reaction mixture of B. The product was isolated quantitatively by column chromatography (benzene): wax; IR (neat) 3300, 1710, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.84 (d, 2 H, J = 6.4 Hz, $COCH_2$) 3.66-3.77 (m, 5 H, OCH_3 and $BrCH_2$), 5.23-5.47 (m, 1 H, OCH), 6.70 (br, 1 H, NH), 7.20-7.30 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 34.0, 37.4, 52.1, 69.6, 118.8, 123.7, 129.0, 137.4, 152.1, 170.1.

1-Phenyl-4-hydroxy-2-pyrrolidinone (19). Compound **2** (0.42 g, 1.8 mmol) was dissolved in 10 mL of acetone and 20 mL of HCl solution (6 N). The mixture was heated at reflux for 24 h and then quenched by the addition of aqueous KOH (2 N). The mixture was diluted with ether (50 mL) and washed with brine, and the ether layer was dried over $MgSO_4$. Removal of ether left a colorless oil, which was chromatographed over silica gel: mp 87 °C (lit.[15] mp 88 °C); IR (KBr) 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10 (br, 1 H, OH), 2.50-3.10 (m, 2 H, CH_2C=O), 3.60-4.20 (m, 2 H, NCH_2), 4.50-4.80 (m, 1 H, OCH), 7.10-7.70 (m, 5 H, Ph); MS m/z 177 (M^+).

1-Phenyl-*cis*-3-benzyl-4-hydroxy-2-pyrrolidinone (20): mp 110-111 °C; IR (KBr) 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (br, 1 H, OH), 2.95-3.05 (m, 2 H, CHC=O), 3.36 (dd, 1 H, J = 2.9 and 13.2 Hz, one of $PhCH_2$), 3.72 (dd, 1 H, J = <1.0 and 11.2 Hz, one of NCH_2), 3.98 (dd, 1 H, J = 4.2 and 12.0 Hz, one of NCH_2), 4.39 (m, 1 H, OCH), 7.34-7.40 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 29.3, 50.6, 55.7, 64.0, 118.8, 123.4, 125.6, 128.0, 128.6, 128.6, 139.7, 140.3, 173.2; MS m/z 267 (M^+). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.15; H, 6.32; N, 5.33.

***N*-Phenyl-3-phenyl-5-[(methoxycarbonyl)methyl]-1,3-oxazolidin-2-imine (21)**: Bu_3SnOMe (1.60 g, 5 mmol) was added to 1 (0.83 g, 5 mmol) in benzene (5 mL) under nitrogen atmosphere. This mixture was stirred at 80 °C for 4 h to give the intermediate A. The solution was cooled to room temperature, and diphenylcarbodiimide (PhN=C=NPh) (0.97 g, 5 mmol) was added. After 10 min, HMPA (0.9 g, 5 mmol) was added, and heated at 60 °C for 1 h. Solvent was removed under reduced pressure, and the residue was chromatographed on silica gel. The byproduct, Bu_3SnBr, was removed easily by using hexane as an eluent, and with benzene, the product **21** was obtained as white needles which was purified by recrystallization from benzene-hexane: mp 125-126 °C; IR (KBr) 1660, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40-2.90 (m, 2 H, OC=OCH_2), 3.71 (s, 3 H, OCH_3), 3.95-4.60 (m, 2 H, NCH_2), 4.80-5.05 (m, 1 H, OCH), 6.90-7.70 (m, 10 H, Ph); MS m/z 310 (M^+).

***N*-Phenyl-5-[(methoxycarbonyl)methyl]-1,3-oxathiolan-2-imine (22).** To the solution of A was added phenyl isothiocyanate (PhN=C=S) (0.68 g, 5 mmol) at room temperature. After 10 min, HMPA (0.90 g, 5 mmol) was added, and the mixture was heated at 60 °C for 1 h. Solvent was removed under reduced pressure, and the residue was chromatographed on silica gel. With benzene as an eluent, **22** was isolated as a colorless oil: wax; IR (neat) 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.60-3.10 (m, 2 H, OC=OCH_2), 3.40-4.50 (m, 5 H, NCH_2 and OCH_3), 4.80-5.30 (m, 1 H, OCH), 6.90-7.70 (m, 5 H, Ph); MS m/z 251 (M^+).

5-[(Methoxycarbonyl)methyl]-1,3-dioxolan-2-one (23). Carbon dioxide was bubbled through a solution of A at room temperature. After 1 h, HMPA (0.90 g, 5 mmol) was added, and the mixture was heated at 60 °C for 1 h. Solvent was removed under reduced pressure, and the residue was chromatographed on silica gel. With benzene as an eluent, **23** was isolated as a colorless oil: wax; IR (neat) 1740, 1800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.60-3.20 (m, 2 H, OC=OCH_2), 3.74 (s, 3 H, OCH_3), 4.22 (dd, 1 H, J = 6.9, 8.7 Hz, one of OCH_2), 4.67 (t, 1 H, J = 8.7 Hz, one of OCH_2), 4.90-5.20 (m, 1 H, OCH); MS, m/z 160 (M^+).

1-Tosyl-3-phenyl-[5-(methoxycarbonyl)methyl]-1,3-imidazolidin-2-one (25). Bu_3SnOMe (1.85 g, 5 mmol) was added to β-lactam **24** (1.94 g, 5 mmol) in benzene (5 mL) under nitrogen atmosphere. This solution was stirred at 80 °C for 4 h to form F. The IR absorption at 1780 cm^{-1} due to the β-lactam ring shifted to 1710 cm^{-1}. This solution was cooled to room temperature, and PhN=C=O (0.60 g, 5 mmol) and HMPA (0.90 g, 5 mmol) were added. After heating at 60 °C for 1 h, the mixture was chromatographed on silica gel. The byproduct, Bu_3SnBr, was removed easily by using hexane as an eluent. With benzene, **25** was obtained as white needles and was purified by recrystallization from benzene-hexane: mp 148-149 °C; IR (KBr) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.43 (s, 3 H, $ArCH_3$), 2.84 (dd, 1 H, J = 10.0 and 16.9 Hz, one of OC=OCH_2), 3.36 (dd, 1 H, J = 3.2 and 16.9 Hz, one of OC=OCH_2), 3.61 (dd, 1 H, J = 3.9 and 9.8 Hz, oen of NCH_2), 3.71 (s, 3 H, OCH_3), 4.17 (t, 1 H, J = 9.8 Hz, one of NCH_2), 4.65-4.80 (m, 1 H, NCH), 7.00-8.20 (m, 9 H, Ar); ^{13}C NMR ($CDCl_3$) δ 21.6, 39.5, 48.8, 49.7, 52.0, 118.7, 124.4, 128.3, 128.9, 129.6, 135.6, 138.1, 145.0, 151.2, 170.5; MS m/z 388 (M^+). Anal. Calcd for $C_{19}H_{20}N_2O_5S$: C, 58.75; H, 5.19; N, 7.21. Found: C, 58.63; H, 5.14; N, 7.10.

Registry No. **1**, 125762-98-3; **2**, 125762-99-4; **3**, 125763-00-0; **4**, 125763-01-1; **5**, 125780-99-6; **6**, 125827-29-4; **7**, 125763-02-2; **8**, 125763-03-3; **9**, 125763-04-4; **10**, 125763-05-5; **11**, 125763-06-6; **12**, 125763-07-7; **13**, 125763-08-8; **14**, 125763-09-9; **15**, 125827-30-7; **16**, 125763-10-2; **17**, 125763-11-3; **18**, 125763-12-4; **19**, 125763-13-5; **20**, 125763-14-6; **21**, 125763-15-7; **22**, 125763-16-8; **23**, 125763-17-9; **24**, 125780-87-2; **25**, 125763-18-0; H_2C=$CHCH(CH_3)CO_2H$, 50304-40-0; H_2C=$CHCH(Bu)CO_2H$, 125763-19-1; H_2C=$CHCH(CH_2Ph)CO_2H$, 89022-02-6; H_2C=$CHCH_2CO_2H$, 625-38-7; (*E*)-$EtCH$=$CHCH_2CO_2H$, 1577-18-0; (*E*)-$H_3C(CH_2)_3CH$=$CHCH_2CO_2H$, 5163-67-7; Bu_3SnOMe, 1067-52-3; PhNCO, 103-71-9; *p*-MeC_6H_4NCO, 622-58-2; *p*-ClC_6H_4NCO, 104-12-1; *p*-$MeC_6H_4SO_2NCO$, 4083-64-1; PhN=C=NPh, 622-16-2; PhNCS, 103-72-0.

Acetyl Chloride Promoted Cyclopropanations of Alkenes with Dibromomethane Using Zinc Dust and Copper(I) Chloride in Ether

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Acetyl chloride strongly accelerates the cyclopropanation reactions of alkenes with dibromomethane or diiodomethane using zinc dust and copper(I) chloride in ether and results in improved yields of cyclopropane products.

We have recently reported[1] our discovery that the addition of catalytic amounts of titanium(IV) chloride strongly promotes the rates of cyclopropanation of alkenes in ether with dibromomethane or diiodomethane using zinc dust and copper(I) chloride. Satisfactory yields of cyclopropanation products, however, were only obtained when using this method with simple hydrocarbon alkenes not bearing Lewis acid sensitive functional groups.

We now disclose that the replacement of titanium(IV) chloride by as little as 1 mol % of acetyl chloride based on zinc not only strongly accelerates alkene cyclo-

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Table I. Comparison of Yields of Acetyl Chloride Promoted Cyclopropanations of Various Alkenes Using Dibromomethane, Zinc Dust, and Copper(I) Chloride in Ether with Those of Other Procedures

	yield of cyclopropane product, %			
starting alkene	CH_2Br_2, CH_3COCl promoted[a,b]	CH_2Br_2, $TiCl_4$ promoted[a,c]	CH_2Br_2, not promoted (ref)[d]	CH_2I_2, not promoted (ref)[d]
1-octene	61	48	18 (4)	48 (5)
cyclohexene	61	58	38 (6)	57 (7)
cyclooctene	88	73	28 (6)	58 (8)
indene	33	–	22 (9)	30 (10)
2-carene	76	–	–	45 (11)
3-carene	76	–	–	43 (11)
α-pinene	53[e]	52	–	21 (11)
β-pinene	67	74	–	28 (12)
crotyl alcohol	58	26	68 (13)	54 (14)
3,4-dihydro-2*H*-pyran	45	17	–	65 (15)
(1-cyclohexenyloxy)-trimethylsilane	60	–	–	65 (16)
1-pyrrolidino-1-cyclohexene	22	–	–	8 (17)

[a] Yields are for distilled material and are based on starting alkene. [b] Reactions were generally carried out at 45–50 °C for 1–2 h on a 0.1- or 0.2-mol alkene scale in 75 or 125 mL of ether using a 1:3:4 mole ratio of alkene to dibromomethane to zinc, using 10 mol % copper(I) chloride and 2 mol % acetyl chloride based on zinc, and with the dibromomethane added in portions. [c] Reactions were generally carried out at 45–50 °C for 2 h in 100 mL of ether on a 0.2-mol alkene scale using a 1:3:4 mole ratio of alkene to dibromomethane to zinc and 10 mol % of copper(I) chloride based on zinc and 2 mol % titanium(IV) chloride based on dibromomethane.[1] [d] Reactions were carried out under a variety of conditions given in the original references cited. [e] About 20% unreacted alkene was recovered.

propanations using the inexpensive, convenient dibromomethane with zinc dust and copper(I) chloride but also causes no special problems with Lewis acid sensitive substrates. Thus, this new procedure replaces the titanium(IV) chloride method[1] and our earlier method employing ultrasonic cavitation[2] for facilitation of the use of dibromomethane in alkene cyclopropanations. Furthermore, in most cases the yields of cyclopropane products formed are better than those obtained using other procedures including those employing diiodomethane.[3]

Table I presents the yields of cyclopropanation products obtained after a reaction period of 1–2 h from a variety of structurally different alkenes using dibromomethane with acetyl chloride promotion, and compares them with the corresponding yields obtained using dibromomethane with titanium(IV) chloride or no promotion as well as using diiodomethane with no promotion. For the cases of the nonpromoted runs using dibromomethane or diiodomethane, reaction times of 20–30 h or greater are common. For the acetyl chloride promoted runs no special drying of reagents or precautions to keep water or air away from the reaction mixtures were employed. With all of the reactions, material balances were excellent. Except for the one case noted, alkene conversions were >95%. It is seen from the Table that in most cases the acetyl chloride promoted dibromomethane reactions give yields that are as good as or better than those obtained under the other conditions listed.

Acetyl chloride was also found to be beneficial both for the rates and yields of products in the reactions of alkenes in ether with diiodomethane. With the hydrocarbon alkenes which were examined, the yields obtained after 1–2 h reaction using 1:2:3 mole ratios of alkene to diiodomethane to zinc dust and 2 mol % of acetyl chloride and 10 mol % of copper(I) chloride based on zinc were similar (cyclohexene, 56%; β-pinene, 73%) to those found using dibromomethane. On the other hand, with the oxygen function containing alkenes examined, the yields for the acetyl chloride promoted reactions using diiodomethane (3,4-dihydro-2*H*-pyran, 72%; 1-cyclohexenyloxytrimethylsilane, 78%) were somewhat better than those found using dibromomethane. This may be related to the lower Lewis acid strength and lower concentrations (due to lower alkene to diiodomethane mole ratios) of the zinc iodide side product formed in the diiodomethane reactions as compared to that of the zinc bromide formed in the dibromomethane reactions. It may also be due to the more rapid reaction of diiodomethane with zinc, thus decreasing the amount of zinc halide catalyzed side reaction of unreacted dihaloalkane with the alkene.[18] With the single nitrogen function containing alkene examined, 1-pyrrolidino-1-cyclohexene, the yield with diiodomethane (4%) was considerably lower than that obtained using dibromomethane (22%). This may be due to the higher reactivity of diiodomethane to nucleophilic attack by the enamine.

In the acetyl chloride promoted cyclopropanations the rates of reaction are so rapid that in larger scale preparations the dihaloalkanes have to be added gradually in portions to keep the reactions from going out of control. This is due both to the exothermicity of the rapid reactions and also to a side reaction in which ethylene, formed by coupling of the dihalomethane, is evolved.[19] Generally, however, the reactions can be completed in 1–2 h. The ethylene-forming side reaction, which we have found to be more pronounced with dibromomethane than with diiodomethane, is not unique to the acetyl chloride promoted cyclopropanations but is also seen under other conditions. However, under the usual nonpromoted reaction conditions, ethylene formation is not rapid enough to cause problems with condensation of the boiling ether solvent.

Concerning the mode of action of the acetyl chloride in promoting the reactions of alkenes and dihaloalkanes with zinc dust and copper(I) chloride, we have observed that increasing the amount of acetyl chloride used over a 10-fold concentration range has no significant effect on the reac-

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tion rate. Also, it was noted by ^1H NMR examination of a reaction of acetyl chloride in ether with zinc dust and copper(I) chloride at room temperature that after about 15 min an exothermic reaction occurred in which ethyl acetate and ethyl chloride were formed.[20]

Further information of relevance to questions concerning the promoting action of acetyl chloride can be deduced from our early observation that titanium(IV) chloride[1] and later independent observation that chlorotrimethylsilane[21] also act as efficient promoters for cyclopropanations of alkenes with dihalomethanes. We had initially thought that the action of titanium(IV) chloride may have been due to the formation of an organotitanium intermediate. However, the observations that chlorotrimethylsilane and acetyl chloride exhibit perhaps even greater efficacy in their promoting ability casts serious doubt on this.

We now suggest that the effects of all three cyclopropanation promoters may be just to react with water and other hydroxylic impurities present in the solvent and reactants. This may "super dry" the reaction mixture, something which is known to be helpful in getting reluctant reactions of alkyl halides and metals to start. At the same time some HCl is released which may aid in cleaning the oxide coating off the surface of the zinc, another process known to be important in zinc activation.[22]

Studies are in progress to learn more of the mechanisms of promotion of reactions of dihaloalkanes with zinc dust and copper(I) chloride by acetyl chloride as well as by titanium(IV) chloride and chlorotrimethylsilane. Also, investigations of the extension of the promoting ability of acetyl chloride to other reactions involving alkyl or aryl halides and metals are being carried out.

Experimental Section

Methods. Boiling points are uncorrected. ^1H and ^{13}C NMR spectra were measured at 300 MHz with a GE QE-300 instrument. The physical properties and spectral data for products previously prepared[1,2] were identical with those given earlier and thus are not repeated here. Compositions of distilled reaction mixtures were determined by GLC methods using a SE-30 or Carbowax 20M column. Zinc dust, copper(I) chloride, and anhydrous ether (Fischer Scientific), dibromomethane, diiodomethane, and acetyl chloride (Aldrich) were used without further purification. The various alkenes, with the exception of (1-cyclohexenyloxy)trimethylsilane,[23] were obtained commercially and when necessary redistilled before use.

General Procedure for Acetyl Chloride Promoted Cyclopropanations Using Dibromomethane. A 500-mL, three-neck, round-bottom flask is fitted with a double condenser system (Allihn on bottom, Friedrich on top) and a mechanical stirrer. For a 0.2 mol scale alkene cyclopropanation, the zinc dust (52.3 g, 0.80 mol), copper(I) chloride (7.92 g, 0.080 mol), about 75 mL of ether, and 1 equiv (34.8 g, 0.20 mol) of the dibromomethane based on alkene are added to the flask in the order indicated. Immediately following the addition of the acetyl chloride promoter (1.26 g, 0.016 mol) by syringe, a stoppered pressure-equalizing dropping funnel containing the alkene (0.20 mol) and about 25 mL of ether is fitted to the remaining neck of the flask, a preheated oil bath (45–50 °C) is raised to heat the flask, and stirring is commenced. After about 5 min, at which time reflux has begun and the initially light gray suspension has become dark gray, the alkene/ether mixture is added dropwise over a period of several minutes. A mixture of the remaining dibromomethane (69.5 g, 0.40 mol) and about 25 mL of ether are then placed in the dropping funnel and added to the reaction mixture in portions over a period of about 30 min at a rate such as to maintain a managable reflux.

Upon completion of the reaction (usually within 1 h following the addition of all reagents), as indicated by a slowing in the rate of reflux or, if desired, by a slowing or stopping of gas evolution from the reaction mixture as indicated by a gas bubbler attached to the Friedrich condenser, the contents of the reaction flask are transferred to a large Erlenmeyer flask, cooled in an ice bath, and treated with 125 mL of saturated aqueous ammonium chloride. Initial addition of the ammonium chloride must be done dropwise to avoid serious foaming. The solids are removed by vacuum filtration using a Büchner funnel, and the flask and filtered solids are washed with several portions of pentane and saturated ammonium chloride solution. (**Caution**! Potential fire hazard if air is drawn through the zinc residue. The residue should be thoroughly wet with water before disposal.) The aqueous layer of the filtrate is washed twice with 50-mL portions of pentane, and the combined organic layers are washed three times with 100-mL portions of 10% aqueous sodium hydroxide and once with saturated aqueous sodium chloride solution. After drying over anhydrous sodium sulfate, the solvents are removed on a steam bath through a Vigreux column or on a rotary vacuum evaporator and the remaining oil is distilled.

Physical Constants and Spectroscopic Data for Cyclopropanation Products Not Reported Recently[1,2] from This Laboratory. (a) From Indene. The cycloprop[*a*]indene product was collected at bp 68–82 °C (10 Torr) [Lit.[9] bp 85 °C (18.5 Torr)]: ^1H NMR ($CDCl_3$) δ 0.02, 1.01, 1.78, 2.30 (all m, 1 H), 2.89 (d, J = 17 Hz, 1 H), 3.13 (dd, J = 17 and 6.7 Hz, 1 H), 7.05 (m, 3 H), and 7.25 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.0, 16.7, 23.9, 35.4, 123.3, 125.3, 125.4, 125.8, 141.8, and 147.0.

(b) From 2-Carene. The 3,3,7-trimethyltricyclo[5.1.0.0^{2,4}]-octane product was collected at bp 84–92 °C (40 Torr): n^{23}_D 1.4682 [lit.[11] bp not given, n^{20}_D 1.4678]; ^1H NMR ($CDCl_3$) δ 0.09 (br t, 1 H), 0.42–0.54 (m, 3 H) 0.60 (br d, 1 H), 0.95 (s, 3 H), 0.97 (s, 3 H), 1.0 (m, 1 H), 1.01 (s, 3 H), 1.14, 1.57, 1.65 (all m, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.5, 15.8, 16.1, 17.0, 18.7, 19.8, 21.6, 21.9, 25.4, 28.5, 29.9.

(c) From 3-Carene. The 1,4,4-trimethyltricyclo[5.1.0.0^{3,5}]-octane product was collected at bp 88–96 °C (40 Torr): n^{25}_D 1.4694 [lit.[11] bp not given, n^{20}_D 1.4688]; ^1H NMR ($CDCl_3$) δ 0.07 (br dd, 1 H), 0.29 (m, 2 H), 0.40 (m, 1 H), 0.49 (m, 1 H), 0.79, 0.97, 1.00 (all s, 3 H), 1.10 (br dd, 1 H), 1.38 (br dt, 1 H), 1.90 (dd, J = 14.7 and 9.5 Hz, 1 H), 1.98 (ddd, J = 14.7, 9.5, 1.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.6, 12.6, 15.0, 15.1, 16.5, 16.9, 17.2, 17.5, 23.5, 25.7, 28.3.

(d) From (1-Cyclohexenyloxy)trimethylsilane. The (bicyclo[4.1.0]hept-1-yloxy)trimethylsilane product obtained under the usual conditions, except with washing of the organic layer being done rapidly with the 10% NaOH at 0 °C and repeatedly with saturated aqueous NaCl until a neutral aqueous layer was obtained, was collected at bp 73–82 °C (15 Torr) [lit.[16] bp 84–87 °C (17 Torr)]: ^1H NMR ($CDCl_3$) δ 0.10 (s, 9 H), 0.26 (br t, 1 H), 0.79 (ddd, J = 10.7, 5.3, and 1.4 Hz, 1 H), 1.05 (m, 2 H), 1.20 (m, 2 H); 1.34, 1.45, 1.87, 1.98, 2.08 (all m, 1 H); ^{13}C NMR ($CDCl_3$) δ 1.3 (3 C), 18.5, 19.2, 21.4, 21.8, 24.5, 32.5, 56.3.

(e) From 1-Pyrrolidino-1-cyclohexene. The 1-pyrrolidinobicyclo[4.1.0]heptane product was prepared using a modified workup procedure[17] and was collected at bp 73–83 °C (5 Torr) [lit.[17] bp 70–74.5 °C (4 Torr)]: ^1H NMR ($CDCl_3$) δ 0.17 (dd, J = 5.8 and 4.4 Hz, 1 H), 0.67 (dd, J = 10.0 and 4.4 Hz, 1 H), 1.00 (m, 2 H), 1.22 (m, 3 H), 1.56 (m, 2 H), 1.68 (m, 4 H), 1.85 (m, 2 H), 2.60 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 18.3, 19.5, 21.1, 22.6, 22.7, 23.6 (2 C), 24.1, 38.1, 47.4 (2 C).

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Registry No. CH_2Br_2, 74-95-3; CH_3COCl, 75-36-5; 1-octene, 111-66-0; 1-hexylcyclopropane, 4468-61-5; cyclohexene, 110-83-8; bicyclo[4.1.0]heptane, 286-08-8; cyclooctene, 931-88-4; bicyclo-

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[6.1.0]nonane, 286-60-2; indene, 95-13-6; cycloprop[a]indene, 15677-15-3; 2-carene, 554-61-0; 3,3,7-trimethyltricyclo-[5.1.0.0^{2,4}]octane, 33046-07-0; 3-carene, 13466-78-9; 1,4,4-trimethyltricyclo[5.1.0.0^{3,5}]octane, 125495-68-3; α-pinene, 80-56-8; 2,7,7-trimethyltricyclo[4.1.1.0^{2,4}]octane, 32549-17-0; β-pinene, 127-91-3; 6,6-dimethylspiro[bicyclo[3.1.1]heptane-2,1′-cyclopropane], 35117-81-8; crotyl alcohol, 6117-91-5; 1-(hydroxymethyl)-2-methylcyclopropane, 6077-72-1; 3,4-dihydro-2*H*-pyran, 110-87-2; 2-oxabicyclo[4.1.0]heptane, 286-16-8; (1-cyclohexenyloxy)trimethylsilane, 6651-36-1; 1-(trimethylsiloxy)bicyclo-[4.1.0]heptane, 38858-74-1; 1-pyrrolidino-1-cyclohexene, 1125-99-1; 1-pyrrolidinobicyclo[4.1.0]heptane, 4668-96-6.

Arylation and Heteroarylation of the Phosphole Ring

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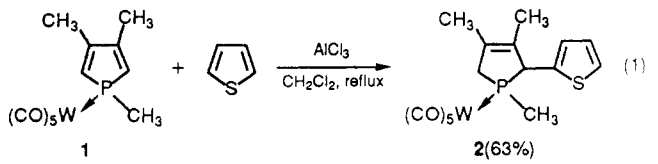
In the presence of $AlCl_3$, the dienic system of a phosphole P–$W(CO)_5$ complex can serve to alkylate electron-rich arenes such as anisole or heteroarenes such as furan and thiophene. The 2-aryl-2,5-dihydrophosphole complexes thus obtained can be converted into the corresponding 2-arylphospholes via decomplexation, reduction, bromination, and dehydrobromination. The overall yields are satisfactory. The thiophene ring can serve as a functionalizable carrier for the phosphole ring. Thus, a 2-(2-thienyl)phosphole P–$W(CO)_5$ complex can be easily acetylated or formylated on the C_5 position of the thiophene ring by CH_3 C(O)Cl + $AlCl_3$ or HC(O)N(Me)Ph + PO Cl_3, respectively.

Contrary to the analogous pyrrole, furan, and thiophene rings, the phosphole ring is almost totally devoid of aromatic chemistry. The nonplanarity of the phosphorus atom prevents the full delocalization of the electronic sextet.[1] As a consequence, it is quite difficult to functionalize a phosphole[2] or to couple it with other preformed structures contrary to its nitrogen, oxygen, and sulfur counterparts. In view of that situation, we thought that it would be interesting to graft a phosphole onto an aromatic heterocycle which, then, could act as a "carrier" for the phosphorus heterocycle. We describe here how it is possible to link a phosphole with a furan or a thiophene ring and how it is possible to functionalize the sulfur heterocycle without destroying the bonded phosphole unit.

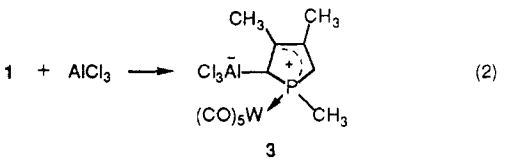
Results and Discussion

Our starting point was a previous observation[3] concerning the possible use of the dienic system of a phosphole complex as alkylating agent for a thiophene ring (eq 1).



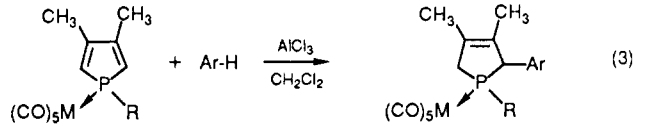
(1)

The reaction mechanism probably involves a zwitterionic complex **3** between $AlCl_3$ and the dienic system which is able to act as an electrophile toward the thiophene ring (eq 2). Indeed, when $AlCl_3$ is mixed with **1** in CH_2Cl_2 solution, complex **1** (δ ^{31}P −8.2 ppm vs H_3PO_4) disappears and a new product is formed (δ ^{31}P −23.9 ppm). Upon subsequent addition of water, this new product is destroyed and the initial complex **1** is reformed.



(2)

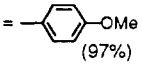
While this reaction gives a single isomer, its stereochemistry could not be assigned with certainty. The α-C*H* Ar ring proton shows no coupling with phosphorus, but we cannot transpose to phospholene complexes the relationship between the H–C–P lone pair dihedral angle and ^2J(H–P) coupling constant which was established for the corresponding free phosphines.[4] As a first step, we decided to check the generality of this coupling reaction. It soon appeared that it could be generalized to electron-rich arenes such as anisole and to furan (eq 3).



(3)

4: R = Ph; M = W
5: R = Ph; M = Mo
6: R = Me; M = Mo

7: R = Ph; M = W; Ar =  (60%)

8: R = Ph; M = Mo; Ar =  (97%)

9: R = Me; M = Mo; Ar =  (76%)

On the contrary, a normal arene such as toluene failed to react and pyrroles gave intractable products. It clearly appears that zwitterions such as **3** are relatively weak electrophiles. In each cases, the final products **7**–**9** are pure

(1) The chemistry of phospholes has been recently reviewed. The review includes a discussion on phosphole aromaticity: Mathey, F. *Chem. Rev.* **1988**, *88*, 429.

(2) A few functional phospholes have been described in the literature but no general method is available for their synthesis: Quin, L. D.; Borleske, S. G. *Tetrahedron Lett.* **1972**, 299. Mathey, F. *Tetrahedron* **1976**, *32*, 2395. Santini, C. C.; Mathey, F. *J. Org. Chem.* **1985**, *50*, 467. Marinetti, A.; Mathey, F. *Tetrahedron Lett.* **1987**, *28*, 5021. Wai Hé-Line, Wai Tan; Foucaud, A. *Tetrahedron Lett.* **1988**, *29*, 4581.

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(4) Albrand, J. P.; Martin, J.; Robert, J. B. *Bull. Soc. Chim. Fr.* **1969**, 40.

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