Notes

Syntheses of *β,β*-Diarylvinyl Phenyl Ketones by Benzotriazole-Mediated Tandem Coupling-Elimination

Alan R. Katritzky,* Sergey N. Denisenko, Daniela C. Oniciu, and Ion Ghiviriga

Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200

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Introduction

β,β-Diarylvinyl phenyl ketones are frequently observed in natural products and are widely used versatile organic synthons; for example, (i) they can be epoxidized[1,2] and then converted into cumarones and flavones,[2] (ii) they can be added to aromatics to give polyaryl substituted ketones,[3] or (iii) they can be simply hydrogenated to give ketones.[4]

The most important synthesis of *β,β*-diarylvinyl phenyl ketones, direct aldol condensation, suffers limitations due to cross-coupling and Michael-type reactions, which cannot be always overcome by recent alternatives.[5,6] The well-known acylation of olefins to such α,*β*-enones is frequently limited by the formation of numerous byproducts.[7] Photodecarbonylation of aryl-substituted furanones affords *β,β*-diarylvinyl phenyl ketones in good yields.[8,9] A recent comprehensive review[10] confirms that additional general and versatile pathways to *β,β*-diarylvinyl phenyl ketones would be valuable.

We now present a new benzotriazole-mediated route to *β*-substituted α,*β*-enones utilizing the corresponding diarylmethanols or diarylmethyl halides and α-bromoacetophenone.

Results and Discussion

N-(Diarylmethyl)benzotriazoles **2a**−**g** were prepared by the reaction of their corresponding secondary alcohols **1a**−**g** and benzotriazole under acid conditions.[11,12] They were usually obtained as mixtures of their 1- and 2-benzotriazolyl isomers (Bt-1 and Bt-2) and used without further purification. Lithiated *N*-(diarylmethyl)benzotriazoles **2a**−**g** reacted with α-bromoacetophenone to give benzotriazole derivatives **3a**−**g** with high conversions (Scheme 1, Table 1) according to the GC and NMR analysis of the crude reaction mixtures. Only intermediate **3a** was separated, as an example for analytical purposes, whereas intermediates **3b**−**g** were transformed without isolation. The removal of benzotriazole from isolated **3a** to give the *β*-substituted α,*β*-enones **4a** was achieved with zinc bromide (0.05 equiv, in refluxing 1,2-dichloroethane); enones **4b**−**g** were prepared using BuLi (0.05−0.08 equiv, at room temperature), in one-pot syntheses directly from **2a**−**g**. For compounds **4c**−**f**, the conversion is improved by using *s*-BuLi instead of BuLi (yields and experimental conditions are presented in Table 1). With one exception (compound **4d**), yields are particularly good for the synthesis of symmetrically substituted enones.

Table 1. Experimental Conditions for the Synthesis of *β,β*-Diarylvinyl Phenyl Ketones 4a−f

	reaction conditions				intermediate 3		
entry	RLi	solv	temp, °C	time, h	isolated yield, %	conversion[a] of **2**, %	yield of **4**, %
a	BuLi	THF	rt	3	52[b]	100	91[c]
a[d]	BuLi	THF	reflux	3		100	90
b	BuLi	THF	rt	12		85	70
c	*s*-BuLi	THF	rt	12		100	60
d	*s*-BuLi	THF	rt	72		75	43
e[f]	*s*-BuLi	THF	rt	10		95	84
f[e]	*s*-BuLi	THF	rt	10		95	90
g[f]	BuLi	THF	rt	10		95	81

[a] The conversion of compound **2** to intermediate **3** were measured by performing of GC and NMR analysis of the reaction mixture. [b] The crude product was pure by NMR and further purification by column chromatography was performed only for analytical purposes. [c] From intermediate **3** by refluxing in 1,2-dichloroethane for 3 h. [d] Reference 18. [e] Reference 19. [f] Reference 18.

Benzotriazol-1-ylphenyl(4-tolyl)methane (**2c**) reacted with α-bromoacetophenone by following the same pattern, and afforded the enone **4c**, as a mixture of isomers in a ratio of 1:2.

The structure of products **4a**−**g** was confirmed by ^{1}H, ^{13}C, and two-dimensional NMR: signals at ca. 6.90−7.15 ppm provided clear evidence for the presence of a hydrogen atom connected to a conjugated double bond. In the ^{13}C NMR spectrum, signals at ca. 138−156 ppm for *C*H=C and at ca. 192−195 ppm for *C*=O are characteristic for an enone system and were unequivocally assigned in each case.

This approach is not applicable to the synthesis of *β*-alkyl-*β*-arylvinylphenyl ketones, as the analogous compounds of type **3** were not obtained. We also failed to

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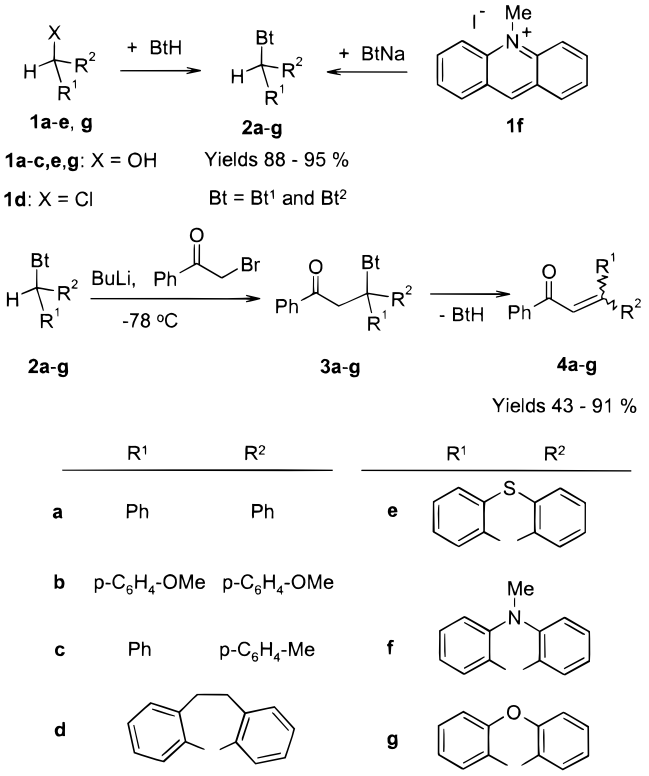
Scheme 1



synthesize β-heteroaryl-β-arylvinylphenyl ketones. For furan the precursor to **3** underwent deprotonation at the α-carbon in the furan ring. For benzothiophene, the reaction took another course: compound **6** (obtained by reacting benzotriazole with alcohol **5**) on treatment with BuLi (1 equiv) and α- bromoacetophenone gave a mixture of **7** and **9** in ratio 2:1. Compound **7** is formed as result of electrophilic attack of α-bromoacetophenone at the 3 position of the benzothiophene ring b. Such γ-regioselectivity is known[13] for a benzotriazolyl-stabilized allyl anions. The mechanism of formation of **9** is unclear: it appears not to involve intermediate **8**; treatment of compound **7** with 1 equiv of BuLi in THF did not lead to the formation of **9** (Scheme 2). Heteroatom-bridged pyranes of type **9** appear to have previously been unknown.

Structural Assignment of Compounds 7 and 9. The structures of compounds **7** and **9** were elucidated by NMR, on basis of the direct and long-range $^1H-^{13}C$ correlations [HETCOR and LRHETC[15] experiments for **7** and indirect detection experiments (HMQC and HMBC) for **9**, which was available in smaller amounts], $^1H-^1H$ correlations (COSY), and NOE difference experiments. The HETCOR experiment was run with preservation of the $^1H-^1H$ couplings in f_1. The ^1H and ^{13}C chemical shifts, together with the observed long-range heteronuclear correlations, are presented in Figure 1.

Compound **7** contained a benzotriazole moiety as revealed by the ^{13}C signals at 145.1, 119.3, and 110.9 ppm, which are typical for positions 3a, 4, and 7 in 1-benzotriazole. Irradiation of the proton at 8.20 ppm produced positive NOE's at the AB (4.90, 4.95 ppm), at 7.36 ppm, and at position 7 on the benzotriazol-1-yl (7.81 ppm). This later NOE, together with the chemical shift of its attached carbon (59.3 ppm) proves that the proton at 8.20 ppm is α to a benzotriazol-1-yl. The protons at 7.36 ppm are directly connected to a carbon of double intensity which should be in the ortho position of one of the phenyl groups; there are four double intensity carbons in the spectrum. The other phenyl group is attached to the carbonyl at 195.8 ppm because this carbon experiences polarization transfer from the protons at 7.98 ppm. In addition, this carbonyl is correlated to the AB protons (4.90 and 4.95 ppm). Irradiation of these protons in the NOE difference experiment produced an increase of the signals at 7.98 ppm (which confirms the phenacyl fragment), at 8.20 ppm (which confirms the proximity of the aliphatic methine and methylene), and for the doublet at 7.67 ppm. This latter NOE indicated that the phenacyl moiety is in the position 3 of the remaining fragment, a benzothiazole, and that the protons at 7.67 ppm are in position 4. If the phenacyl group was in position 2, an NOE to the phenylene protons would be less likely to be seen. Besides, no NOE to the phenylene protons was observed when the proton at 8.20 ppm was irradiated.

In compound **9**, the only aliphatic carbon is linked to the oxygen as revealed by its chemical shift (78.3 ppm). The proton bound to this carbon (6.59 ppm) displays long-range correlations in the HMBC with the carbons at 127.4 and 151.0 ppm. The carbon at 127.4 ppm is of double intensity and the proton directly bound to it is a doublet at 7.51 ppm; thus it is in the ortho position of a phenyl which is connected to the aliphatic methine. This is also confirmed by the positive NOE observed at 7.51 ppm when the proton at 6.59 ppm was irradiated. As indicated by its long-range correlation with the proton at 6.59 ppm and its chemical shift, the quaternary carbon at 151.0 ppm is also bound to the oxygen. In addition, this carbon has a phenyl group attached to it because it displays polarization transfer from the proton at 7.73 ppm (doublet) which is bound to a carbon of double intensity (125.0 ppm). The methine group at 94.6 and 6.72 ppm is connected to the carbon at 151.0 ppm, as indicated by the polarization transfer from its proton to this carbon and by its low ^{13}C chemical shift typical for an enol ether. In addition, the protons at 7.73 ppm experienced a positive NOE when this methine proton (6.72 ppm) was irradiated.

The elemental analysis of **9** indicated that the rest of the molecule is a benzothiophene moiety. The attachment of the unsaturated methine group to position 3 of the benzothiophene was demonstrated by the positive NOE at 7.81 ppm when the proton at 6.72 ppm was irradiated and by the long-range correlations of this proton with the carbons at 135.7 and 134.3 ppm.

Conclusion

The reaction of *N*-(diarylmethyl)benzotriazoles with α-bromoacetophenone, followed by elimination of benzotriazole, as a tandem reaction, furnished β,β-diarylvinyl phenyl ketones in good to excellent yields. Nonsymmetrically substituted enones are obtained as mixtures of cis and trans isomers. A different reaction course was evidenced for 1-(α-benzothiophenyl)-1-phenylmethylbenzotriazole: the heterocycle was capable of forming a carbanion in the presence of *s*-BuLi and hence made

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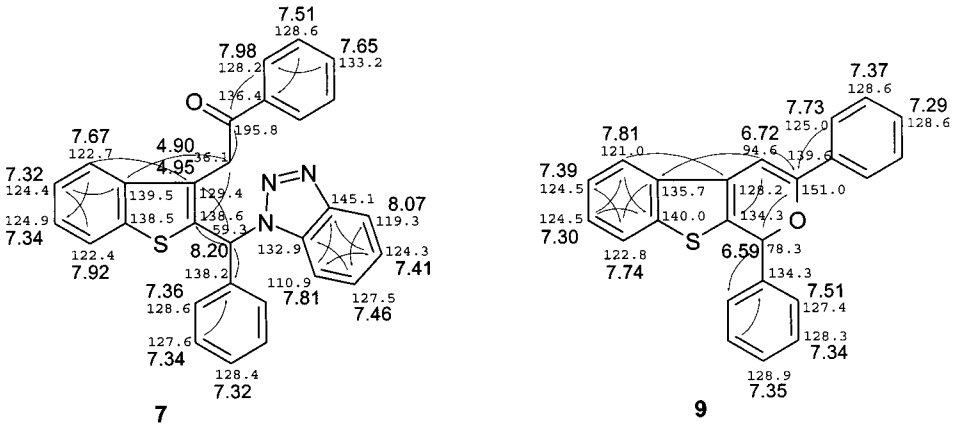
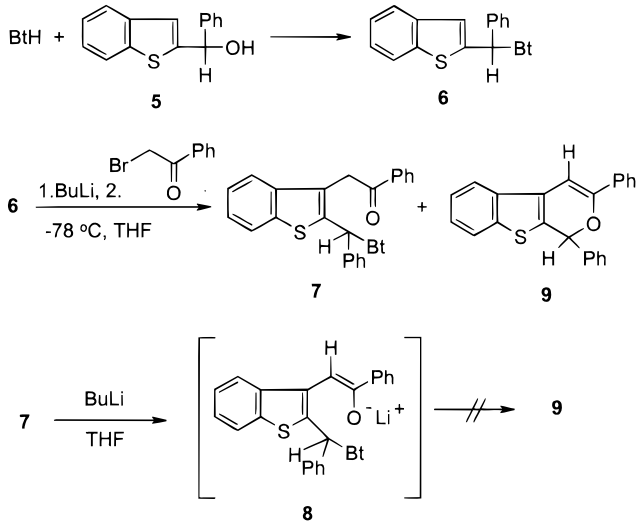


Figure 1. Complete ^{1}H and ^{13}C NMR Assignments for 2-{2-[1*H*-1,2,3-Benzotriazol-1-yl(phenyl)methyl]benzo[*b*]thiophen-3-yl}-1-phenyl-1-ethanone (**7**) and 1,3-Diphenyl-1-*H*-benzo[4,5]thieno[2,3-*c*]pyran (**9**).

Scheme 2



possible the annulation to a fused 7*H*-thieno[3,4-*c*]pyran. This synthon is envisaged as a valuable precursor in the synthesis of thienopyrylium salts.[16]

Experimental Section

General. Melting points were determined with a hot-stage apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard for ^{1}H (300 MHz) and solvent as the internal standard for ^{13}C (75 MHz), unless otherwise stated. The abbreviations for the multiplicity of the proton signals are as follows: qv for quintet, sx for sextet, and h for heptet. THF was distilled under nitrogen immediately prior to use from sodium/benzophenone. All reactions with air-sensitive compounds were carried out under an argon atmosphere. Column chromatography was conducted with silica gel 230-400 mesh.

Thioxantene-9-ol (**1e**) was prepared according to the literature method.[17] Benzotriazol-1-yl-diarylmethanes **2a**−**d** were prepared as previously reported.[11,12]

(Benzothiophen-2-yl)phenylmethanol (5). To a solution of benzothiophene (2.6 g, 19.37 mmol) in THF (50 mL) at −78 °C was added BuLi (13.3 mL, 1.6 M in cyclohexane, 21 mmol). After 10 min at −78 °C and 20 min at room temperature, the temperature was lowered to −78 °C and benzaldehyde (2.13 g, 20 mmol) in THF (10 mL) was added. The mixture was allowed to warm to room temperature and after 1.5 h was treated with saturated NH_4Cl and extracted with CH_2Cl_2. The organic layer was washed with 5% NaOH and brine and then dried ($MgSO_4$). The solvent was removed in vacuo to give 4.5 g (18.7 mmol, 97%) of crystals with a purity of 98.5% (by GC). Recrystallization from diethyl ether/hexanes yielded 3.58 g (80%) of light yellow prisms with mp 85.0−86.0 °C: ^{1}H NMR 7.78−7.72 (m, 1H), 7.68−7.62 (m, 1H), 7.49−7.20 (m, 7H), 7.08 (s, 1H), 6.10 (s, 1H), 2.63 (br s, 1H); ^{13}C NMR δ 148.8, 142.4, 139.6, 139.2, 128.2 (2C), 127.7, 126.2 (2C), 123.9, 123.8, 123.3, 122.1, 120.8, 72.4. Anal. Calcd for $C_{15}H_{12}OS$: C, 74.96; H, 5.04. Found: C, 74.76; H, 4.67.

General Procedure for the Preparation of 1-Diarylmethylbenzotriazoles 2e,g and 6. A mixture of benzotriazole (7.26 g, 61 mmol) and the appropriate carbinol **1** (55.6 mmol) was stirred for 8 h in benzene (200 mL) under reflux, in the presence of a catalytic amount of *p*-toluenesulfonic acid monohydrate. The water formed during the reaction was azeotropically removed by using a Dean−Stark apparatus. The reaction mixture was washed with Na_2CO_3 (10%), dried ($MgSO_4$), and concentrated, to give a mixture of the benzotriazol-1-yl and -2-yl isomers. The benzotriazol-1-yl isomer was separated by flash column chromatography or recrystallization, for analytical purposes.

9*H*-9-(Benzotriazol-1-yl)thioxanthene (2e). Hexanes/ethyl acetate (4:1) was used as the eluent to give white crystals (52%, yield of both isomers 95%): mp 159.0−160.5 °C; ^{1}H NMR δ 8.03−8.08 (m, 1H), 7.50−7.45 (m, 3H), 7.35−7.22 (m, 4H), 7.21−7.07 (m, 5H); ^{13}C NMR δ 146.3, 146.3, 131.8 (2C), 131.6, 129.1 (3C), 128.5 (2C), 127.3, 126.6 (2C), 126.2 (2C), 123.8, 119.8, 110.8, 62.1. Anal. Calcd for $C_{19}H_{13}N_3S$: C, 72.35; H, 4.16; N, 13.33. Found: C, 72.40; H, 4.22; N, 13.39.

9*H*-9-(Benzotriazol-1-yl)xanthene (2g) was recrystallized from toluene/diethyl ether to give colorless crystals (79%, yield of both isomers 95%): mp 190.0−192.0 °C; ^{1}H NMR δ 8.02 (d, J = 8.3 Hz, 1H), 7.63 (s, 1H), 7.45−7.10 (m, 8H), 7.04 (t, J = 7.4 Hz, 2H), 6.86 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 151.0 (2C); 147.0; 131.0; 130.4 (2C), 129.3 (2C), 127.3, 124.0 (2C), 123.8, 120.0, 117.0 (2C), 116.9 (2C), 110.1, 55.4. Anal. Calcd for $C_{19}H_{13}N_3O$: C, 76.23; H, 4.39; N, 14.04. Found: C, 76.27; H, 4.17; N, 14.22.

(Benzotriazol-1-yl)(benzothiophen-2-yl)phenylmethane (6). Recrystallized from diethyl ether to give white crystals (60%, yield of both isomers 88%); mp 113.0−127.0 °C; ^{1}H NMR δ 8.14−8.10 (m, 1H), 7.78−7.71 (m, 1H), 7.71−7.65 (m, 1H), 7.64 (s, 1H), 7.42−7.20 (m, 10H), 7.13 (s, 1H); ^{13}C NMR δ 146.4, 141.3, 140.2, 138.8, 137.1, 132.6, 128.9 (3C), 127.8 (2C), 127.5, 124.9, 124.9, 124.6, 124.0, 123.9, 122.3, 120.2, 110.5, 63.5. Anal. Calcd for $C_{21}H_{15}N_3S$: C, 73.87; H, 4.44; N, 12.31. Found: C, 73.52; H, 4.38; N, 12.24.

9,10-Dihydro-10-methyl-9-(benzotriazol-1-yl)acridine (2f). A mixture of benzotriazole (1.19 g, 10 mmol), NaH (0.40 g of 60% solution in mineral oil, 10 mmol), and the 10-methylacridinium iodide **1f** (10 mmol) was stirred for 1 h in dry THF (50 mL) at room temperature. The reaction mixture was washed with Na_2CO_3 (10%), dried ($MgSO_4$), and concentrated, to give a

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mixture of the benzotriazol-1-yl and -2-yl isomers. The benzotriazol-1-yl isomer was separated by recrystallization from 2-propanol to give white crystals (75%, yield of both isomers 89%): mp 168.0−169.5 °C; ^{1}H NMR δ 8.00−7.93 (d, J = 7.6 Hz, 1H), 7.63 (s, 1H), 7.34 (t, J = 8.3 Hz, 2H), 7.30−7.06 (m, 7H), 6.9 (t, J = 7.0 Hz, 2H), 3.60 (s, 3H); ^{13}C NMR δ 146.5, 141.4 (2C), 131.1, 118.0 (2C), 129.5 (4C), 126.8, 123.4, 120.7 (2C), 119.6, 112.9 (2C), 110.3, 59.8, 33.0. Anal. Calcd for $C_{20}H_{16}N_4$: C, 76.89; H, 5.17; N, 17.94. Found: C, 76.76; H, 5.13; N, 17.93.

1-(Benzotriazol-1-yl)-1,1,3-tris(phenyl)propan-3-one (3a). To a stirred solution of benzotriazol-1-yl-diphenylmethane **2a** (0.77 g, 2.7 mmol) in THF (25 mL) at −78 °C was added a solution of BuLi (1.88 mL, 1.6 M in cyclohexane, 3 mmol). The mixture was stirred at this temperature for 30 min, then 2-bromoacetophenone (0.537 g, 2.7 mmol) in THF (5 mL) was slowly added while the solution stirred. The reaction mixture was kept at −78 °C for 2 h and for an additional 12 h at room temperature and then was quenched with cold saturated NH_4-Cl. The reaction mixture was extracted with diethyl ether (50 mL), and the organic layer was dried ($MgSO_4$). The solvent was evaporated under vacuum to give the crude product, which was purified by recrystallization from diethyl ether, to afford the pure compound as white crystals (0.57 g, 52%): mp 149.0−151.0 °C; ^{1}H NMR δ 8.05 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 7.1 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46−7.38 (m, J = 8.0 Hz, 2H), 7.36−7.21 (m, 11H), 7.12 (t, J = 7.7 Hz, 1H), 6.44 (d, J = 8.5 Hz, 1H), 5.0 (s, 2H); ^{13}C NMR δ 194.3, 146.4, 140.3 (2C), 137.2, 133.3, 132.9, 128.4 (2C), 128.3 (4C), 128.0 (2C), 127.9 (6C), 126.7, 123.5, 119.9, 112.8, 72.4, 50.7. Anal. Calcd for $C_{27}H_{21}N_3O$: C, 80.36; H, 5.26; N, 10.42. Found: C, 80.51; H, 5.51; N, 10.50.

1,3,3-Tris(phenyl)propen-1-one (4a). To a stirred solution of 3-benzotriazol-1-yl-1,3,3-tris(phenyl)propan-1-one **3a** (0.45 g, 1.12 mmol) in 1,2-dichloroethane (10 mL) at 20 °C a were added few crystals of $ZnBr_2$, and the mixture was stirred at reflux for 3 h. The precipitate was filtered, and the organic layer was washed with water (2 mL) and dried ($MgSO_4$). In vacuo removal of the solvent gave the pure product as a yellow oil, which crystallized on standing, to give yellow crystals (290 mg, 91%): mp 88.0−90.0 °C (diethyl ether);[18] ^{1}H NMR δ 7.94 (dd, J = 7.1, 1.4 Hz, 2H), 7.50 (tt, J = 7.4, 7.1, 1.4 Hz, 1H), 7.46−7.34 (m, 7H), 7.33−7.25 (m, 3H), 7.25−7.17 (m, 2H), 7.15 (s, 1H); ^{13}C NMR δ 192.7, 154.7, 141.3, 138.9, 138.1, 132.6, 129.7 (2C), 129.3, 128.7 (2C), 128.5 (2C), 128.4 (2C), 128.3 (3C), 128.0 (2C), 124.0.

General Procedure for the Preparation of Substituted 1-Propenones 4b−g. To a stirred solution of the mixture of 1- and 2-isomers of compound **2** (3.1 mmol) in THF (25 mL) at −78 °C was added BuLi (2.2 mL, 1.6 M in cyclohexane, 3.4 mmol). The mixture was stirred at this temperature for 30 min, then 2-bromoacetophenone (0.611 g, 3.1 mmol) in THF (5 mL) was slowly added while the solution stirred. The reaction mixture was kept at −78 °C for 2 h and for an additional 12 h at room temperature and then was quenched with cold saturated NH_4Cl. The reaction mixture was extracted with diethyl ether (50 mL), and the organic layer was dried ($MgSO_4$). The solvent was removed under vacuum to give the crude product, which was isolated by column chromatography or recrystallization. When compound **2b** was used as a starting material, compound **3b** was obtained after the reaction was quenched (by NMR), but the benzotriazole was eliminated during the separations.

2-{2-[1*H*-1,2,3-(Benzotriazol-1-yl)(phenyl)methyl]benzo-[*b*]thiophen-3-yl}-1-phenyl-1-ethanone (7). To a stirred solution of benzotriazol-1-yl-(2-benzothiophenyl)phenylmethane (0.973 g, 2.85 mmol) in THF (25 mL) at −78 °C was added a solution of BuLi (2 mL, 1.6 M in cyclohexane, 3.2 mmol). The mixture was stirred at −78 °C for 30 min, then 2-bromoacetophenone (0.570 g, 2.85 mmol) in THF (5 mL) was added slowly. After the mixture stirred for 30 min at −78 °C and 12 h at room temperature, diethyl ether (50 mL) was added and the reaction mixture was washed with saturated NH_4Cl solution and dried ($MgSO_4$). The solvent was evaporated in vacuo, and the oily residue was separated by column chromatography on silica gel with hexane/ethyl acetate (20:1) as eluent to give the product as a first fraction (655 mg, 50%): white crystals, mp 172.0−174.0 °C; for ^{1}H and ^{13}C NMR assignments, see Figure 1. Anal. Calcd for $C_{29}H_{21}N_3OS$: N, 9.15. Found: N, 8.87.

1,3-Diphenyl-1-*H*-benzo[4,5]thieno[2,3-*c*]pyran (9) was separated by column chromatography on silica gel with hexane/ethyl acetate (20:1) as eluent, as the second fraction of the above-mentioned procedure to yield an oil (235 mg, 25%); for ^{1}H and ^{13}C NMR assignments, see Figure 1; HRMS (CI) calcd for $C_{23}H_{16}$-OS 340.0921, found 340.0938.

Supporting Information Available: Characterization data for compounds **4b−g** and discussion of structure assignment by NMR for compounds **7** and **9**; spectral data for **4b,c** and **9** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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