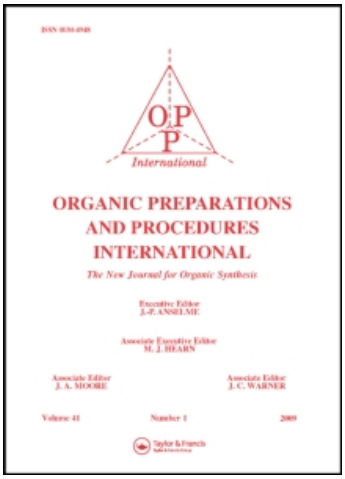

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SYNTHESIS OF 5-BROMO-3,3-DIPHENYL-1-PENTENE

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1. F. d'Angelo and G. Revial, *Tetrahedron Lett.*, **24**, 2103 (1983).

2. A. T. Nielsen and W. R. Carpenter, *Org. Synth.*, **45**, 25 (1965).

3. S. M. Ruder and V. R. Kulkarni, *Synthesis*, 945 (**1993**).

4. A. Von Baeyer, *Ber.*, **25**, 2122, (1892).

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SYNTHESIS OF 5-BROMO-3,3-DIPHENYL-1-PENTENE

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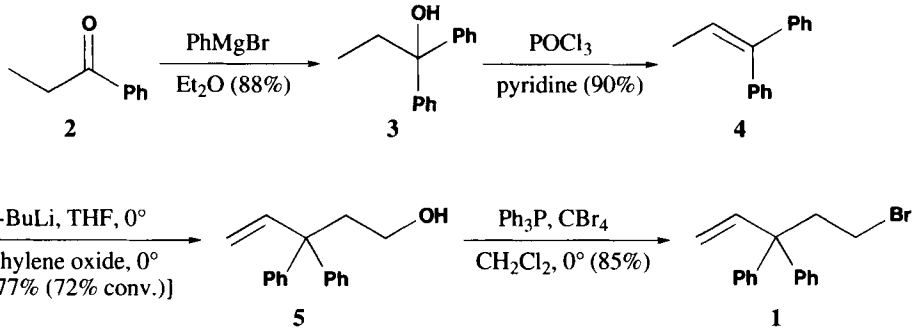
A current synthetic study required the use of 5-bromo-3,3-diphenyl-1-pentene (**1**). A review of the literature revealed that neither **1** nor its alcohol precursor 3,3-diphenyl-4-penten-1-ol (**5**) had been previously reported. Earlier work[1] on alkylations of 1,1-diphenylallyllithium demonstrated that reaction occurs predominantly at the diphenyl substituted carbon (C-1) of the allylic system. Thus, it was expected that reaction of this lithium compound with ethylene oxide would afford **5** which could then be easily converted to the title compound. This report describes the successful application of this strategy to the synthesis of **1** in four steps with an overall yield of 52% (see Scheme).



2 **3** **4** **5** **1**

The synthesis of 1,1-diphenyl-1-propene (**4**) was carried out by Grignard synthesis of 1,1-diphenyl-1-propanol (**3**) followed by dehydration using phosphorous oxychloride in pyridine. The best yield in the Grignard reaction (88%) was realized by addition of phenylmagnesium bromide to propiophenone (**2**) while dehydration proceeded in 90%. Treatment of **4** with *n*-butyllithium at 0°

followed by addition of 2 equivalents of ethylene oxide afforded 77% of 3,3-diphenyl-4-penten-1-ol (**5**), based on 72% conversion of **4** to its anion. GC and ^{1}H NMR indicated that this alcohol contained less than 5% of the isomeric 5,5-diphenyl-4-penten-1-ol resulting from reaction at C-3 of the allylic system. The best ratio of C-1:C-3 addition product was achieved at 0°, though the reaction typically proceeded to only *ca.* 70% conversion. Lower temperatures (-22°) slowed deprotonation of the alkene and suppressed the reaction with ethylene oxide; higher temperatures (35°) gave greater conversion of starting material but a significantly larger proportion (up to 20%) of C-3 addition. The alcohol was converted directly to the bromide by treatment with triphenylphosphine and carbon tetrabromide (85%).[2] The alternative route via the mesylate gave inconsistent and generally unsatisfactory results.

EXPERIMENTAL

THF was distilled from $LiAlH_4$; all other solvents and reagents were used as received. All reactions were run under dry N_2. Unless otherwise indicated, the NH_4Cl, $NaHCO_3$ and NaCl used in workup procedures refer to saturated aqueous solutions. Reactions were monitored by one of the following methods: 1) TLC on hard layer silica gel GF plates using UV detection or 2) capillary GC with FI detection (SE-30 column, 6 m x 0.25 mm i.d., 0.25 μm film thickness) programmed between 50-300°. Preparative separations were performed by flash chromato-graphy[3] on silica gel (Grace, grade 62, 60-200 mesh) containing UV-active phosphor (Sylvania no. 2282); band elution was monitored using a hand-held UV lamp. Melting points are uncorrected. IR spectra are referenced to polystyrene. ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ at 400 and 100 MHz, respectively and are referenced to internal $(CH_3)_4Si$. High resolution mass spectra (HRMS, EI/DP) were obtained at 70 eV. Elemental analyses are ±0.3%.

1,1-Diphenyl-1-propanol (3).- This alcohol was prepared by treatment of 0.35 mol of propiophenone with 0.40 mol of phenylmagnesium bromide (88%) in ether according to the procedure described by Ottenbrite and co-workers, mp. 90-91°, lit.[4] mp. 90-92°. Other workers have prepared this compound by reaction of phenylmagnesium bromide with ethyl propionate (60%)[5] and addition of ethylmagnesium bromide to benzophenone (87%).[6]

IR (thin film): 3530, 1602, 1498, 750, 700 cm^{-1}; ^{1}H NMR: δ 7.41 (d, 4H, J = 7.3 Hz), 7.30 (m, 4H), 7.20 (t, 2H, J = 7.0 Hz), 2.31 (q, 2H, J = 7.3 Hz), 2.05 (bs, 1H), 0.87 (t, 3H, J = 7.3 Hz); ^{13}C NMR: δ 146.9, 128.1, 126.7, 126.1, 78.4, 34.4, 8.1; HRMS: *m/e* Calcd for $C_{15}H_{16}O$: 212.1201. Found: 212.1202.

1,1-Diphenyl-1-propene (4).- To a stirred 0-5° (ice bath) solution of 43.0 g (0.20 moles) of **3** in 400 mL of pyridine was added 62.9 g (38.2 mL, 0.41 mol) of phosphorous oxychloride dropwise during 30 min. The mixture was heated to reflux for 2 hrs, cooled to rt, poured onto 1 kg of crushed ice and ether extracted (3 x 250 mL). The combined ether extracts were washed with 1 *M* HCl (3 x 300 mL), water, $NaHCO_3$ and NaCl, then dried ($MgSO_4$) and concentrated under vacuum. The crude alkene was purified by chromatography on a 30 cm x 6 cm silica gel column eluted with hexanes. Concentration of the eluent gave 35.2 g (0.18 mol, 90%) of **4** as a clear oil which crystallized to a white solid, mp. 46-47°, lit.[7] mp. 49°.

IR (thin film): 1598, 1495, 1360, 755, 699 cm^{-1}; ^1H NMR: δ 7.40-7.18 (complex, 10H), 6.18 (q, 1H, J = 7.0 Hz), 1.76 (d, 3H, J = 7.0 Hz); ^{13}C NMR: δ 142.9, 142.4, 140.0, 130.0, 128.1, 128.0, 127.2, 126.8, 126.7, 124.2, 15.7; HRMS: *m/e* Calcd for $C_{15}H_{14}$: 194.1095. Found: 194.1090.

3,3-Diphenyl-4-penten-1-ol (5).- To a magnetically stirred 50-mL THF solution of 5.82 g (30.0 mmol) of **4** at 0° (ice-salt bath) was added 20.3 mL of 1.5 *M* *n*-butyllithium (30.5 mmol) dropwise during 15 min. The reaction was stirred for 15 min and a 10-mL THF solution of 2.64 g (3.0 mL, 60 mmol) of ethylene oxide was added dropwise. The reaction was stirred for 10 min, then quenched at 0° with 20 mL of saturated NH_4Cl, diluted with 200 mL of H_2O and ether extracted (2 x 100 mL). The combined ether extracts were washed with NH_4Cl, H_2O and NaCl, dried ($MgSO_4$) and concentrated under vacuum. The crude alcohol was purified on a 50 cm x 2.5 cm silica gel column. Elution with hexane yielded 0.78 g (4.0 mmol, 13.4%) of unreacted **4**; 5% ether in hexane removed several minor side products; 10% ether in hexane gave 3.96 g (16.6 mmol, 55.5%, 77% based on 72% conversion) of alcohol **5** as a colorless viscous oil which crystallized to a white solid, mp. 54-55°.

IR (thin film): 3415, 3080, 3060, 3025, 1635, 1600, 1498, 1030, 920, 758, 702 cm^{-1}; ^1H NMR: δ 7.31-7.18 (complex, 10H), 6.44 (dd, 1H, J = 17.5, 10.7 Hz), 5.21 (d, 1H, J = 10.7 Hz), 4.87 (d, 1H, J = 17.5 Hz), 3.53 (m, 2H), 2.60 (t, 2H, J = 7.3 Hz), 1.60 (bs, 1H); ^{13}C NMR: δ 146.4, 144.3, 128.2, 128.1, 126.2, 114.2, 60.0, 52.4, 41.2; HRMS: *m/e* Calcd for $C_{17}H_{18}O$: 238.1356. Found: 238.1351.

Anal. Calcd for $C_{17}H_{18}O$: C, 85.71; H, 7.56. Found: C, 85.63; H, 7.59

5-Bromo-3,3-diphenyl-1-pentene (1).- To a magnetically stirred 0-5° (ice bath) solution of 2.00 g (8.4 mmol) of **5** and 3.41 g (10.4 mmol) of carbon tetrabromide in 15 mL of CH_2Cl_2 was added 3.37 g (12.8 mmol) of triphenylphosphine portionwise during 45 min. The reaction was stirred for an additional 5 min, 2 g of silica gel was added and the mixture was concentrated under vacuum. The product was purified by silica gel column (50 x 2.5 cm) using increasing concentrations of ether in hexane. Band 2 afforded 2.15 g (7.14 mmol, 85%) of **1** as a colorless oil.

IR (thin film): 3075, 3050, 3020, 1630, 1595, 1490, 1000, 920, 753, 698 cm^{-1}; ^1H NMR: δ 7.29-7.15 (complex, 10H), 6.37 (dd, 1H, J = 17.5, 10.7 Hz), 5.25 (d, 1H, J = 10.7 Hz), 4.92 (d, 1H, J = 17.5 Hz), 3.13 (m, 2H), 2.85 (m, 2H); ^{13}C NMR: δ 145.4, 143.3, 129.8, 128.3 (2), 128.1 (2), 127.2, 126.5, 114.5, 54.4, 42.1, 29.3; HRMS: *m/e* Calcd for $C_{17}H_{17}Br$: 300.0514. Found: 300.0513.

Anal. Calcd for $C_{17}H_{17}Br$: C, 67.77; H, 5.65. Found: C, 67.96; H, 5.78

REFERENCES

1. a) J. Tanaka, M. Nojima and S. Kusabayashi, *J. Am. Chem. Soc.*, **109**, 3391 (1987); b) J. Tanaka, H. Morishita, M. Nojima and S. Kusabayashi, *J. Chem. Soc., Perkin Trans. 2*, 1009 (**1989**).

2. P. J. Kocienski, G. Cernigliaro and G. Feldstein, *J. Org. Chem.*, **42**, 353 (1977).

3. W. C. Still, M. Kahn and A. Mitra, *ibid.*, **43**, 2923 (1978).

4. R. M. Ottenbrite, J. W. Brockington and K. G. Rutherford, *ibid.*, **38**, 1186 (1973).

5. A. Jung and M. Brini, *Bull. Soc. Chem. Fr.*, 693 (**1964**).

6. a) M. Tuot and M. Guyard, *ibid.*, 1087 (**1947**); b) A. Klages, *Ber.*, **35**, 2646 (1902); occasionally, the addition of benzophenone to ethylmagnesium bromine to yields small amounts of benzhydrol as a by-product.

7. R. Greenwald, M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).