Experimental Section[13]

Reactions of Sodium Dialkylphosphonates with Propargyl Bromide (1).—A solution of the sodium dialkylphosphonate, prepared from sodium hydride and the dialkylphosphonate by an established procedure,[14] was added dropwise to a solution of 1 (1 equiv.) in tetrahydrofuran in the manner reported by Guthrie and co-workers.[3] The dark reaction mixtures were worked up as reported and distilled to give a forefraction containing trialkyl phosphate and dialkyl alkylphosphonate and a higher boiling fraction containing the desired dialkyl 1-propynylphosphonate (**2a** or **2b**). A viscous dark undistillable oil remained in the distillation flask.

Dimethyl 1-propynylphosphonate (**2b**) was obtained as a clear colorless liquid distilling at 100–101° (2.0–2.1 mm.): infrared spectrum (CCl_4 solution): 2985 (w), 2950 (m), 2857 (m), 2217 (s), 2092 (w), 1629 (w), 1456 (m), 1285 (s) (sh), 1272 (s), 1186 (m), 1095 (s) (br), and 914 (w) cm.$^{-1}$.

Diethyl 1-propynylphosphonate (**2a**) was obtained as a clear colorless liquid distilling at 101–106° (0.9 mm.), lit.[3] b.p. 105.5–110.0° (1 mm.): infrared spectrum (film): 2980 (m), 2926 (m), 2894 (m), 2194 (s), 2071 (w), 1618 (w), 1478 (w), 1443 (m), 1390 (w), 1260 (vs), 1160 (m), 1090 (m) (sh), 1025 (s) (br), 956 (s), 790 (s), 755 (s), and 610 s cm.$^{-1}$; p.m.r. spectrum: $\mathrm{C}H_3\text{–C–O}$, triplet, $\tau = 8.70$ p.p.m.; $\mathrm{C}H_3\mathrm{C{\equiv}C}$–, doublet, $\tau = 7.98$ p.p.m., ${}^4J_{\mathrm{PH}} = 4.6$ c.p.s.; and $–\mathrm{C}H_2\text{–O}$, quintet, $\tau = 6.00$ p.p.m.

Reactions of Trialkyl Phosphites with Propargyl Bromide (1).—The reactions were carried out by heating a mixture of 1 and the phosphite to 90° in exactly the same fashion used by Jensen and co-workers.[7] After the initial vigorous reaction had subsided, the solution was refluxed for a total of 2 hr. Distillation of the dark solutions gave a forefraction of trialkyl phosphite and a higher boiling fraction containing the desired phosphonate.

Dimethyl propargylphosphonate (**3b**) was obtained as a clear, colorless liquid distilling at 58° (0.2 mm.): infrared spectrum (CCl_4 solution): 3322 (s), 3003 (w), 2950 (m), 2899 (w), 2849 (w), 2212 (w), 2123 (w), 1976 (w), 1942 (w), 1449 (m), 1397 (w), 1271 (s), 1224 (w) (sh), 1183 (m), 1062 (s), 1037 (s), 962 (w), 914 (w), and 855 (m) cm.$^{-1}$.

Diethyl 1-propynylphosphonate (**2a**) was obtained as a clear, colorless liquid distilling at 112° (2 mm.). Jensen and co-workers[7] reported b.p. 98–103° (2 mm.) for the product from this reaction. The infrared and p.m.r. spectra of this material were identical with those of the sample of **2a** prepared by the Nylen reaction.

A less volatile fraction, b.p. 152–165° (0.2 mm.), was also obtained from the reaction of triethyl phosphite and 1, but could not be identified: infrared spectrum (film): 2994 (s), 2933 (m), 2899 (m), 2212 (w), 1961 (w), 1631 (w), 1600 (w), 1479 (w), 1443 (m), 1395 (m), 1370 (w), 1255 (s), 1164 (m), 1098 (w) (sh), 1065–1014 (vs), 962 (s), and 786 (s) (br) cm.$^{-1}$; p.m.r. spectrum: triplet, $\tau = 8.70$ p.p.m. (39.0H)[15]; multiplets, $\tau = 8.25$–7.42 p.p.m. (4.3H); broad singlet and multiplet, $\tau = 6.80$ and 6.55 p.p.m. (4.5H); quintet, $\tau = 5.98$ p.p.m. (26.0H); multiplet, $\tau = 5.37$ p.p.m. (1.0H); multiplet, $\tau = 4.85$ p.p.m. (2.7H).

A similar unidentified fraction of b.p. 150–152° (0.2 mm.) was also isolated by Jensen and co-workers[7] from this Arbuzov reaction. In view of the pronounced infrared absorptions characteristic of diethyl phosphonate functions and the ratio of $\mathrm{P{–}OCH_2{–}CH_3}$ to other protons observed in the p.m.r. spectrum, it is probable that this material represents a mixture of products arising from the thermal reaction of either **2a** or **2b** with triethyl phosphite. The ease of formation of phosphonates by the thermal reaction of trialkyl phosphites with acetylenes has been noted previously.[3,7,16]

---

[13] Infrared spectra were determined on a Beckman IR-8 spectrophotometer calibrated with a polystyrene film. P.m.r. spectra were obtained on a Varian Associates Model A-60 spectrometer at 37° (probe temperature) on 5–10% solutions in carbon tetrachloride. Chemical shifts are reported on the τ scale from internal tetramethylsilane ($\tau = 10.00$ p.p.m.); these values are the average of at least two spectral determinations and are accurate to at least ±0.015 p.p.m. The coupling constants were obtained from 50-c.p.s. sweep width spectra and are the average of at least three runs; the values are accurate to ±0.15 c.p.s. or better.

[14] R. G. Harvey, T. C. Myers, H. I. Jacobson, and E. V. Jensen, *J. Am. Chem. Soc.*, **79**, 2612 (1957).

[15] Relative integrated intensity.

[16] C. E. Griffin and T. D. Mitchell, *J. Org. Chem.*, **30**, 1935 (1965).

Chemistry of Ylids. XII. Effect of Phosphorus Substituents on the Stereochemistry of the Wittig Reaction[1a]

A. WILLIAM JOHNSON[1b,c] AND VERNON L. KYLLINGSTAD[1d]

Chemistry Department, University of North Dakota,
Grand Forks, North Dakota

Received August 2, 1965

Commencing with some of the earliest work on the Wittig reaction between phosphonium ylids and carbonyl compounds, the stereochemistry of the product olefins has been of interest.[2] Most such reactions lead to dominance of the *trans* isomer in the reaction mixture, sometimes to the complete exclusion of the *cis* isomer.[3] The flexibility of the Wittig reaction would be vastly improved were there available a means of forcing the *cis* olefins to dominate. This means relying on kinetic control of the reaction.

Bergelson and Shemyakin[4] claimed that addition of a variety of substances, lithium halides, amines, polar solvents, etc., to a Wittig reaction medium led to dramatic increases to near 9.0 in the *cis/trans* ratio of the olefins produced. However, House, *et al.*,[5] recently have shed doubt on some of this work and found, at the most, *cis/trans* ratios of 1.0 using a variety of phosphonium ylids and additives.

Ketcham, *et al.*,[6] found that the *cis/trans* ratio of 0.11 for the 4-nitro-4′-methoxystilbenes (**1**) formed from the reaction of *p*-nitrobenzylidenetriphenylphosphorane (**2a**) with *p*-anisaldehyde (**3a**) could be raised to 0.92 by interchanging the ylid and aldehyde substituents, using *p*-methoxybenzylidenetriphenylphosphorane (**2b**) and *p*-nitrobenzaldehyde (**3b**). However, this still is not a very satisfactory yield of *cis* isomer. They concluded that a more reactive ylid would afford the maximum yield of *cis* isomer (approaching 50%) owing to diminished reversibility of the betaine-forming step (*i.e.*, smaller k_2). House and Rasmusson[7] reached similar conclusions.

In contrast to this somewhat too general conclusion, Bestmann and Kratzer,[8] Speziale and Bissing,[9] and Bissing[10] all found that trialkylphosphonium ylids afforded almost exclusively *trans* isomers while the analogous but less nucleophilic triphenylphosphonium ylids afforded larger but still very small *cis/trans* ratios of olefins. For example, carbethoxymethylene-*triphenyl*phosphorane (**4**) and benzaldehyde gave a

---

[1] (a) Paper XI: *Chem. Ind.* (London), in press. For paper X, see A. W. Johnson, V. J. Hruby, and J. L. Williams, *J. Am. Chem. Soc.*, **86**, 918 (1964). (b) To whom inquiries should be addressed: University of Saskatchewan, Regina Campus, Regina, Saskatchewan, Canada. (c) We acknowledge the partial support of this research by the U. S. Public Health Service, Grant No. GM-10488-01. (d) Taken from the senior thesis of V. L. K. submitted in partial fulfillment of the requirements for the degree of B.S. in Chemistry, June 1965.

[2] G. Wittig and U. Schollkopf, *Chem. Ber.*, **87**, 1318 (1954).

[3] For a review of data to 1963, see S. Trippett, *Quart. Rev.* (London), **17**, 406 (1963).

[4] L. D. Bergelson and M. M. Shemyakin, *Pure Appl. Chem.*, **9**, 271 (1964); *Bull. Acad. Sci. USSR*, 1053 (1963); *Tetrahedron*, **19**, 149 (1963).

[5] H. O. House, V. K. Jones, and G. A. Frank, *J. Org. Chem.*, **29**, 3327 (1964).

[6] R. Ketcham, D. Jambotkar, and L. Martinelli, *ibid.*, **27**, 4666 (1962).

[7] H. O. House and G. H. Rasmusson, *ibid.*, **26**, 4278 (1961).

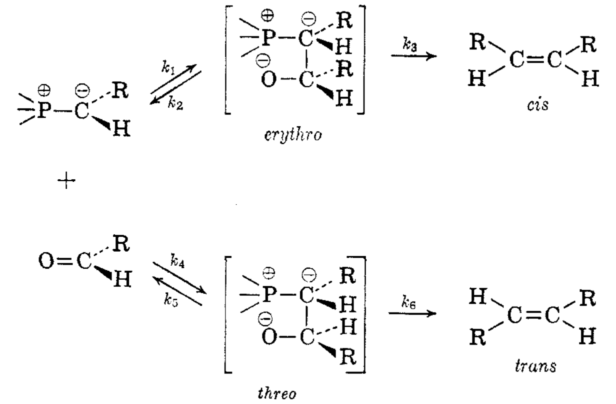
[8] H. J. Bestmann and O. Kratzer, *Chem. Ber.*, **95**, 1894 (1962).

[9] A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc.*, **85**, 3878 (1963).

[10] D. E. Bissing, *J. Org. Chem.*, **30**, 1296 (1965).

cis/trans ratio of 0.19 for the ethyl cinnamate, whereas carbethoxymethylene*tri-n-butyl*phosphorane (**5**) gave a *cis/trans* ratio of 0.05 even though the latter is the most nucleophilic and the most reactive.[9]

On the basis of the kinetic stereochemical studies by Speziale and Bissing,[9] it appeared that the geometric isomer distribution was affected mainly by the ratios k_4/k_1, k_3/k_2, and k_6/k_3. Comparing reaction of the ylids **4** and **5** with benzaldehyde, the former gave the largest *cis/trans* ratio and had the smaller k_4/k_1 ratio, the larger k_3/k_2 ratio, and the smaller k_6/k_3 ratio. It is obvious that a larger k_3/k_2 ratio (*i.e.*, relative ease of betaine decomposition) should lead to a smaller k_6/k_3 ratio, both leading to a larger *cis/trans* ratio, and that these conditions should prevail for **4** over **5**. However, it is not clear why the least nucleophilic ylid (**4**) should be the least discriminating in its reaction (*i.e.*, k_4/k_1 ratio smaller than that for **5**), although it is obvious that the least discriminating should give a k_4/k_1 ratio closest to unity.



On an *a priori* basis the larger *cis/trans* ratios should be obtainable if k_4/k_1 were small, k_3/k_2 were large, and k_6/k_3 were small. These criteria would necessitate the use of a phosphorane that was very nucleophilic (*i.e.*, k_1 large and k_2 small) but which produced a betaine whose decomposition was facile (*i.e.*, k_3 large). The latter condition would place less reliance on conjugation of the ylid and carbonyl substituents with the incipient double bond of the transition state. Under such conditions the difference in energies between the *erythro* and *threo* transition states diminishes and k_3 approaches k_6.

We have studied the effect of ylid structure on the preparation of 4-nitro-4′-methoxystilbenes (**1**) being concerned with the *cis/trans* ratio of the following reaction. We have been especially concerned with

$$\underset{\mathbf{2}}{R^1{}_3P{=}CH{-}C_6H_4R^2\text{-}p} + \underset{\mathbf{3}}{p\text{-}R^3C_6H_4CHO} \longrightarrow \underset{\mathbf{1}}{CH_3OC_6H_4CH{=}CHC_6H_4NO_2} + R^1{}_3PO$$

variations in R^1 designed to afford larger k_3 values than for **2a** and **2b**, thereby affording high *cis/trans* ratios of olefin **1** and providing a preparative route for *cis* olefins. The results of the reactions are recorded in Table I.

These reactions all were run in benzene solution under nitrogen and using *n*-butyllithium to generate the ylid. Since it was shown that the *cis* isomer of **1** isomerized readily to the *trans* upon chromatography or recrystallization, the *cis/trans* ratio was obtained by recording the n.m.r. spectrum of the reaction mixture. Use of known ratios of isomers indicated an error of less than 3% for this method. The methoxyl protons of the *cis* and *trans* isomers of **1** were at 228.0 and 230.5 c.p.s. downfield from TMS, respectively, and the peaks could be separately integrated. The ylids where $R^1 = C_4H_9$, $R^2 = OCH_3$ and $R^1 = p\text{-}CH_3OC_6H_4$, $R^2 = NO_2$ or CH_3O also were prepared and subjected to the appropriate Wittig reaction. However, we were unable to determine the *cis/trans* ratios owing to the complexity of the n.m.r. spectra.

TABLE I

cis/trans RATIO OF OLEFINS FROM REACTION OF $R^1{}_3P{=}CHC_6H_4R^2$ (**2**) + $R^3C_6H_4CHO$ (**3**)

Reaction	Ylid	R^1	R^2	Aldehyde	R^3	*cis/trans* of **1**
1	**2a**	C_6H_5	NO_2	**3a**	OCH_3	0.35
2	**2b**	C_6H_5	OCH_3	**3b**	NO_2	0.79
3	**2c**	p-ClC_6H_4	NO_2	**3a**	OCH_3	1.10
4	**2d**	p-ClC_6H_4	OCH_3	**3b**	NO_2	4.10
5	**2e**	n-C_4H_9	NO_2	**3a**	OCH_3	0.20

Ketcham, *et al.*,[6] obtained no *cis* isomer from reaction of **2a** with **3a** but their analysis involved chromatography on alumina and crystallization, both operations known to effect isomerization of *cis*-**1** to *trans*-**1** (see Experimental Section). We found a 25.8/74.2 *cis/trans* ratio in a total yield of 78% of stilbenes (**1**).

It is clear from these results that, when using the same phosphonium group, the most effective means of obtaining maximum yields of *cis* olefin is to employ the most nucleophilic of the two possible ylids, a methoxybenzylidenephosphorane rather than a nitrobenzylidenephosphorane (*i.e.*, **2b** over **2a** and **2d** over **2c**). This agrees with the conclusions of Ketcham[6] and House.[7] The more nucleophilic ylid should lead to a k_4/k_1 ratio closer to unity and a smaller k_2 value, both factors leading to the formation of more *erythro* betaine. The effect on the *cis/trans* ratio by such a choice is a factor of about 2.2 (reaction 1 *vs.* reaction 2).

The most interesting observation is the effect of structural variation in the phosphonium group on the *cis/trans* ratio. Use of *p*-methoxybenzylidenetri(*p*-chlorophenyl)phosphorane (**2d**) in place of **2b** led to an increase from 0.79 to 4.10 in the *cis/trans* ratio, a factor of 5.2 (reaction 4 *vs.* reaction 2). In the nitrobenzylidene series the *cis/trans* ratio increased as the phosphorus substituent was successively changed from *n*-butyl (**2e**) to phenyl (**2a**) to *p*-chlorophenyl (**2c**). Therefore, whereas Ketcham, *et al.*,[6] concluded that maximum *cis/trans* ratios (approaching 1.0) could be obtained by altering the carbanion substituents on an ylid, it appears now that altering the nature of the phosphonium group has an even larger effect. As indicated in Table I, combining the effects of these two structural alterations (reaction 4 *vs.* reaction 5) permits the *cis/trans* ratio to be changed from 17/83 to 80/20, a factor of 20 in the *cis/trans* ratio.

The nature of the phosphorus substituents probably affects both betaine formation and betaine decomposition, but mainly the latter. In the nitrobenzylidene series the order of ylid nucleophilicity should be **2e** > **2a** > **2c**.[11] On the basis of Speziale and Bissing's[9]

---

[11] A. W. Johnson, unpublished results.

experience with the ylids **4** and **5**, the least nucleophilic ylid (**2c**) would be expected to afford the smallest k_4/k_1 value, contributing to a higher *cis/trans* ratio. The betaine decomposition step should be fastest with **2c** and least so with **2e** owing to the increased positive character of the phosphorus atom in the former facilitating oxyanion attack. In other words, **2c** should afford the smallest k_6/k_3 ratio, also contributing to the largest *cis/trans* ratio. Therefore, both the betaine formation and decomposition steps favor the highest *cis/trans* ratio for the tri(*p*-chlorophenyl) ylid (**2c**). This combination of effects led to the unusually high *cis/trans* ratio when the phosphorus atom carried electron-withdrawing groups.

The fact that in the methoxybenzylidenephosphorane series the *cis/trans* ratio increased by a factor of 5.2 when the triphenylphosphonium group was replaced by the tri(*p*-chlorophenyl)phosphonium group, but in the nitrobenzylidenephosphorane series the ratio increased by a factor of only 3.1, probably indicates that the k_6/k_3 ratio was small for both tri(*p*-chlorophenyl)phosphonium ylids. The difference in the two factors may indicate that the k_4/k_1 ratio was closer to unity for the methoxy series than for the nitro series, the latter being the least nucleophilic and therefore most discriminating. The *cis/trans* ratios must be determined by a delicate balance of the rate constant ratios k_4/k_1 and k_6/k_3.

Wittig reactions normally involve the use of triphenylphosphonium ylids, presumably because of the availability of triphenylphosphine. From this work it appears that formation of *trans* olefins can be strongly favored by use of phosphonium ylids carrying electron-donating phosphorus substituents (*e.g.*, tri-*n*-butylphosphonium ylids) while formation of *cis* olefins can be favored by use of ylids carrying electron-withdrawing phosphorus substituents [*e.g.*, tri(*p*-chlorophenyl)phosphonium ylids]. Tri-*n*-butylphosphine required for the former is a commercial product and tri(*p*-chlorophenyl)phosphine is readily prepared.[12]

Experimental Section[13]

Phosphines.—Triphenylphosphine and tri-*n*-butylphosphine were used directly as received from commercial sources. Tri-(*p*-chlorophenyl)phosphine was prepared as described by Mann and Chaplin,[12] m.p. 102–103°.

Phosphonium Salts.—The phosphonium salts were prepared by heating 40 mmoles of *p*-methoxybenzyl bromide or *p*-nitrobenzyl bromide with 40 mmoles of phosphine in 100 ml. of benzene for about 12 hr. The precipitated salts were removed by filtration and recrystallized from benzene–chloroform. The following were prepared: *p*-methoxybenzyltriphenylphosphonium bromide, m.p. 236–238°; *p*-nitrobenzyltriphenylphosphonium bromide, m.p. 269–270°; *p*-methoxybenzyltri(*p*-chloro phenyl)phosphonium bromide, m.p. 269–271°; *p*-nitrobenzyltri(*p*-chlorophenyl)phosphonium bromide, m.p. 260–261°; *p*-methoxybenzyltri(*p*-methoxyphenyl)phosphonium bromide, m.p. 254–256°; *p*-nitrobenzyltri(*p*-methoxyphenyl)phosphonium bromide, m.p. 222–223°; *p*-methoxybenzyltri-*n*-butylphosphonium tetraphenylborate, m.p. 184–186°; and *p*-nitrobenzyltri-*n*-butylphosphonium bromide, m.p. 165–166°.

Wittig Reactions.—To 2.5 mmoles of phosphonium salt slurried in 80 ml. of benzene flushed with nitrogen was added 2.5 mmoles of *n*-butyllithium in hexane. The colored solution was stirred at room temperature for 1 hr. after which time 2.5 mmoles of the appropriate substituted benzaldehyde was added. After stirring overnight (at room temperature for the methoxybenzylides but with gentle warming to 40° for the nitrobenzylides), the reaction was hydrolyzed with 20 ml. of 40% sodium bisulfite. Water was added, the organic components were extracted with ether, and the organic layer was dried over magnesium sulfate. The solvents were removed *in vacuo* at or below room temperature, leaving an oily crude residue containing *cis*- and *trans*-4-nitro-4′-methoxystilbenes, phosphine oxide, and unreacted starting materials.

For purposes of quantitative analysis a portion of the crude residue was taken up in hexadeuterioacetone and its n.m.r. spectrum was recorded. The *cis/trans* ratios obtained are recorded in Table I.

For isolation purposes the crude residue was chromatographed on Merck 71707 alumina. Elution with 1:1 benzene–hexane afforded *cis*-4-nitro-4′-methoxystilbene, m.p. 65–67° (lit.[6] m.p. 69–70). Elution with 9:1 benzene–chloroform afforded *trans*-4-nitro-4′-methoxystilbene, m.p. 132–133° (lit.[6] m.p. 131–132°). Attempts to recrystallize the *cis* isomer invariably led to very low recovery of *cis* olefin and the isolation of considerable amounts of the *trans* isomer. The total yield of both isomers from reaction between **2a** and **3a** (reaction 1) was 0.52 g. (78%).

Placing 0.12 g. of *cis* olefin on an alumina column and eluting with 1:1 benzene–hexane led to the recovery of only 0.09 g. of the *cis* isomer, the remainder being the *trans* isomer. The same procedure with a 55.8/44.2 mixture of *trans* and *cis* olefins afforded a 69.6/30.4 mixture of *trans* and *cis* isomers.

N.m.r. Analyses.—The n.m.r. spectra of the crude Wittig reaction products were recorded in hexadeuterioacetone at ambient temperatures. The methoxyl protons were at 228.0 c.p.s. for the *cis* isomer and at 230.5 c.p.s. for the *trans* isomer. *p*-Anisaldehyde did not interfere (232 c.p.s.) but tri(*p*-methoxyphenyl)phosphine oxide did (231 c.p.s.). The peaks were integrated using a sweep width of 100 c.p.s. The ratio of the integrated peaks heights was taken as directly proportional to the ratio of the two isomers present in the solution.

Known ratios of *cis*- and *trans*-4-nitro-4′-methoxystilbenes were weighed out and their spectra were recorded in hexadeuterioacetone. The theoretical *cis/trans* ratios compared with the observed ratios as follows: calcd. 31.6/68.4, found 28.6/71.4; calcd. 46.4/53.6, found 44.0/56.0; calcd. 59.9/40.1, found 57.5/42.5; calcd. 73.5/26.5; found 71.4/28.6. The maximum deviation from the theoretical values was 3%. The observed values for the *cis/trans* ratios always were low, a direction consistent with the known facile *cis*-to-*trans* isomerization of the stilbenes.

---

[12] F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 527 (1937). This compound was prepared by R. Swor whose assistance we acknowledge.

[13] Melting points are uncorrected. N.m.r. spectra were recorded on a Varian A-60 n.m.r. spectrometer, the purchase of which was aided by a grant from the National Science Foundation.

Cycloadditions. VI. Photosensitized Dimerization of α-Phellandrene[1]

JOHN E. BALDWIN AND JAMES P. NELSON[2]

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61803

Received August 17, 1965

Photosensitized dimerizations of conjugated dienes are believed to take place by a mechanism involving transfer of excitation from a triplet sensitizer to the diene; the resulting excited triplet diene combines with an unactivated diene giving a biradical intermediate, which collapses to products through spin inversion and cyclization.[3,4] Modes of cycloaddition

---

[1] Paper V: J. E. Baldwin and R. A. Smith, *J. Am. Chem. Soc.*, **87**, 4819 (1965).

[2] National Science Foundation Undergraduate Research Participant, summer 1965.

[3] D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964), and earlier papers cited therein.

[4] D. J. Trecker, R. L. Brandon, and J. P. Henry, *Chem. Ind.* (London), 652 (1963).