to the C-5 methylene while the more electronegative benzoate ester was placed at C-3.

The preparation of 3-*O*-benzoyl-5-bromo-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (**4**) was carried out by refluxing **2** either in *n*-propyl bromide solu tion or in a chloroform solution containing cyanogen bromide. In this case the two-proton doublet for the C-5 hydrogens appeared at δ 3.55 ($J_{4,5} = 7$ Hz) with the C-3 one-proton doublet at 5.58 ($J_{3,4} = 3$ Hz, $J_{2,3} = 0$). The reaction with cyanogen bromide appears to be a special case of the von Braun reaction[4] whereby bromide ion attacks the C-5 position either simultaneously or after elimination of dimethylcyanamide.

Cyclic α-(dimethylamino)benzylidene acetals are useful intermediates for functionalizing glycols under very mild conditions. It would appear that the reaction could be carried out with any reagent which would cause elimination of the dimethylamino moiety and supply a suitable nucleophile to open the resulting acyloxonium ion intermediate.

Experimental Section

Melting points were taken on a Fisher-Johns apparatus. Ir spectra were measured on a Beckman IR-9 spectrometer. Nmr spectra were measured on a Varian Associates A-60 instrument with tetramethylsilane as the internal standard. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. Gas chromatography was performed with an F & M 810 chromatograph equipped with a 4 ft × 0.25 in. glass column containing 100–120 mesh 3% OV-17 Gas-Chrom Q and programmed for 150–300° at 10°/min and 25 ml/min. Tlc was carried out on silica gel Quanta/Gram plates obtained from Quantum Industries. Silica gel for column chromatography was 70–325 mesh from EM Reagents, distributed by Brinkman Instruments.

3,5-*O*-[α-(Dimethylamino)benzylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose (**2**).—A solution of 5.00 g of 1,2-*O*-isopropylidene-α-D-xylofuranose[5] and *N*,*N*-dimethylbenzamide diethyl acetal[6] in 25 ml of CH_2Cl_2 was allowed to stand overnight at room temperature. After evaporation of the solvent the residual oil was distilled at reduced pressure to yield 7.12 g (84%) of a thick syrup: bp 143–145° (0.1 mm); $[\alpha]^{25}\mathrm{D}$ +25.4° (*c* 1.01, $CHCl_3$); nmr ($CDCl_3$) δ 1.33 (3 H, s, $CHCH_3$), 1.43 and 1.50 (3 H combined, s, s, partially resolved, ratio of ~1:5, respectively, *C*-CH_3), 2.08 and 2.27 (6 H combined, s, s, resolved, ratio of 6:1, *N*-CH_3), 3.80–4.75 (5 H, m, H-2, -3, -4, and -5), 5.97 and 6.07 (1 H combined, d, d, H-1), 7.4 (5 H, m, C_6H_5). The product crystallized after standing for several weeks at room temperature and was recrystallized from pentane: mp 74–75.5°; $[\alpha]^{25}\mathrm{D}$ +30.6° (*c* 1.04, $CHCl_3$). The nmr was the same as for the distilled product. Gas chromatography showed only one peak at 8.5-min retention time.

Anal. Calcd for $C_{17}H_{23}NO_5$: C, 63.54; H, 7.21; N, 4.36. Found: C, 63.58; H, 7.12; N, 4.42.

3-*O*-Benzoyl-5-deoxy-5-iodo-1,2-*O*-isopropylidene-α-D-xylofuranose (**3**).—A solution of 0.62 g of 3,5-*O*-[α-(dimethylamino)-benzylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose (**2**) in 15 ml ethyl iodide was refluxed for 5 hr. Filtration afforded a white solid which was very water soluble and precipitated AgI on addition of $AgNO_3$ solution. Tlc ($CHCl_3$) of the filtrate showed two spots,[7] R_f 0.8 (major) and 0.1 (minor). Evaporation to a syrup and chromatography on a column of 15 g of silica gel with $CHCl_3$ gave 0.67 g (82%) of a colorless syrup (only R_f 0.8 spot by tlc): $[\alpha]^{25}\mathrm{D}$ −50.8° (*c* 1.02, $CHCl_3$); ir (liquid film) 1727 cm^{-1}; nmr ($CDCl_3$) δ 1.33 (3 H, s, *C*-CH_3), 1.56 (3 H, s, *C*-CH_3), 3.33 (2 H, d, $J_{4,5} = 7$ Hz, CH_2I), 4.68 (sextet, $J_{3,4} = 3$ Hz, $J_{4,5} = 7$ Hz, H-4), 4.70 (d, overlaid on the H-4 signal, $J_{1,2} = 4$ Hz, $J_{2,3} = 0$, H-2; 2 H for H-2 plus H-4), 5.58 (1 H, d, $J_{3,4} = 3$ Hz, $CHOCOC_6H_5$), 6.03 (1 H, d, $J_{1,2} = 4$ Hz, H-1), 7.35–8.15 (5 H, m, $CO_2C_6H_5$).

Anal. Calcd for $C_{15}H_{17}IO_5$: C, 44.57; H, 4.24; I, 31.39. Found: C, 44.48; H, 4.29; I, 31.60.

3-*O*-Benzoyl-5-bromo-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (**4**). **Method A.**—A solution of 0.50 g of **2** and 0.30 g of cyanogen bromide in 15 ml of $CHCl_3$ was refluxed for 17 hr. Tlc ($CHCl_3$) showed a major spot at R_f 0.6 and two minor spots at 0.1 and 0.5.[7] The major spot also moved at R_f 0.3 with toluene. After concentrating the mixture to a syrup it was chromatographed on a column of 10 g of silica gel with toluene. Combining fractions with only the major spot and evaporating gave 0.30 g of a syrup: $[\alpha]^{25}\mathrm{D}$ −46.6° (*c* 1.00, $CHCl_3$); ir (liquid film) 1734 cm^{-1}; nmr ($CDCl_3$) δ 1.32 (3 H, s, *C*-CH_3), 1.55 (3 H, s, *C*-CH_3), 3.55 (2 H, d, $J_{4,5} = 7$ Hz, CH_2Br), 4.68 (d, $J_{1,2} = 4$ Hz, $J_{2,3} = 0$, H-2; superposed sextet, $J_{3,4} = 3$ Hz, $J_{4,5} = 7$ Hz, H-4; total of 2 H), 5.58 (1 H, d, $J_{3,4} = 3$ Hz, $CHOCOC_6H_5$), 6.03 (1 H, d, $J_{1,2} = 4$ Hz, H-1), 7.3–8.2 (5 H, m, C_6H_5).

Anal. Calcd for $C_{15}H_{17}BrO_5$: C, 50.44; H, 4.80; Br, 22.37. Found: C, 50.54; H, 4.83; Br, 22.28.

Method B.—A solution of **2** in 5 ml of *n*-propyl bromide was refluxed overnight and filtered from the insoluble dimethyldi-*n*-propylammonium bromide. Gas chromatography showed only one peak with a retention time of 9.8 min, the same as for the product from method A.

Registry No.—**1**, 19429-87-9; **2**, 41164-23-2; **3**, 41164-24-3; **4**, 41164-25-4; 1,2-*O*-isopropylidene-α-D-xylofuranose, 20031-21-4.

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[4] H. A. Hageman, in *Org. React.*, **7**, 198 (1953).

[5] P. A. Levene and A. L. Raymond, *J. Chem. Soc.*, **102**, 317(1933).

[6] H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Chem. Ber.*, **96**, 2671 (1963).

[7] Plates were sprayed with a solution prepared from 5 g of ammonium molybdate, 5 ml of concentrated H_2SO_4, and 5 ml of 86% H_3PO_4 in 100 ml of water and heated at 120°. Gray spots turned blue on standing at room temperature: S. Hanessian and N. R. Plessas, *J. Org. Chem.*, **34**, 2163 (1969).

γ Substitution of Allyl Ylides in the Wittig Reaction

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Received December 26, 1972

There are several reports in the literature describing electrophilic capture of phosphonate- or phosphonamide-stabilized allylic anions by ketones or aldehydes at both the α and γ carbons.[3] Also, allylidenetriphenylphosphorane reacts at the α and γ carbons with ethyl chloroformate, and cinnamyltriphenylphosphonium salt undergoes deuterium exchange in basic solution at both allylic positions.[4] A further example of γ substitution has been reported by Buchi and Wuest in the course of attempted Wittig reaction of allylidenetriphenylphosphorane and an enone,[5] but this appears to be a special case since 1,4 addition to the enone occurs as well. To our knowledge, there is no previously reported instance of γ substitution in a typical Wittig reaction.

We have found that allyltriphenylphosphonium fluoroborate reacts with benzaldehyde and diazabicycloundecene (DBU) in refluxing tetrahydrofuran to form a dienol **1** (26%) in addition to the expected Wittig product 1-phenylbutadiene. The structure of **1** is proved by the nmr spectrum [δ 7.2–7.5 (10 H),

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[1] Alfred P. Sloan Fellow, 1971–1973.

[2] Support of this work by the National Science Foundation is acknowledged.

[3] E. J. Corey and D. E. Cane, *J. Org. Chem.*, **34**, 3053 (1969); G. Lavielle, *C. R. Acad. Sci.*, **270**, 86 (1970).

[4] H. J. Bestmann and H. Schulz, *Angew. Chem.*, **73**, 27 (1961); H. J. Bestmann and H. Schulz, *Justus Liebigs Ann. Chem.*, **674**, 11 (1964).

[5] G. Buchi and H. Wuest, *Helv. Chim. Acta*, **54**, 1767 (1971).

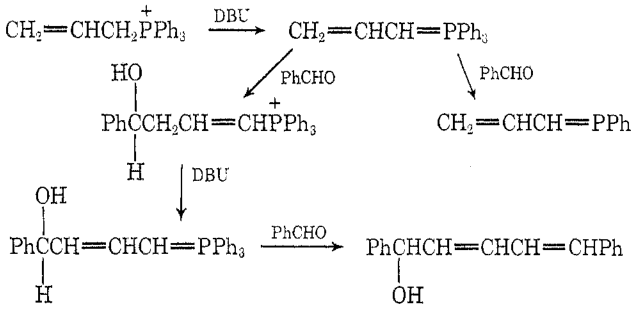
TABLE I

REACTION OF BENZALDEHYDE WITH ALLYLIC PHOSPHONIUM FLUOROBORATES AND DBU IN TETRAHYDROFURAN

Registry no.	Salt	Conditions	Yield of Wittig diene, %	Yield of dienol, %
	DBU			
41143-49-1	$CH_2{=}CHCH_2\overset{+}{P}Ph_3$	18-hr reflux	59	26
	$CH_2{=}CHCH_2\overset{+}{P}Ph_3$	50 hr, 25°	49	35
41143-50-4	$CH_3CH{=}CHCH_2\overset{+}{P}Ph_3$	18-hr reflux	67	13
41143-51-5	$PhCH{=}CHCH_2\overset{+}{P}Ph_3$	18-hr reflux	67	0
41143-52-6	$CH_3CH{=}C(CH_3)\overset{+}{P}Ph_3$	18-hr reflux	5	42
41187-93-3	$CH_3CH{=}C(CH_3)\overset{+}{P}CH_3Ph_2$	18-hr reflux	30	24
	Methanolic DBU			
	$CH_2{=}CHCH_2\overset{+}{P}Ph_3$	18-hr reflux	5	49
	$CH_3CH{=}CHCH_2\overset{+}{P}Ph_3$	18-hr reflux	19	39
	$CH_3CH{=}C(CH_3)PCH_3Ph_2$	18-hr reflux	0.4	28

5.8–7.2 (4 H), 5.26 (1 H, dd, J = 7, 2.5 Hz), 2.15 (1 OH)] and conversion into 1,5-diphenylpenta-2,4-dienone[6] with activated manganese dioxide. The dienol results from γ substitution of the allyl ylide followed by proton transfer to form a new ylide and normal Wittig reaction with a second mole of benzaldehyde.

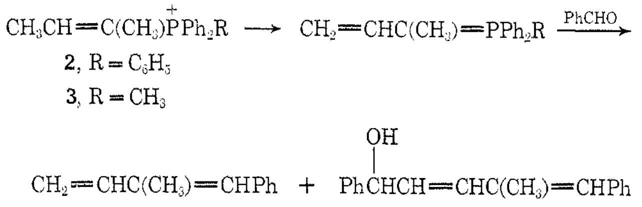
SCHEME I



1

Under similar conditions, crotyltriphenylphosphonium fluoroborate gives relatively less dienol (Table I). Cinnamyltriphenylphosphonium fluoroborate produces only the normal Wittig product, indicating that the ratio of $\alpha:\gamma$ ylide substitution increases with steric crowding at the γ carbon.

As expected, increased hindrance at the α carbon favors γ substitution. 2-Butenyltriphenylphosphonium fluoroborate[7] (**2**), benzaldehyde, and DBU afford the dienol **4** (42%) and only 5% of the Wittig product,



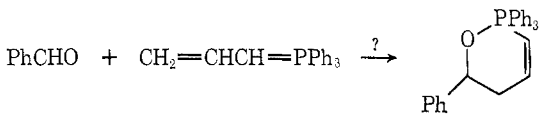
2, R = C_6H_5
3, R = CH_3

4

1-phenyl-2-methylbuta-1,3-diene. Approximately equal amounts of diene and dienol are obtained using 2-butenylmethyldiphenylphosphonium fluoroborate[8] (**3**) as the ylide precursor; so reduced hindrance by the phosphorus substituents favors α substitution.

A dramatic increase in the ratio of $\gamma:\alpha$ substitution product is observed when allylic ylides are generated with DBU in refluxing methanol (Table I). The ratio of dienol:diene is *ca.* 10:1 for allyltriphenylphosphonium fluoroborate and 2:1 for the crotyl analog. No significant solvent effect is observed when the allylidene ylide reaction is performed using excess methanolic sodium methoxide as the base in place of DBU. These observations are in accord with the simple ionic mechanism of Scheme I. Proton transfer to the developing negative charge on the aldehyde oxygen is more important for γ attack than for α attack owing to greater charge separation in the former, and the $\gamma:\alpha$ ratio increases in methanol relative to THF. In the presence of excess methoxide, the medium is too basic to exert as strong a catalytic effect.[9]

The solvent effects are inconsistent with a Diels–Alder mechanism for γ substitution *via* the pentavalent phosphorane **5**. Also, we have observed formation of a dienol from reaction of benzaldehyde and the



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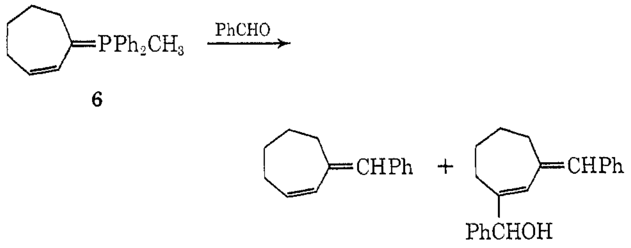

6

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(6) J. T. Thomas and G. Branch, *J. Amer. Chem. Soc.*, **75**, 4793 (1953).

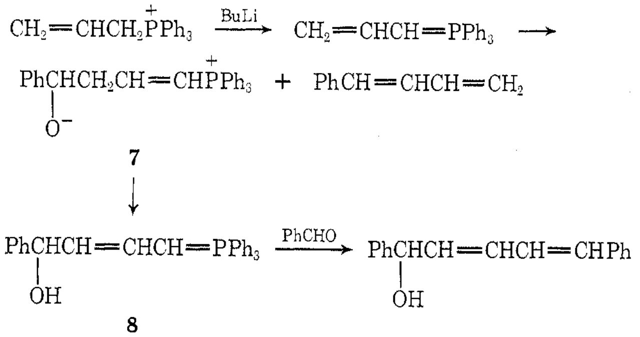
(7) D. Seyferth and J. Fogel, *J. Organometal. Chem.*, **6**, 205 (1966).

(8) Prepared from 2-butenyllithium and chlorodiphenylphosphine followed by methyl iodide and excess sodium fluoroborate. The noncrystalline product is characterized by the nmr spectrum ($CDCl_3$): δ 7.4–7.9 (10 H, m), 6.5–6.8 (1 H, m), 2.65 (3 H, d, J = 13 Hz), 2.07 (3 H, br, d, J = 14 Hz), 1.47 (3 H, m).

(9) Methanolic methoxide does affect the $\gamma:\alpha$ ratio in the reaction of **3** with benzaldehyde. The ratio changes from *ca.* 1:1 in THF–DBU to 9:1 in methanol–sodium methoxide.

transoid allylic ylide 6[10] which is incapable of a cycloaddition process.

To determine the generality of γ substitution, we have examined the reaction of allylidenetriphenylphosphorane and benzaldehyde under more typical Wittig conditions. Treatment of allyltriphenylphosphonium fluoroborate with a small excess of *n*-butyllithium (positive Gilman test) in tetrahydrofuran followed by benzaldehyde and aqueous work-up affords 1-phenylbutadiene (65%). Under these conditions, 1,5-diphenylpenta-2,4-dien-1-ol is not formed in amounts detectable by thin layer chromatography. However, the dienol is formed in 11% yield in addition to 1-phenylbutadiene if the same experiment is performed without aqueous work-up and the THF solution is treated with DBU, benzaldehyde, and the fluroroboric acid salt of DBU to approximate the latter stages of reactions listed in Table I. Clearly, the γ-substituted vinylphosphonium salt **7** is formed to a small extent even under aprotic Wittig conditions, but requires a proton transfer agent (DBU·HBF_4 or methanol) in order to be converted into the hydroxyl ylide **8**.[11]



$$\mathrm{CH_2{=}CHCH_2\overset{+}{P}Ph_3 \xrightarrow{BuLi} CH_2{=}CHCH{=}PPh_3 \longrightarrow}$$

$$\mathrm{Ph\underset{O^-}{\underset{|}{C}}HCH_2CH{=}CH\overset{+}{P}Ph_3 + PhCH{=}CHCH{=}CH_2}$$

7

$$\downarrow$$

$$\mathrm{Ph\underset{OH}{\underset{|}{C}}HCH{=}CHCH{=}PPh_3 \xrightarrow{PhCHO} Ph\underset{OH}{\underset{|}{C}}HCH{=}CHCH{=}CHPh}$$

8

Allyl- or crotyltriphenylphosphonium salts also react with isobutyraldehyde (DBU, THF at reflux) to form dienols (10–20%) in addition to the dienes. We conclude that γ substitution of allyl ylides is general and probably has not been observed previously in the Wittig reaction because the initially formed salt (*i e.*, **7**) is not converted to dienol under aprotic conditions, and is discarded along with other polar byproducts in the course of aqueous work-up.

Experimental Section

2-(2-Butenyl)methyldiphenylphosphonium Fluoroborate.—A 250-ml three-neck flask was equipped with mechanical stirring and argon inlet and outlet. Lithium wire (1.3 g, 0.185 mol) cut into small pieces was added together with dry ether (60 ml) under argon and the mixture was cooled to −30° and stirred vigorously. (*E*)-2-bromobut-2-ene (5.4 g, 0.04 mol) was added dropwise over 20 min and the mixture was stirred for an additional 1 hr at −30°. The ether solution was transferred at −30° by syringe to a second flask, unreacted lithium being left behind. To this solution was added chlorodiphenylphosphine (Aldrich, distilled, 5.5 g, 0.025 mol) and the reaction mixture was stirred at −30° for 3 hr. Excess methyl iodide (17 g) was then added under argon and the reaction was allowed to stand at room temperature for 18 hr. The ether was evaporated to dryness, and the residue was taken up in methanol (*ca.* 100 ml) and stirred vigorously with a large excess of aqueous sodium fluoroborate. The product was then extracted into chloroform (3 × 50 ml), and the chloroform was dried over magnesium sulfate and evaporated under high vacuum. The residual yellow oil could not be crystallized but the nmr spectrum indicated <90% 2-(2-butenyl)methyldiphenylphosphonium fluoroborate, nmr ($CDCl_3$) δ 7.4–8 (10 H, m), 6.2–6.8 (1 H, m), 2.7 (3 H, d, J = 14 Hz), 2.1 (3 H, m), 1.6 (3 H, m).

Reaction of Allylic Phosphonium Salts with Benzaldehyde. General Procedure.—The phosphonium salt (0.005 mol), DBU (0.0055 mol), and benzaldehyde (0.025 mol) were dissolved in the appropriate solvent (dry tetrahydrofuran or reagent grade methanol, 10 ml) and allowed to react under nitrogen as indicated in Table I. The products were then extracted by aqueous pentane work-up. The pentane layer was concentrated, an internal standard (toluene) was added, and the diene yields were determined by glpc on 5 ft × 0.25 in. SE-30. The aqueous layer and all pentane—insoluble residues were then extracted with chloroform, and all of the organic fractions were combined and evaporated. The crude product was separated by preparative layer chromatography over silica gel using 4:1 hexane–ether. Three zones were observed in addition to polar base line material, R_f 0.8 (diene), 0.6–0.7 (recovered benzaldehyde), and 0.2–0.3 (dienol). All dienol products were oils and were characterized by nmr and exact mass. Elution of the base-line material with chloroform–ether afforded the phosphine oxide, generally in 3–8% higher yield than the combined yields of diene and dienol.

γ Substitution under Aprotic Conditions.—Allyltriphenylphosphonium fluoroborate (1.8 g, 0.0045 mol) suspended in dry tetrahydrofuran (25 ml) was treated dropwise with *n*-butyllithium (0.0046 mol) in hexane (3 ml) at 0°. Benzaldehyde (2.38 g, 0.0225 mol, freshly distilled) was then added to the homogeneous red solution and the reaction mixture was stored under nitrogen for 18 hr at 25°. Work-up as above afforded phenylbutadiene (65%, cis:trans 1:3) but no dienol by tlc analysis.

The above experiment was repeated. After overnight reaction of benzaldehyde with the ylide, 0.0045 mol each of DBU, DBU·$H^+BF_4^-$, and benzaldehyde was added, and the mixture was heated at reflux for 18 hr. Work-up as before afforded phenylbutadiene (52%) and 1-phenylpenta-2,4-dienol (11%). Addition of 3,4-dichlorobenzaldehyde after the initial Wittig condensation did not alter the product ratios and produced no new products by tlc or glpc analysis.

Registry No.—Benzaldehyde, 100-52-7; (*E*)-2-bromobut-2-ene, 3017-71-8; chlorodiphenylphosphine, 1079-66-9; methyl iodide, 74-88-4; sodium fluoroborate, 13755-29-8.

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[10] E. Vedejs, K. A. J. Snoble, and P. L. Fuchs, *J. Org. Chem.*, **38**, 1178 (1973).

[11] It is conceivable that **7** is not formed initially if the Wittig betaine has not completely decomposed to phenylbutadiene at the time that benzaldehyde, DBU, and DBU·HBF_4 are added. Dissociation of the betaine under protic conditions followed by readdition to form **7** could then explain formation of the dienol. To exclude this possibility, we have conducted a crossover experiment where 3,4-dichlorobenzaldehyde is added instead of benzaldehyde after the initial Wittig condensation. The products contain no trace of 3,4-dichlorophenylbutadiene, which would have to be formed if dissociation of the betaine plays any role in the reaction.

The Reaction of Triethylamine with *N*-*p*-Toluenesulfonylarylhydrazidoyl Chlorides

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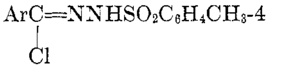
The reaction of triethylamine with *N*-*p*-toluenesulfonylhydrazidoyl chlorides (**2**) was investigated as a method for preparing nitrilesulfonimides (**1**).

$$\mathrm{ArC{\equiv}\overset{+}{N}\overset{-}{N}SO_2Ar}$$

1



$$\mathrm{Ar\underset{Cl}{\underset{|}{C}}{=}NNHSO_2C_6H_4CH_3\text{-}4}$$

2a, Ar = C_6H_5
b, Ar = 2,4,6-$(CH_3)_3C_6H_2$

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[1] Abstracted in part from the Ph.D. Thesis of J. N. K., 1973.