_6H_5)_3\overset{+}{P}-\overset{-}{N}-N{=}N-C(C_6H_5)_3 \rightarrow (C_6H_5)_3\overset{+}{P}\overset{-}{N}\cdot + (C_6H_5)_3C\cdot + N_2$ is surprising in view of the facile decomposition of trityl azo compounds in general. Interest in the radical $(C_6H_5)_3\overset{+}{P}-\overset{-}{N}\cdot$ was our original motive for this investigation.

TABLE I

Yields of Nitrogen in Acetic Acid at 25°

Reagents	Concentrations, Mole/L.		Nitrogen Yield, Mole/L.
	Phosphine	Ar_3CN_3	
$(C_6H_5)_3P$ and $(C_6H_5)_3CN_3$	0.74[a]	0.74[a]	0.68
	0.26	1.01	0.23
	0.53	0.55	0.53
	0.25	0.50	0.24
$(C_6H_5)_3P$ and 9-phenyl-9-fluorenyl azide	0.72[a]	0.72[a]	0.68
	0.25	1.00	0.24

[a] Added as the 1:1 complex.

ous and the acid is *dilute* requires high temperatures, and then the decomposition rate is about that predicted for the azide alone.[5]

The rate of the acetic acid-catalyzed decomposition is very sensitive to the nature of the solvent. In *dilute* solutions of acetic acid in refluxing chloroform, acetone, or benzene, the rate is too low for convenient measurement, and it may be that only the independent decomposition of the azide is occurring. The rate becomes measurable spectrophotometrically in refluxing chloroform containing 0.08*M* acetic acid, four times the initial concentration of the complex. Table II gives the approximate half-lives of the azide band in various solvents.

TABLE II

Half-Life of the Azide in Acidic Solutions of the Triphenylphosphine–trityl Azide Complex[a]

Solvent	Temperature	Half-Life, Hr.
Chloroform[b]	Refluxing	70
Acetone	Refluxing	100
Nitrobenzene	25°	8
Nitrobenzene	60°	4
Benzene	Refluxing	Very slow
Dimethylformamide	73°	Very slow
Chloroform[c]	Refluxing	20
Chloroform[d]	Refluxing	6
Methanol	Refluxing	0.2

[a]The initial concentration of the complex is 0.022 and the acetic acid 0.088. [b]The chloroform is stabilized with ethanol. [c]Contains 0.015 molar additional $(C_6H_5)_3P$. [d]Contains 0.059 molar additional $(C_6H_5)_3P$.

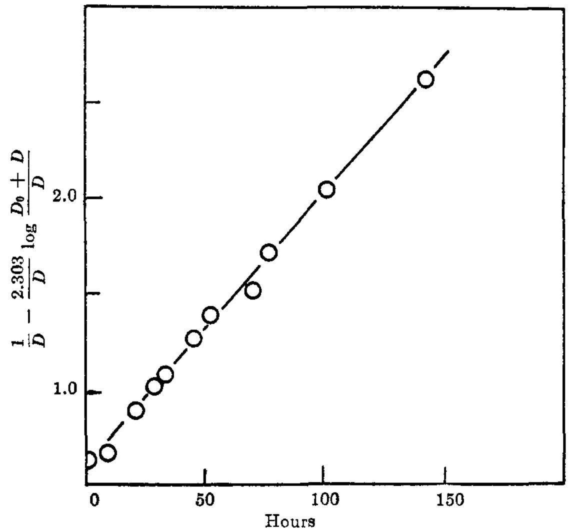

Fig. 1. Rate of reaction of 0.022 *M* trityl azide–triphenylphosphine complex with 0.088 *M* acetic acid in refluxing acetone

Figure 1 shows a kinetic plot for the decomposition of the trityl azide complex in acetone under the reaction conditions of Table II. The function plotted assumes a rate-determining decomposition of the protonated complex and a consumption of two moles of acetic acid per mole of azide decomposed. A similar fit is obtained, with rate constants reproducible to within ±15%, for duplicate experiments in refluxing chloroform. The acid-catalyzed decomposition of the 9-phenyl-9-fluorenyl azide–triphenylphosphine complex in refluxing chloroform is only about one fifth as fast as that of the trityl azide complex. This is the structural effect to be expected if a carbonium ion is formed in the rate-determining step.

In methanol and in nitrobenzene the nitrogen evolution rates are not reproducible. A series of experiments using the triphenylphosphine–trityl azide complex and an equimolar amount of acetic acid in methanol at 62° gave half-lives, *listed in the order in which the experiments were carried out in the same reaction vessel*, of seven, twelve, sixteen, nineteen, twenty-four, and thirty-three minutes. Putting in freshly broken glass chips did not interrupt this trend. A vessel washed with ammonia gave a half-life of eighteen minutes in the first subsequent experiment and a half-life of twenty-one minutes in the second. In nitrobenzene at 62° the results conform to no single order of reaction and the initial rates vary by a factor of two or more in apparently identical experiments. The presence of air or of hydroquinone appears to make no significant difference.

In acetic acid. The decomposition of the trityl-azide-triphenylphosphine complex in glacial acetic acid or in glacial acetic acid plus small amounts of chloroform (to increase the solubility) gives reproducible rates of nitrogen evolution, but follows a complicated rate law. From the initial zero order rate constants (Table III and Fig. 2) it appears that the reaction is first order with respect to triphenylphosphine. With respect to trityl azide the reaction is of mixed first and second order, as shown in Fig. 3.[7]

$$\text{Rate} = k[(C_6H_5)_3P][(C_6H_5)_3CN_3] + k'[(C_6H_5)_3P][(C_6H_5)_3CN_3]^2 \quad (7)$$

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[7] Rates of higher than the first order in azide are also found for the reaction of benzenesulfonyl azide with triphenylphosphine in dry benzene without added acid (Tsuno and Leffler, unpublished).

TABLE III

RATES IN ACETIC ACID–CHLOROFORM AT 25°

Total Azide, Mole/L.	Triphenylphosphine, Mole/L.	Initial Rate (M.L.$^{-1}$ Sec.$^{-1}$ × 10^{-5})
In 10 Vol. % $CHCl_3$		
0.044	0.44	4.1
0.087	0.44	9.9
0.087	0.44	11
0.084	0.63	16
0.21	0.42	34
0.21	0.42	38
0.42	0.42	114
0.092	0.23	5.5
0.095	0.095	2.4
In 25 Vol. % $CHCl_3$		
0.048	0.096	1.3
	0.120	1.4
	0.239	2.9

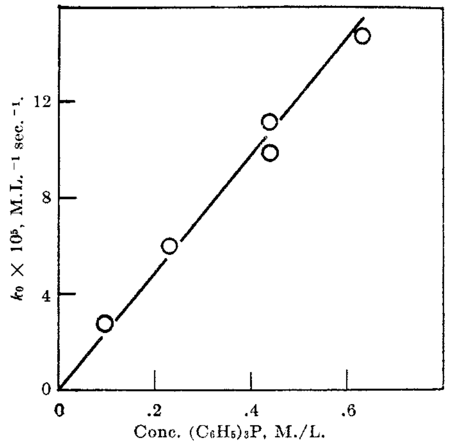

Fig. 2. Dependence of initial rates at 25° in 10 vol. % chloroform–acetic acid on the concentration of triphenylphosphine at a concentration of tritryl azide equal to 0.087 mole/l.

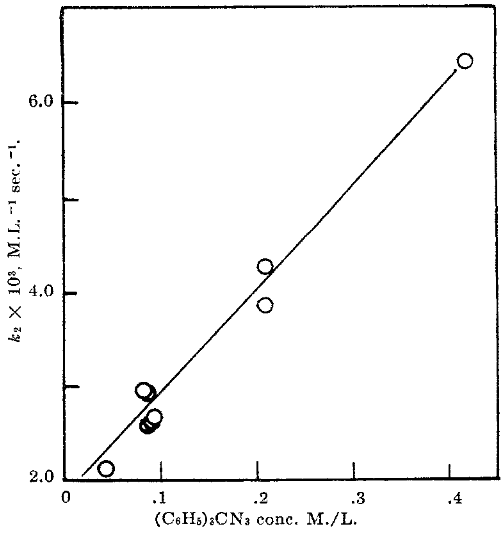

Fig. 3. Dependence of the initial rate divided by the product of the azide and phosphine concentrations on the azide concentration in 10% $CHCl_3$ = 90% HOAc at 25°

The higher order reaction is not due to radical chains,[8] as neither hydroquinone nor 10% styrene has any effect on the rate of the reaction in glacial acetic acid. The styrene is not polymerized.

It can also be shown that the higher order reaction is not due to hydrazoic acid, although that hypothesis seemed attractive at first. Trityl azide in glacial acetic acid is solvolyzed into trityl acetate and hydrazoic acid only to a very small extent, as shown by its nearly normal cryoscopic molecular weight. The concentration of hydrazoic acid due to solvolysis is therefore proportional to the square root of the trityl azide concentration. Reaction of the trityl azide–triphenylphosphine complex with hydrazoic acid would lead to a rate term of 1.5 order with respect to trityl azide. The results can in fact be roughly fitted to such an expression, but only if the rate of the spontaneous decomposition of the complex (without participation by hydrazoic acid) is zero. Added hydrazoic acid (in the form of sodium azide, Table IV) accelerates the reaction.

TABLE IV

SALT EFFECTS OF ACETIC ACID–CHLOROFORM AT 25°

Added Salt	Conc. Mole/L.	Initial Rate (M.L.$^{-1}$ Sec.$^{-1}$ × 10^{-1})
In 25 Vol. % $CHCl_3$; Trityl Azide, 0.048 Mole/L.; Triphenylphosphine, 0.120 Mole/L.		
None		1.39
NaN_3	0.0048	1.67
	0.0095	1.96
	0.0143	2.14
LiCl	0.0069	1.53
	0.0157	1.58
	0.0218	1.60
	0.0347	2.03
	0.0480	1.99
In 10 Vol. % $CHCl_3$; Trityl Azide, 0.087 Mole/L.; Triphenylphosphine, 0.44 Mole/L.		
None		10.5
NaN_3	0.013	11.4
	0.026	14.1
	0.0087[a]	10.9
	0.013[a]	11.6
	0.013[b]	12.8

[a] Also contained 0.0087 mole/l. of hydrochloric acid.
[b] Also contained 0.013 mole/l. of sodium acetate.

Using the observed effect of added hydrazoic acid and assuming a reasonable value for the trityl azide solvolysis equilibrium constant, it is possible to calculate what the rate should be in the absence of added hydrazoic acid; the result of the calculation is an order of magnitude too low. Finally, if hydrazoic acid from the solvolysis is an important reagent, then added trityl acetate should slow down the reaction; no such effect is observed (Fig. 4).

It will be seen from Table IV that the decomposi-

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[8] The decomposition of benzenesulfonyl azide is accelerated by *t*-butyl hydroperoxide (Tsuno and Leffler, unpublished data).

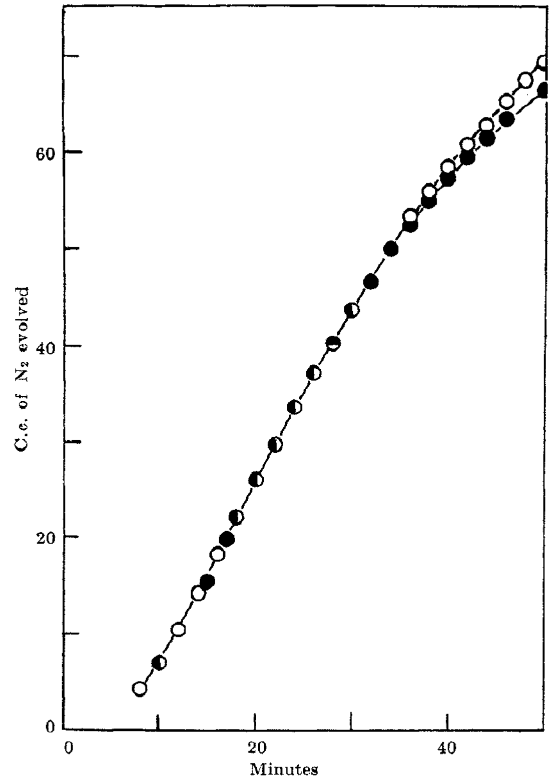


Fig. 4. Effect of trityl acetate (0.05 *M*), open circles, on the rate of the reaction of 0.05 *M* trityl azide with 0.05 *M* triphenylphosphine in 25 vol. % chloroform–acetic acid. The closed circles are for an experiment with no trityl acetate

tion of the trityl azide–triphenylphosphine complex in acetic acid at 25° is accelerated by lithium chloride, as expected on the basis of Equation 2.

Hydrazoic acid in acetic acid. Hydrazoic acid can react directly with triphenylphosphine.[2a]

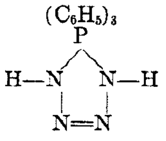
$$(C_6H_5)_3P + 2HN_3 \longrightarrow (C_6H_5)_3PNH{\cdot}HN_3 + N_2 \qquad (8)$$

This reaction is not a complication in the absence of deliberately added hydrazoic acid, as the initial rate of reaction of 0.25 molar triphenylphosphine with 0.04 molar sodium azide in 10% chloroform–90% acetic acid at 25° is only about 0.3% that of the decomposition of 0.25 molar trityl azide–triphenylphosphine complex.

Table IV shows that the nitrogen evolution from the trityl azide–triphenylphosphine complex in acetic acid is markedly accelerated by hydrazoic acid, the increase in rate being approximately proportional to the concentration of added sodium azide.

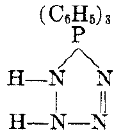
$$\begin{aligned}(C_6H_5)_3PN_3C(C_6H_5)_3 + HN_3 &\longrightarrow [(C_6H_5)_3PN_3C(C_6H_5)_3{\cdot}HN_3] \\ &\longrightarrow (C_6H_5)_3PNH + (C_6H_5)_3CN_3 + N_2 \qquad (9)\end{aligned}$$

In connection with the latter reaction the nature of the compound $(C_6H_5)_3PNH{\cdot}HN_3$ is significant. This compound reacts only very slowly with silver ion[2a] and hence must have a nonionic structure such as II or III.



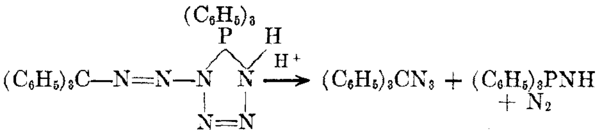
II

or



III

For the intermediate or transition-state for the reaction of hydrazoic acid with the trityl azide–triphenylphosphine complex we would like to propose the analogous structure IV.



IV

The intermediate or transition-state for the reaction of a second molecule of trityl azide with the trityl azide-triphenylphosphine complex might also have a structure of that general type.

EXPERIMENTAL

Triphenylmethyl azide. Triphenylmethyl azide was prepared by the method of Saunders and Ware[5] and purified by elution from alumina with hexane.

Triphenylmethyl azide-triphenylphosphine complex.[4] Ether solutions of the components were mixed and allowed to stand in the refrigerator for several hours., m.p. 103–104°.

9-Phenyl-9-fluorenyl azide. This material was prepared by the method of Arcus and Coombs.[9]

9-Phenyl-9-fluorenyl azide-triphenylphosphine complex. A solution of 1 g. of the azide in 2 cc. of dry ether was added to a filtered solution of 1 g. of triphenylphosphine in 1 cc. of dry ether. The mixture was refrigerated for 15 hr., and the white crystalline precipitate was washed with ether, m.p. 73–74°, yield, 1.8 g. Its infrared spectrum in Nujol is similar to that of the trityl azide complex.

Diphenylcarbamyl azide. This compound was prepared by the method of Stollé[10] and recrystallized from *n*-hexane, m.p. 78–79.5°.

N-(Diphenylcarbamyl)triphenylphosphineimine. To a solution of 1.5 g. of triphenylphosphine in 5 cc. of dry ether was added a solution of 1.3 g. of diphenylcarbamyl azide in 5 cc. of dry ether. The complex remained in solution but decomposed slowly with evolution of nitrogen. On standing over night in the refrigerator the solution deposited crystals of the phosphineimine, m.p. 178–180°. This substance has infrared bands at 1110, 1170, and at 720, in agreement with the spectra reported for other phosphineimines.[11]

Decomposition of the trityl azide-triphenylphosphine complex in neutral solvents. In benzene the products were a complex mixture containing small amounts of triphenylmethane (5–20% yield), triphenylphosphine (5–10% yield), and benzophenone anil. In nitrobenzene the products were triphenylphosphine oxide (60–90% yield) and benzophenone anil.

Decomposition of the trityl azide-triphenylphosphine complex in organic solvents containing acetic acid. From the reaction in refluxing chloroform containing small amounts of acetic acid there were isolated unchanged trityl azide, triphenyl carbinol, trityl acetate, and triphenylphosphine

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(9) C. L. Arcus and M. M. Coombs, *J. Chem. Soc.*, 3977 (1954).

(10) R. Stollé, *Ber.*, **57B**, 1063 (1924).

(11) L. Horner and H. Oediger, *Ann.*, **627**, 142 (1959).

oxide, the material balance being 96–97%. From the reaction in refluxing acetone containing acetic acid the products were similar and the material balance was 94%. The main products of the reaction in methanol in the presence of acetic acid were methyl trityl ether and triphenylphosphine oxide. These products accounted for 88% of the starting material, but there was also formed about 3% of an unknown material, melting at 190–210°.

Decomposition of the triarylmethyl azide-triphenylphosphine complexes in glacial acetic acid. From 1.85 g. of the trityl azide–triphenylphosphine complex decomposed in 5 cc. of glacial acetic acid under nitrogen were obtained, after distillation of the solvent and chromatography on alumina, 0.66 g. of triphenylcarbinol and 0.82 g. of triphenylphosphine oxide. Elution of the column with water gave ammonium acetate. A similar experiment with 2.0 g. of the 9-phenyl-9-fluorenyl azide–triphenylphosphine complex gave 0.60 g. of 9-phenyl-9-fluorenyl acetate, 0.61 g. of triphenylphosphine oxide, and 0.63 g. of *N*-(9-phenyl-9-fluorenyl)triphenylphosphineimine, m.p. 223–224°.

Anal. Calcd. for $C_{37}H_{28}NP$: C, 85.9; H, 5.45; N, 2.7. Found: C, 85.9, H, 5.13; N, 2.68.

The other products were identified by their infrared spectra and mixed melting points. Similar experiments in the presence of excess triarylmethyl azide gave similar results; the excess azide was recovered unchanged.

Trapping of triphenylphosphineimine. A solution of 10 cc. of benzoyl chloride and 4.4 g. of the trityl azide–triphenylphosphine complex in benzene was refluxed for 24 hr., washed with K_2CO_3, and concentrated by distillation. *N*-Benzoyltriphenylphosphineimine, which crystallized from the residual oil in good yield, was identified by a mixed melting point. Other products were triphenylcarbinol, triphenylphosphine oxide, trityl chloride, and benzoic anhydride.

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Study of the Chromium(VI) Oxide–Pyridine Complex

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The chromium(VI) oxide–pyridine complex was found to be a good oxidizing agent at room temperature for the conversion of primary benzylic and allylic alcohols to their corresponding aldehydes. Data for twenty-one compounds are presented. Simple aliphatic and aromatic secondary alcohols are converted to ketones in fair to good yields; data for six are presented.

The chromium(VI) oxide–pyridine complex was introduced as an oxidant for the conversion of primary and secondary alcohols to aldehydes and ketones by Poos, Arth, Beyler, and Sarett.[1] They reported that the reagent, in a pyridine dispersion at room temperature, did not attack such readily oxidized groups as olefinic double bonds and thiol ether linkages. Acetal groups were not affected by the reagent, for the medium was basic. First applied in the steroid field, the reported use of the reagent has been almost entirely in that area since.[2] In most cases, the application has been to the conversion of a secondary alcohol to a ketone, and it has been routinely observed that olefinic linkages and acetal groups are little affected by the reagent.

Aldehyde syntheses *via* the reagent have been seldom reported. Mazur, Danieli, and Sondheimer reported the conversion of 3,16-biscycloethylenedioxybisnor-5α-cholan-22-ol, a primary aliphatic alcohol, to the corresponding C-22 aldehyde in 83% yield by employing the reagent at a moderately elevated temperature (37°) for a briefer than normal reaction time.[2h] The few reports of attempts to accomplish the same type of aldehyde synthesis by using the reagent at room temperature have been discouraging. (*cf.* ref. 2a, 2m) Zimmerman, Singer, and Thyagarajan, for example, did not obtain aldehyde by action of the reagent on the epoxyalcohol, 2,3-*cis*-diphenyl-2,3-epoxypropan-1 ol.[3] α,β-Epoxy secondary alcohols, however, readily yielded ketones.[3,4] In the present study, citronellol was converted to citronellal by the chromium(VI) oxide–pyridine complex in pyridine in only 25%

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(1) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 425 (1953).

(2) The following list of references does not constitute an exhaustive search of the literature. (a) L. F. Fieser, T. Goto, and B. K. Bhattachoryya, *J. Am. Chem. Soc.*, **82**, 1704 (1960). (b) J. A. Zderic, E. Batres, D. C. Limon, H. Carpio, J. Lisci, G. Monroy, E. Necoechea, and H. J. Ringold, *J. Am. Chem. Soc.*, **82**, 3404 (1960). (c) W. S. Johnson, W. A. Vredenburgh, and J. E. Pike, *J. Am. Chem. Soc.*, **82**, 3409 (1960). (d) S. Bernstein and R. H. Lenhard, *J. Am. Chem. Soc.*, **82**, 3683 (1960). (e) S. Bernstein, M. Heller, L. I. Feldman, W. S. Allen, R. H. Blank, and C. E. Linden, *J. Am. Chem. Soc.*, **82**, 3685 (1960). (f) H. E. Kenney, S. Serota, E. A. Weaver, and M. E. Wall, *J. Am. Chem. Soc.*, **82**, 3689 (1960). (g) W. S. Allen, S. Bernstein, L. I. Feldman, and M. J. Weiss, *J. Am. Chem. Soc.*, **82**, 3696 (1960). (h) Y. Mazur, N. Danieli, and F. Sondheimer, *J. Am. Chem. Soc.*, **82**, 5889 (1960). (i) J. C. Sheehan, R. L. Young, and P. A. Cruickshank, *J. Am. Chem. Soc.*, **82**, 6147 (1960). (j) D. N. Kirk and V. Petrow, *J. Chem. Soc.*, 4667 (1960). (k) R. Neher and A. Wettstein, *Helv. Chim. Acta*, **43**, 1191 (1960). (l) E. S. Rothman and M. E. Wall, *J. Org. Chem.*, **25**, 1396 (1960). (m) See also B. E. Cross, *J. Chem. Soc.*, 3032 (1960), who applied the reagent with little success in working with derivatives of gibberellic acid. (n) J. Fishman, E. R. H. Jones, G. Lowe, and M. C. Whiting, *J. Chem. Soc.*, 3948 (1960) applied the reagent in studying the stereochemistry of tricothecin. (m) K. Heusler, J. Kalvoda, C. Meystre, P. Wieland, G. Anner, A. Wettstein, G. Cainelli, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **44**, 502 (1961).

(3) H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959).

(4) H. H. Wasserman and N. E. Aubrey, *J. Am. Chem. Soc.*, **77**, 590 (1955).