1580, 1460, 1415, 1395, 1380, 1255, 1200, 1175, 1120, 1080, 1030, 1010, 990, 960; MS, *m/e* (relative intensity) 317 (M + 1, 24), 316 (M^+, 70), 258 (20), 257 (100), 242 (11), 227 (10), 215 (21), 199 (11), 156 (9), 128 (14), 101 (10), 75 (12).

Anal. Calcd for $C_{16}H_{16}O_5N_2$: C, 60.75; H, 5.10; N, 8.86. Found: C, 60.35; H, 5.29; N, 8.66.

General Procedure for the Preparation of 2-Cyanoquinolines: 2-Cyano-6-methoxyquinoline (8b). A mixture of 6-methoxyquinoline (11.1 g, 70.0 mmol) in CH_2Cl_2 (140 mL) and H_2O (40 mL) containing KCN (13.70 g, 210 mmol, 3.0 equiv) was treated dropwise (30 min) with a solution of *p*-toluenesulfonyl chloride (*p*-TsCl; 22.0 g, 115.0 mmol, 1.6 equiv) in CH_2Cl_2 (150 mL) at 25 °C. After being stirred for 120 h at 25 °C, the mixture was filtered through Celite (washed with CH_2Cl_2, 4 × 30 mL) and the filtrate was concentrated in vacuo. The crude product was dissolved in $CHCl_3$ and passed through a plug of SiO_2 ($CHCl_3$ eluant). The combined $CHCl_3$ fractions were concentrated in vacuo and the product was recrystallized from ethanol–water, affording 10.40 g (12.81 g theoretical, 81%) of pure 8b: mp 175–176 °C (ethanol–water) (lit.[3] mp 177–178 °C); ^1H NMR ($CDCl_3$) δ 8.15 (1 H, d, J = 9 Hz), 8.04 (1 H, d, J = 9 Hz), 7.62 (1 H, d, J = 9. Hz), 7.42 (1 H, dd, J = 9, 2 Hz), 7.09 (1 H, d, J = 2 Hz), 3.96 (3 H, s, $ArOCH_3$); ^{13}C NMR ($CDCl_3$) δ 160.0 (C-6), 144.6 (C-8a), 135.6 (C-4), 131.5 (C-8), 130.8 (C-4a/C-2), 130.3 (C-2/C-4a), 124.6 (C-5), 123.8 (C-3), 117.9 (CN), 104.7 (C-7); IR (KBr) ν_{max} 2949, 2228, 1622, 1499, 1472, 1412, 1387, 1246, 1201, 1167, 1115, 1019, 860, 835 cm^{-1}; MS, *m/e* (relative intensity) 184 (M^+, base), 169 (8), 155 (12), 154 (37), 142 (4), 141 (63), 115 (4), 114 (28), 89 (4), 88 (5), 87 (4), 63 (5), 62 (6), 61 (2).

Anal. Calcd for $C_{11}H_8N_2O$: C, 71.72; H, 4.38; N, 15.21. Found: C, 71.45; H, 4.21; N, 15.00.

2-Cyanoquinoline (7b) (Table I): mp 94–95 °C (ethanol) (lit.[7] mp 91–93 °C); ^1H NMR ($CDCl_3$) δ 8.25 (1 H, d, J = 9 Hz), 8.25–8.05 (1 H, m), 7.82–7.55 (4 H, m); IR (KBr) ν_{max} 3016, 2234, 1501, 1304, 1215 cm^{-1}.

Acknowledgment. The financial support of the National Institutes of Health (CA 33668) and the Chicago Community Trust/Searle Scholars Program is gratefully acknowledged.

Registry No. **1a**, 119-65-3; **1a** Reissert intermediate, 3340-68-9; **1b**, 1198-30-7; **2a**, 36982-71-5; **2a** Reissert intermediate, 91523-13-6; **2b**, 58189-36-9; **3a**, 81925-37-3; **3a** Reissert intermediate, 91523-14-7; **3b**, 91523-06-7; **4a**, 91523-07-8; **4a** Reissert intermediate, 91523-15-8; **4b**, 91523-08-9; **5a**, 91523-09-0; **5a** Reissert intermediate, 91523-16-9; **5b**, 91523-10-3; **6a**, 91523-11-4; **6a** Reissert intermediate, 91523-17-0; **6b**, 91523-12-5; **7a**, 91-22-5; **7a** Reissert intermediate, 91523-18-1; **7b**, 1436-43-7; **8a**, 5263-87-6; **8a** Reissert intermediate, 91523-19-2; **8b**, 5467-79-8; 8-quinolinol, 148-24-3; 8-(benzyloxy)quinoline, 84165-42-4; 6-methoxy-5-nitroquinoline, 6623-91-2.

Activation of Reducing Agents. Sodium Hydride Containing Complex Reducing Agents. 20.[1] Pdc, a New, Very Selective Heterogeneous Hydrogenation Catalyst

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Catalytic semihydrogenation of acetylenes to (*Z*)-olefins constitutes a very important process in organic chemistry.[2] However, although numerous studies have been devoted to this problem,[3] no catalyst of general applicability has been reported so far that exhibits both quantitative bond selectivity (alkene/(alkene + alkane) ratio) and stereoselectivity ($Z/(Z + E)$ ratio).[4] Moreover, as underlined by Friefelder,[3] some catalysts which had been claimed to exhibit high selectivities and stereoselectivities appeared somewhat less successful since chromatographic techniques have been improved. So, numerous works are still aimed at devising highly selective catalysts.[5] Indeed, obtention of highly pure (*Z*)-olefins is often a key step during the synthesis of important substances such as pheromones,[6] biological or natural products,[7] etc.

Among the catalysts reported as efficient in performing selective semihydrogenations of acetylenes, the well-known Lindlar palladium[8] (used in the presence of quinoline) and the more recent P_2 nickel[9] (used in the presence of ethylenediamine) are the most usual.[6]

As part of our study on complex reducing agents,[10] we have recently described a new nickel heterogeneous hydrogenation catalyst (prepared from NaH, *t*-AmOH, and $Ni(OAc)_2$), referred to as Nic.[11] Nic exhibits selectivities and stereoselectivities comparable to those of P_2Ni for the semihydrogenation of acetylenes to (*Z*)-alkenes, even on a preparative scale.[12] The interesting outcomes of this study encouraged us to extend our investigations to catalysts prepared in the same way from other metallic salts.

We present here our first results concerning the atmospheric pressure semihydrogenation of acetylenes over Pdc (prepared from $Pd(OAc)_2$).

Results and Discussion

Preliminary experiments led us to find that the semihydrogenation of monosubstituted acetylenes must be conducted in solvents such as hexane or octane whereas the semihydrogenation of disubstituted ones must be conducted in ethanol, ethanol–hydrocarbon mixtures, or ethanol–THF mixtures.[13] Moreover, in all cases, the presence of quinoline as a catalyst modifier was found to be necessary. In these conditions, Pdc was found to allow highly selective, *self-terminating* semihydrogenations of acetylenes.

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(2) Gutmann, H.; Lindlar, H. In "Chemistry of Acetylenes", Viehe, H. G., Ed.; Marcel Dekker: New York, 1969.

(3) Augustine, R. L. "Catalytic Hydrogenation"; Marcel Dekker; New York, 1965. Friefelder, M. "Practical Catalytic Hydrogenation"; Wiley-Interscience: New York, 1971.

(4) Marwell, E. N.; Li, T. Synthesis **1973**, 457 and references cited therein.

(5) See, for example: Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.* **1981**, *46*, 5340; **1981**, *46*, 5344. Nitta, Y.; Imanaka, T.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1980**, *54*, 3579. Mauret, P.; Alphonse, P. *J. Org. Chem.* **1982**, *47*, 3322. Bogdanovic, B.; Gottsch, P.; Rubach, M. *J. Mol. Catal.* **1981**, *11*, 135. Johnstone, R. A. W.; Wilby, H. *Tetrahedron* **1981**, *37*, 3667. Rajaram, J.; Narula, A. P. S.; Chawla, H. P. S.; Dev, S. *Tetrahedron* **1983**, *39*, 2315. Suzuki, N.; Ayaguchi, Y.; Tsukanaka, T.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 353.

(6) See, for example: Henrick, C. A. *Tetrahedron* **1977**, *33*, 1845; Tetrahedron Rept. no. 34.

(7) See, for example: Bartlett, P. A. *Tetrahedron* **1980**, *36*, 3. Ackroyd, J.; Scheinmann, F. *Chem. Soc. Rev.* **1982**, *11*, 321.

(8) Lindlar, H. *Helv. Chim. Acta* **1952**, *35*, 446. Lindlar, H.; Dubuis, R. Org. Synth. **1966**, *46*, 89. Note, however, that a $Pd/BaSO_4$ catalyst, used in the presence of quinoline, has been reported to be superior to Lindlar catalyst in reproducibility and ease of preparation. Cram, D. J.; Allinger, N. L. *J. Am. Chem. Soc.* **1956**, *78*, 2518.

(9) Brown, C. A.; Ahuja, V. K. *J. Chem. Soc., Chem. Commun.* **1973**, 553. See also: Brown, H. C.; Brown, C. A. *J. Am. Chem. Soc.* **1963**, *85*, 1005. Brown, C. A.; Ahuja, V. K. *J. Org. Chem.* **1973**, *38*, 2226.

(10) For a review, see: Caubere, P. *Angew Chem., Int. Ed. Engl.* **1983**, *22*, 599.

(11) (a) Brunet, J. J.; Gallois, P.; Caubere, P. *Tetrahedron Lett.* **1977**, 3955. (b) Brunet, J. J.; Gallois, P.; Caubere, P. *J. Org. Chem.* **1980**, *45*, 1937.

(12) Gallois, P.; Brunet, J. J.; Caubere, P. *J. Org. Chem.* **1980**, *45*, 1946.

(13) Hydrogenation of disubstituted acetylene (in the presence of quinoline) over Pdc in hexane or octane was found to be extremely slow.

0022-3263/84/1949-4058$01.50/0

Scheme I

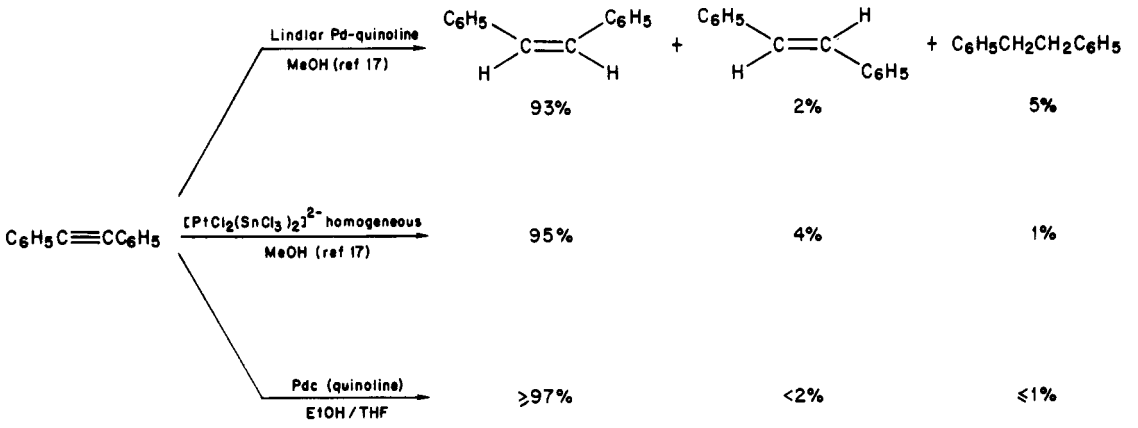

Table I. Semihydrogenation of Acetylenes over Pdc–Quinoline[a] at 20–21 °C (1 atm)

acetylene (10 mmol)	solvent (mL)	% olefin[b]	% fully saturated cmpd[b]	% selectivity (alkene/ alkene + alkane)	% (*Z*)-olefin[b]	% (*E*)-olefin[b]	% stereoselectivity (*Z*/(*Z* + *E*))
$C_6H_5C{\equiv}CH$	hexane (8)	98.5	1.5	98.5			
1-octyne	hexane (8)	98.7	1.3	98.7			
$C_6H_5C{\equiv}CCH_3$	EtOH (1) hexane (7)	99	1	99	98.4	0.6	99.4
2-hexyne	EtOH (4) octane (4)	99[c]	1	99	97.8[c]	1.2[c]	98.8
$C_6H_5C{\equiv}CC_6H_5$	EtOH (3) THF (5)	99	1	99	97.3	1.7	98.3

[a] Pd/acetylene ratio:1/50. Reaction performed with 2 mL of quinoline for 8 mL of other solvent(s). [b] Determined by GLC analysis on capillary columns (see Experimental Section) with internal standards. [c] Small amounts (0.1–0.2%) of 1-hexene were recorded.

The general basic procedure thus determined (see Experimental Section) was then used to perform the semihydrogenation of some representative acetylenes (Table I). Note that in order to provide synthetic chemists with results of practical interest, all results reported in this table have been determined by GLC analysis performed 20 min after complete cessation of hydrogen absorption. In all cases, no trace of any remaining acetylene could be detected.

Moreover, it is important to underline the high reproducibility of both the preparation of the catalyst and the hydrogenation procedure. Indeed, for more than 20 experiments conducted on $C_6H_5C{\equiv}CH$ (with Pdc's from different batches), a selectivity of 98.5 ± 0.3% was always obtained.

Complementary experiments led us to discover some interesting features. First of all, reaction of NaH (60 mmol) with $Pd(OAc)_2$ (10 mmol) in THF[14] led to a catalyst active for the hydrogenation of acetylenes to saturated hydrocarbons. However, even in the presence of quinoline, this material did not allow self-terminating semihydrogenations.[15] Compared hydrogenation curves are given in Figure 1. This observation indicates, once more, the dramatic effect of alkoxides in such catalysts.

Second, not reported experiments performed with phenylacetylene as substrate showed that (i) quinoline was a more efficient inhibitor than pyridine, ethylenediamine, piperidine, triethylamine, dimethylbenzylamine, and 1,2,3,4-tetrahydroquinoline, (ii) using 2 mL of quinoline for 8 mL of hexane led to the same result as using 10 mL of pure quinoline, (iii) with quinoline as inhibitor, hexane, octane, benzene, THF, and DME allowed selectivities ≳98% whereas ethanol and AcOEt did not allow self-terminating semihydrogenations.[16]

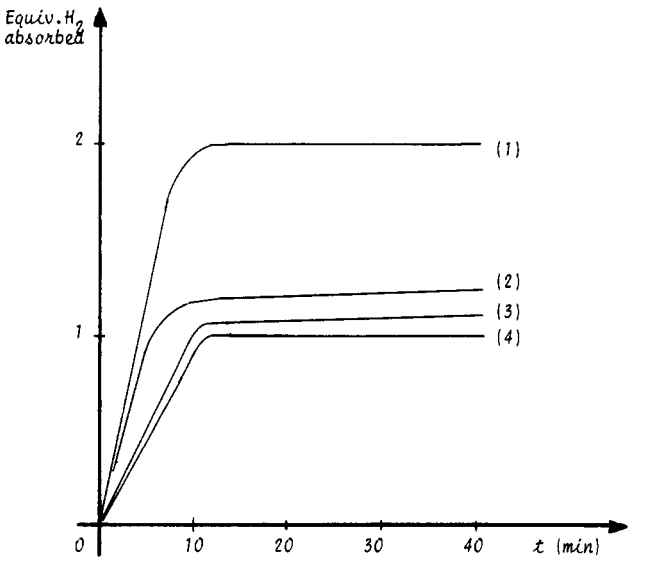

Figure 1. Hydrogenation of 10 mmol of $C_6H_5C{\equiv}CH$ in hexane: ratio Pd/substrate, 1/50 mmol. (Curve 1) catalyst NaH–$Pd(OAc)_2$, hexane (10 mL); (curve 2) catalyst NaH–$Pd(OAc)_2$, hexane (8 mL), quinoline (2 mL); (curve 3) catalyst Pdc, hexane (10 mL); (curve 4) catalyst Pdc, hexane (8 mL), quinoline (2 mL).

Finally, the temperature effect (generally recognized as an important parameter)[17] was also studied. In fact, we found that, in agreement with some authors, the best results are generally obtained by starting the hydrogenation

(14) Reaction performed for 3 h in 40 mL of refluxing THF.

(15) Hydrogenation of phenylacetylene (10 mmol) in hexane (8 mL)–quinoline (2 mL) with 0.2 mmol of this catalyst exhibited a breakdown of the hydrogenation curve only near 1.2 hydrogen equiv absorption and then practically ceased; GLC analyses of the reaction mixture indicated a selectivity <90%.

(16) Elyassini, J. DEA Nancy, 1982, unpublished results.

(17) See, for example: Hennion, G. F.; Schroeder, W. A.; Lu, R. P.; Scanlon, W. B. *J. Org. Chem.* **1956**, *21*, 1142. Payne, G. B. *J. Org. Chem.* **1962**, *27*, 3819. Kimel, W.; Sax, N. W.; Kaiser, S.; Eichmann, G. G.; Chase, G. O.; Ofner, A. *J. Org. Chem.* **1958**, *23*, 153.

at 20–21 °C. (In this case, the temperature increases up to 31–33 °C and then decreases as soon as 1 hydrogen equivalent has been absorbed). Indeed, we found that conducting these semihydrogenations in thermostated flasks at +10 °C, –6 °C, or –20 °C generally resulted in a poorer selectivity without significant improvement of the stereoselectivity. However, hydrogenation of diphenylacetylene appeared to be an exception. Indeed, in this case, the temperature effect was found to be more important, at least with some solvent combinations. For example, in EtOH/THF (1/1) mixtures, the following results were obtained (T °C, Z/E/saturated): +21 °C, 95.4/2.9/1.7; +10 °C, 96.6/2.2/1.2; –20 °C, 97.2/1.6/1.2. However, it must be noted that a comparable result could be obtained at 21 °C by changing the solvent in EtOH/THF (3/5) mixtures (Table I).

Pdc thus appears as very selective and stereoselective. A direct comparison with some of the best catalysts reported so far is possible, owing to a recent, careful, study by Friedlin et al.[18] of the semihydrogenation of diphenylacetylene. Among the many group VIII metal catalysts studied, these authors found that the more selective and stereoselective were Lindlar Pd and $[PtCl_2(SnCl_3)]^{2-}$, this latter being reported as the only one that allows a self-terminating semihydrogenation. The results summarized in the scheme clearly indicate that Pdc is superior to the above catalysts, both for selectivity and stereoselectivity.

A comparison of Pdc with P_2Ni[9] is also important since P_2Ni often appeared more stereoselective than Lindlar Pd.[19] In the cases where a direct comparison is possible,[9] it is clear that Pdc is at least as stereoselective as P_2Ni, and above all, more selective.[20]

In conclusion, the present work shows that Pdc, very easy to obtain with a high reproducibility, from NaH, t-AmOH, and $Pd(OAc)_2$ may be presently considered as one of the best catalysts for the semihydrogenation of simple acetylenes to (Z)-alkenes. Extension of these results to more complex substrates is being pursued and will be reported later.

Experimental Section

Fluka sodium hydride (50–60% in oil)[21] was used and washed twice with THF in the reaction flask under nitrogen. Badische Anilin reagent grade THF was distilled from benzophenone–sodium couple before use. (The absence of peroxides was tested before each run). Fluka palladium acetate was dried under vacuum for 24 h at 80 °C. t-AmOH (2-methyl-2-butanol) was distilled from sodium. All acetylenes were commercial (Fluka or Aldrich). They were purified (distillation, recrystallization, or column chromatography) just before use. In each case they were checked by GLC analysis and found to be free of any possible hydrogenation product. Synthetic quinoline was distilled just before use. Nitrogen R, argon U, and hydrogen (L'Air Liquide) were used. GLC analyses (SE-30 or Carbowax capillary columns) were performed with a 7100 Spectra Physics apparatus (flamme ionization detector) equipped with a 4100 SP computing integrator. In all the cases studied, all compounds likely to be formed were available and GLC analyses were performed in such conditions that they all gave base-line separated signals.

Preparation and Storage of the Catalyst. Pdc was prepared from NaH (60 mmol), t-AmOH (20 mmol), and $Pd(OAc)_2$ (10 mmol) in THF (50 mL) following the procedure previously reported for the preparation of Nic.[11] Addition of t-AmOH was started at 40 °C as it was very important not to exceed 45 °C during either step of the preparation. After 3 h of stirring at 45 °C, the catalyst was ready for use. It was syringed and stored under argon in air-tight bottles in which was placed a magnetic stirrer in order to homogenize the suspension before each sampling (1 mL, 0.2 mmol catalyst).

Semihydrogenation of Acetylenes. All experiments were conducted with a classical apparatus for atmospheric pressure hydrogenations equipped with the modified hydrogenation vessel we have previously described.[11b]

Hydrogenations were performed on a 10-mmol substrate scale (catalyst/substrate ratio; 1/50). Reactants were introduced into the reaction vessel in the following order: solvent (6 mL), quinoline (2 mL), Pdc (0.2 mmol). Then hydrogen was introduced after purging the apparatus 3 times and stirring was then started. After 10 min of stirring (2500 rpm monitored by a stroboscope), the acetylene (10 mmol) with 2 mL of solvent was syringed in the reaction vessel through a septum cap. The progress of the hydrogenation was then followed in a classical manner. All others experimental details may be found in the previous publications on Nic.[11,12]

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Registry No. Pd, 7440-05-3; t-AmOH, 75-85-4; $Pd(OAc)_2$, 3375-31-3; NaH, 7646-69-7; $C_6H_5C{\equiv}CH$, 536-74-3; $C_6H_5CH{=}CH_2$, 100-42-5; $H_2C{=}CH(CH_2)_5CH_3$, 111-66-0; (Z)-$C_6H_5CH{=}ChCH_3$, 766-90-5; (E)-$C_6H_5CH{=}CHCH_3$, 873-66-5; (Z)-$H_3CCH{=}CHCH_2CH_2CH_3$, 7688-21-3; (E)-H,3CCH=$CHCH_2CH_2CH_3$, 4050-45-7; (Z)-$C_6H_5CH{=}CHC_6H_5$, 645-49-8; (E)-$C_6H_5CH{=}CHC_6H_5$, 103-30-0; $C_6H_5CH_2CH_3$, 100-41-4; $H_3C(CH_2)_6CH_3$, 111-65-9; $C_6H_5CH_2CH_2CH_3$, 103-65-1; $H_3C(CH_2)_4CH_3$, 110-54-3; $C_6H_5CH_2CH_2C_6H_5$, 103-29-7; 1-octyne, 629-05-0; 2-hexyne, 764-35-2; 1-phenylpropyne, 673-32-5; diphenylacetylene, 501-65-5; quinoline, 91-22-5.

(18) Litvin, E. F.; Friedlin, L. Kh.; Krokhmaleva, L. F.; Kozlova, L. M.; Nazarova, N. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1981**, *4*, 811 (English translation).

(19) Semihydrogenation of alkynes over Lindlar Pd often led to large amounts of E isomers. See, for example: Dobson, N. A.; Eglington, G.; Krishnamurti, M.; Raphael, R. A.; Willis, R. G. *Tetrahedron* **1961**, *16*, 16.

(20) It can be inferred from results reported in ref 9 that P_2Ni generally led to the formation of 2–4% of overhydrogenated compounds.

(21) Titration of each batch before use was carried out by classical techniques. See: Plesek, J.; Hermanek, S. "Sodium Hydride"; Iliffe: London, 1968.

Syntheses of Macrocyclic Acetals via Cyclization of α,ω-Diols with an Intermediate from Diphenyldiazomethane and 2,3-Dichloro-5,6-dicyanobenzoquinone

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There are numerous procedures available for the syntheses of acetals.[1,2] Conventional methods include the conversion of aldehydes and ketones into their corresponding acetals by use of alcohols in the presence of acidic catalysts such as p-toluenesulfonic acid.[3] These well-known methods, however, fail completely or give low yields when the product is a strained cyclic acetal or an acetal of unusually low stability.

Recently, we developed a new synthetic method for cyclic and noncyclic diphenyl acetals and macrocyclic crown ether acetals that makes use of a redox reaction of diphenyldiazomethane (DDM) with 2,3-dichloro-5,6-di-

(1) Schmitz, E.; Eichhorn, J. In "The Chemistry of the Ether Linkage"; Patai, S., Ed.; Wiley: London, 1967; Chapter 7.

(2) Bergstrom, R. G. In "The Chemistry of Ethers, Crown Ethers, Hydroxy Groups and Their Sulphur Analogues"; Patai, S., Ed.; Wiley: Chichester, 1980; Chapter 20.

(3) Lorette, N. B.; Howard, W. L. *J. Org. Chem.* **1961**, *26*, 3112.

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