1,2- vs 1,4-Addition of Acylbenzotriazoles to α,β-Unsaturated Aldehydes and Ketones. A Novel Route to 3-Alkyl-4,6-diaryl-3,4-dihydropyran-2-ones

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Lithiation of aliphatic 1-acylbenzotriazoles with subsequent reaction with α,β-unsaturated ketones and aldehydes affords either 3,4,6-trisubstituted 3,4-dihydropyran-2-ones or 1,3-dienes depending on the carbonyl reagent used. Substituent effects on product yield and isomer ratio are discussed.

Introduction

Reported ring syntheses of 3,4-dihydro-2-pyrones[1] include (i) acid-catalyzed intramolecular cyclization of δ-oxoalkanoic acids,[2] (ii) dimerization of α,β-unsaturated acyl cyanides[3] or α-(sulfonio)ketone triflates,[4] and (iii) [4 + 2] cycloaddition of ketenes prepared in situ to diverse α,β-unsaturated ketones.[5] A few nucleophilic Michael additions of metalated esters to α,β-unsaturated carbonyl compounds were also reported to form 3,4-dihydro-2-pyrones.[6] However, despite extensive investigation of the chemistry of partially reduced 2-pyrones, apparently no 3-alkyl-4,6-diaryl-3,4-dihydropyran-2-ones have been synthesized.

Nucleophilic additions to conjugated unsaturated systems have been the subject of numerous studies and have been comprehensively reviewed.[7] The influence of the nature of the nucleophile, temperature, and additives on the mode of the reaction (1,2- or 1,4-addition) has been of major interest. Metalated amides and thioamides have received little attention as nucleophiles; however, their lithium derivatives frequently react with chalcones with predominant 1,4-addition,[8] while the corresponding titanium enolates favor 1,2-addition.[9] The orientation of additions to alkenones and alkyl 2-arylethenyl ketones varies depending on the reaction conditions.[7b,8] We know of no reported reactions of amide-derived enolates with cinnamaldehydes.

In 1996, Schick et al.[10] reported a fascinating formation of di- and trisubstituted butyrolactones **3** by intramolecular cyclization of the organolithium intermediates **2**, prepared by 1,2-addition of lithium enolates of *N*-acylbenzotriazoles **1** to carbonyl compounds (Scheme 1). This reaction was demonstrated for nonbranched aliphatic (R^1 = Et, *n*-C_6H_{13}) and arylalkyl (R^1 = $PhCH_2$) acylbenzotriazoles, while aliphatic ketones and alkyl (arylalkyl) aldehydes were used as carbonyl components. No reactions with aromatic or α,β-unsaturated aldehydes or ketones and no reactions of benzylic (R^1 = aryl) or branched aliphatic acylbenzotriazoles were mentioned.

As in Schick's reaction, 1,4-addition of lithiated acylbenzotriazoles **1** to chalcones should generate a reactive enolate anion **5**, which could attack intramolecularly the amide carbonyl group with elimination of benzotriazolyl anion and formation of the corresponding 3,4-dihydropyran-2-ones **6** and/or **7**. We have now found that lithiated 1-alkylcarbonylbenzotriazoles indeed provide a convenient approach to such compounds and extend the variety of accessible 3,4-dihydropyran-2-ones.

Results and Discussion

Reactions of nonbranched aliphatic acylbenzotriazoles **1a**,**b** with chalcones follow the 1,4-addition pathway. Thus, lithiated **1a** (Scheme 1) with unsubstituted chalcone **4a** (under the same conditions as those used by Schick in his reaction with ketones) gave a mixture of diastereomeric 3,4-dihydropyran-2-ones **6a** and **7a** in 70% yield with the *trans*-isomer **6a** predominating (with the ratio of 4:1). A similar ratio of the diastereomers **6b**/**7b** was obtained in the analogous reaction with 4-chlorochalcone (Table 1). However, when 4-nitrochalcone was used, the *trans*-isomer **6c** was formed almost exclusively (with the diastereoisomeric ratio of 20:1). Due to a significant difference in the solubilities of **6c** and **7c**, *trans*-isomer **6c** was isolated pure by washing the diastereomeric mixture with a small amount of diethyl ether.

A similar enhancement in the *trans*/*cis* isomeric ratio was observed in the reactions with *trans*,*trans*-dibenzylideneacetone (**6e**/**7e**, 12:1) and *trans*-dibenzoylethylene (only *trans*-isomer **6d**). This tendency is explained by additional stabilization of the intermediate enolate **5** with

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Scheme 1

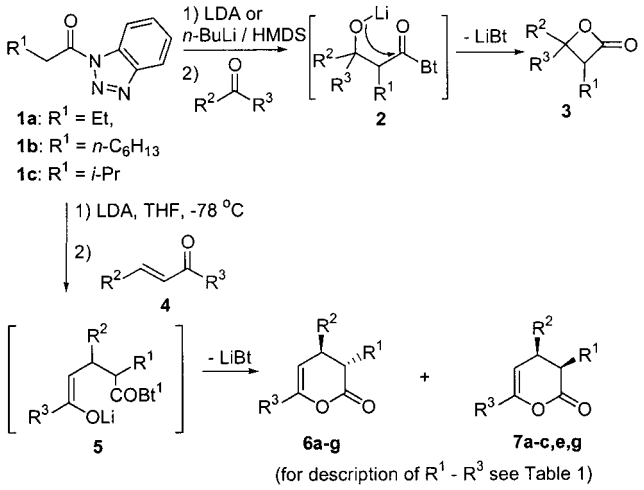

Table 1. 3,4,6-Trisubstituted 3,4-Dihydropyran-2-ones 6 and 7

entry	compd	R^1	R^2	R^3	yield, %	*trans*:*cis*
1	**6a**/**7a**	Et	Ph	Ph	70	4:1
2	**6b**/**7b**	Et	4-ClC_6H_4	Ph	74	4:1
3	**6c**/**7c**	Et	4-$O_2NC_6H_4$	Ph	81	20:1
4	**6d**	Et	PhCO	Ph	72	*a*
5	**6e**/**7e**	Et	Ph	PhCH=CH	53	12:1
6	**6f**	*n*-C_6H_{13}	Ph	Ph	79	*a*
7	**6g**/**7g**	Me_2CH	Ph	Ph	24	15:1

[a] Only *trans*.

an electron-accepting R^2 substituent, allowing for easier C−C bond free rotation and the predominant formation of the sterically favored *trans*-isomer. In each case, the diastereomeric ratios were determined using ^{1}H NMR spectra of the crude reaction mixtures. These ratios were later compared with those obtained after the column chromatography purification: in all cases, no deviations were observed.

Unexpectedly, lengthening the carbon chain in the starting 1-acylbenzotriazole (R^1 = *n*-C_6H_{13}) also favors the formation of the *trans*-isomer (compare entries 1 and 6 in Table 1). This and the predominant formation of the *trans*-isomer (entry 7) from 1-isovalerylbenzotriazole (**1c**) are ascribed to increased steric demands in the intermediate enolate **5**. In the case of **1c**, these steric demands also lead to a significant decline in the product yield (see Table 1). An attempt to carry out this reaction with even more sterically hindered 1-neopentylcarbonylbenzotriazole (**1d**) failed.

Lithiated acylbenzotriazoles were found to be unstable at temperatures above −60 °C and, thus, react in the temperature range −60 to −78 °C. This suggests that the product ratios are the kinetic ones. Despite the use of excess acylbenzotriazole, minor amounts of the starting α,β-unsaturated carbonyl compounds were still present in the reaction mixtures, indicating that the acylbenzotriazole decomposition process competes with the desired cycloaddition reaction. Kinetic control could also explain the lack of reactivity of sterically hindered 1-alkylcarbonylbenzotriazoles.

The behavior of aryl-substituted acylbenzotriazoles in the reaction with chalcones has also been investigated. Under the standard reaction conditions, 1-benzylcarbonylbenzotriazole (**1e**) is more prone to nucleophilic substitution of the benzotriazolyl group with LDA than to the proton abstraction, resulting in the formation of the corresponding *N*,*N*-diisopropylamide. Replacement of LDA with non-nucleophilic bases, such as *n*-butyllithium or LiHMDS, did not lead to the formation of the expected dihydropyranones. Switching to 1-(2-phenylethyl)carbonylbenzotriazole (**1f**), which has an additional methylene group, significantly suppressed the benzotriazolyl group substitution with LDA, but led to a complex reaction mixture with only traces of the desired product present. Thus, the scope of this method for preparation of 3,4,6-trisubstituted 3,4-dihydropyran-2-ones is essentially limited to the derivatives with non-α-branched alkyl substituents at the 3-position.

Scheme 2

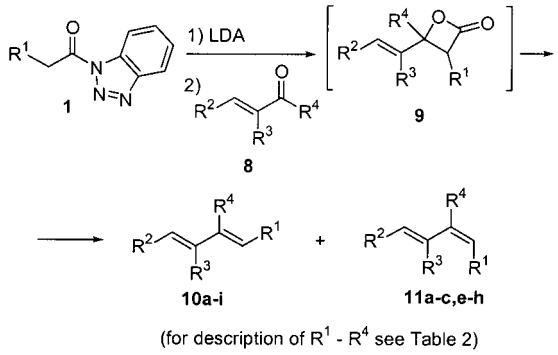

Table 2. 1,3-Dienes 10 and 11

entry	compd	R^1	R^2	R^3	R^4	yield, %	(*E*,*E*):(*E*,*Z*)
1	**10a**/**11a**	Et	Ph	H	H	68	62:38
2	**10b**/**11b**	Et	2-$MeOC_6H_4$	H	H	50	71:29
3	**10c**/**11c**	Et	2-furyl	H	H	66	52:48
4	**10d**	Et	4-*t*-BuC_6H_4	Me	H	25	*a*
5	**10e**/**11e**	Et	Ph	H	Me	82	42:58
6	**10f**/**11f**	*n*-C_6H_{13}	Ph	H	H	66	58:42
7	**10g**	*n*-C_6H_{13}	4-*t*-BuC_6H_4	Me	H	48	*a*, *b*
8	**10h**/**11h**	*n*-C_6H_{13}	Ph	H	Me	58	55:45
9	**10i**	Me_2CH	Ph	H	H	8	*a*

[a] Only (*E*,*E*). [b] Ca. 5% of the (*E*,*Z*)-isomer **11g** was observed in the ^{1}H NMR spectrum.

In contrast to the foregoing results, treatment of lithiated 1-acylbenzotriazoles with cinnamaldehydes results in 1,2-addition and subsequent formation of conjugated dienes. Thus, reaction of *n*-butyrylbenzotriazole **1a** with LDA and then with *trans*-cinnamaldehyde **8a** under the standard reaction conditions afforded a mixture of (*E*,*E*) (**10a**) and (*E*,*Z*) (**11a**) dienes with the *E*,*E*-isomer predominating (Scheme 2, Table 2). *o*-Methoxycinnamaldehyde **8b** and 3-(2-furyl)acrolein **8c** gave the corresponding dienes **10b**/**11b** and **10c**/**11c**. As shown in Table 2, an introduction of an electron-donating substituent into the aromatic ring increases the relative amount of the *E*,*E*-isomer **10**, while with the electron-accepting 2-furyl group an almost equimolar mixture of the isomers was formed. An introduction of a methyl group at the α-position of the starting cinnamaldehyde leads to a general decrease in the product yield; however, the increased steric demands favor the formation of a *trans* double bond (see entries 4 and 7, Table 2). Interestingly, the diene **10g** was obtained reproducibly in double the yield of the homologous diene **10d**. Also, the diene **10g** was contaminated with a minor amount (less than 5%) of the isomeric **11g**, although, from the standpoint of steric hindrance, the opposite results were expected.

The suggested pathway of this reaction is shown in Scheme 2. In contrast to reactions with chalcones, reactions of lithiated 1-acylbenzotriazoles with cinnamaldehydes follow exclusively the 1,2-addition pathway. Although examples of subsequent isomerization of kinetic 1,2-adducts to thermodynamic 1,4-adducts are well-known, in our case the formation of the latter was not observed, probably due to further transformations of 1,2-adducts at low temperatures. Analogous 1,2-adducts of type **9** were previously reported as intermediates in the reaction of acyl chloride derived ketenes with carbonyl compounds;[11] they were also shown to undergo thermal decarboxylation with the formation of the corresponding olefins. Our attempts to avoid CO_2 elimination and to isolate the intermediates **9** by quenching the reaction at low temperature were unsuccessful: only dienes **10**/**11** were obtained. This phenomenon is probably explained by preferential formation of a highly conjugated aryldiene system (R^2 is an aryl (heteroaryl) group in all cases).

Interestingly, 2-phenylethenyl methyl ketone (**8e**, R^2 = Ph, R^3 = H, R^4 = Me) tends to react exclusively by the 1,2-addition route, similarly to the aldehydes discussed above, but not to chalcones. Thus, the reactions of acylbenzotriazoles **1a**,**b** with **8e** gave almost equimolar mixtures of (*E*,*E*) and (*E*,*Z*) dienes **10e**/**11e** and **10h**/**11h**, respectively.

Reactions of lithiated 1-acylbenzotriazoles with cinnamaldehydes and styryl methyl ketone generally afford 1,3-dienes in moderate yields and, except in the cases of sterically hindered substrates, as mixtures of *trans* and *cis* isomers. Thus, this methodology provides no advantages compared to established methods for the preparation of 1,3-dienes.[12]

Conclusions

Lithiated aliphatic nonbranched 1-acylbenzotriazoles undergo 1,4-addition to α,*β*-unsaturated aromatic ketones to afford previously unknown 3-alkyl-4,6-diaryl-3,4-dihydropyran-2-ones, predominantly (or exclusively) as *trans*-isomers, in good yields. An analogous reaction with cinnamaldehydes or with methyl styryl ketone follows the 1,2-addition pathway resulting in formation of various 1,3-dienes. Introduction of a *β*-substituent into the alkyl chain of the acylbenzotriazole leads to a significant decrease in the product yield, although an improvement in the stereoselectivity is observed.

Experimental Section

General Comments. Melting points were measured on a Mel-Temp apparatus and are uncorrected. ^{1}H and ^{13}C NMR data were recorded on Gemini 300 MHz NMR spectrometer (300 and 75 MHz, respectively) in $CDCl_3$ as a solvent and with TMS as an internal standard. For isomeric mixtures, signals common for both isomers are provided without additional specification. Column chromatography was carried out on silica gel (activated, neutral, 50−200 micron). Tetrahydrofuran was distilled from sodium/benzophenone immediately prior to use. Di(isopropyl)amine was distilled from sodium and handled under nitrogen. 1-Acylbenzotriazoles were prepared following the known procedure.[13]

1-Butyrylbenzotriazole (1a): white plates (95%), mp 56−57 °C (from hexanes) (lit.[10] 54−55 °C); ^{1}H NMR δ 1.12 (t, J = 7.4 Hz, 3H), 1.91−2.00 (m, 2H), 3.41 (t, J = 7.4 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.65 (t, J = 7.3 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.30 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 13.7, 17.9, 37.3, 114.4, 120.1, 126.0, 130.3, 131.1, 146.1, 172.5.

1-(*n*-Octanoyl)benzotriazole (1b): colorless oil[10] (96%); ^{1}H NMR δ 0.89 (t, J = 6.6 Hz, 3H), 1.30−1.51 (m, 8H), 1.86−1.94 (m, 2H), 3.42 (t, J = 7.5 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.29 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 14.0, 22.5, 24.4, 28.9, 29.0, 31.6, 35.5, 114.4, 120.0, 126.0, 130.2, 131.1, 146.1, 172.6.

1-(Benzotriazol-1-yl)-3-methylbutan-1-one (1c): colorless liquid (96%); ^{1}H NMR δ 1.11 (d, J = 6.7 Hz, 6H), 2.40−2.50 (m, 1H), 3.31 (d, J = 7.0 Hz, 2H), 7.50 (dd, J = 8.1, 7.3 Hz, 1H), 7.65 (dd, J = 8.0, 7.3 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 8.30 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 22.5, 25.5, 44.0, 114.4, 120.0, 126.0, 130.2, 131.0, 146.1, 171.9. Anal. Calcd for $C_{11}H_{13}N_3O$: C, 65.01; H, 6.45; N, 20.67. Found: C, 65.32; H, 6.65; N, 21.00.

1-(Benzotriazol-1-yl)-3,3-dimethylbutan-1-one (1d): white plates (70%), mp 56−57 °C (from hexanes) (lit.[14] 56−57 °C); ^{1}H NMR δ 1.17 (s, 9H), 3.36 (s, 2H), 7.51 (t, J = 7.7 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.34 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 29.8, 32.0, 47.1, 114.6, 120.1, 126.1, 130.2, 131.1, 146.2, 171.4.

1-(Benzotriazol-1-yl)-2-phenylethanone (1e): white microcrystals (67%), mp 67−68 °C (from hexanes) (lit.[15] 70−71 °C); ^{1}H NMR δ 4.73 (s, 2H), 7.30−7.40 (m, 3H), 7.45−7.52 (m, 3H), 7.63 (t, J = 7.3 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.26 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 42.0, 114.4, 120.1, 126.2, 127.6, 128.8, 129.8, 130.5, 131.2, 132.5, 146.3, 170.2.

1-(Benzotriazol-1-yl)-3-phenylpropan-1-one (1f): white microcrystals (98%), mp 61−62 °C (from hexanes) (lit.[10] 62−63 °C); ^{1}H NMR δ 3.24 (t, J = 7.7 Hz, 2H), 3.77 (t, J = 7.7 Hz, 2H), 7.18−7.28 (m, 1H), 7.30−7.35 (m, 4H), 7.50 (pseudo-t, J = 7.6 Hz, 1H), 7.65 (pseudo-t, J = 7.7 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.29 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 30.2, 37.1, 114.4, 120.1, 126.1, 126.5, 128.4, 128.6, 130.4, 131.0, 139.8, 146.1, 171.6.

General Procedure for the Synthesis of 3,4,6-Trisubstituted 3,4-Dihydropyran-2-ones 6/7 and 1,3-Dienes 10/11. A solution of di(isopropyl)amine (0.6 mL, 4.0 mmol) in dry THF (40 mL) was cooled to −10 °C under nitrogen, and 1.58 N *n*-BuLi in hexanes (2.2 mL, 3.5 mmol) was added dropwise. The colorless solution obtained was allowed to warm up to room temperature during 40 min, and then it was cooled to −78 °C. A solution of 1-acylbenzotriazole (3.5 mmol) in dry THF (20 mL) was added slowly dropwise. The reaction mixture was stirred at −78 °C for 20 min, and then a solution of the α,*β*-unsaturated aldehyde or ketone (3.0 mmol) in THF (20 mL) was added slowly. The reaction mixture was allowed to warm up to room temperature during 3.5 h, and it was stirred at room temperature for an additional 1 h. Then it was quenched with aqueous saturated NH_4Cl and extracted with ether. The organic fraction was washed with water and brine and dried over $MgSO_4$. After solvent removal, the residue was purified by column chromatography (SiO_2; dichloromethane:hexanes = 1:3 to 1:1 (for 3,4-dihydropyran-2-ones) or ethyl acetate:hexanes = 1:10 (for 1,3-dienes)).

3-Ethyl-4,6-diphenyl-3,4-dihydropyran-2-one (6a/7a): colorless oil (70%); ^{1}H NMR δ 0.88−1.07 (m, 3H), 1.19−1.29 (m, 1H), 1.59−1.81 (m, 1H), 2.73 (dd, J = 12.6, 7.1 Hz, 1H (*cis*)), 2.84 (dd, J = 14.0, 6.9 Hz, 1H (*trans*)), 3.71 (dd, J = 7.1, 4.6 Hz, 1H (*cis*)), 3.84 (pseudo-t, J = 6.6 Hz, 1H (*trans*)), 5.84 (d, J = 4.5 Hz, 1H (*cis*)), 6.06 (d, J = 6.5 Hz, 1H (*trans*)), 7.15−7.20 (m, 2H), 7.21−7.42 (m, 6H), 7.65−7.69 (m, 2H); ^{13}C NMR δ 11.3 (*cis*) and 12.0 (*trans*), 19.8 (*trans*) and 22.7 (*cis*), 41.2 (*trans*) and 42.4 (*cis*), 45.9 (*trans*) and 47.9 (*cis*), 103.6 (*cis*) and 104.7 (*trans*), 124.6, 127.4, 127.6, 128.1, 128.5, 128.8, 129.1, 132.2, 138.0, 141.5, 149.4, 150.1, 170.4. HRMS (FAB) calcd for $C_{19}H_{19}O_2$ (M + 1): 279.1385. Found: 279.1401.

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3-Ethyl-4-(4-chlorophenyl)-6-phenyl-3,4-dihydropyran-2-one (6b/7b): colorless oil (74%); ^{1}H NMR δ 1.00 (t, J = 7.3 Hz, 3H), 1.12−1.28 (m, 1H), 1.63−1.82 (m, 1H), 2.67 (dd, J = 12.6, 7.0 Hz, 1H (*cis*)), 2.81 (dd, J = 13.9, 7.0 Hz, 1H (*trans*)), 3.67 (dd, J = 7.0, 4.6 Hz, 1H (*cis*)), 3.79 (t, J = 6.6 Hz, 1H (*trans*)), 5.78 (d, J = 4.5 Hz, 1H (*cis*)), 6.01 (d, J = 6.5 Hz, 1H (*trans*)), 7.08 (d, J = 8.4 Hz, 2H (*trans*)), 7.14 (d, J = 8.4 Hz, 2H (*cis*)), 7.24 (d, J = 8.5 Hz, 2H (*trans*)), 7.29 (d, J = 8.4 Hz, 2H (*cis*)), 7.30−7.41 (m, 3H), 7.64−7.68 (m, 2H); ^{13}C NMR δ 11.2 (*cis*) and 11.9 (*trans*), 19.7 (*trans*) and 22.6 (*cis*), 40.5 (*trans*) and 41.7 (*cis*), 45.6 (*trans*) and 47.8 (*cis*), 102.8 (*cis*) and 104.1 (*trans*), 124.5, 128.5, 128.7, 128.9, 129.1, 129.2, 129.3, 131.8 (*cis*) and 131.9 (*trans*), 133.1 (*cis*) and 133.3 (*trans*), 136.4, 139.9, 149.7 (*cis*) and 150.3 (*trans*), 169.4 (*cis*) and 169.9 (*trans*). HRMS (FAB) calcd for $C_{19}H_{18}ClO_2$ (M + 1): 313.0995. Found: 313.0975.

***trans*-3-Ethyl-4-(4-nitrophenyl)-6-phenyl-3,4-dihydropyran-2-one (6c):** pale-yellow needles (81%), mp 98−99 °C (from ethyl ether); ^{1}H NMR δ 1.05 (t, J = 7.3 Hz, 3H), 1.16−1.26 (m, 1H), 1.73−1.84 (m, 1H), 2.93 (q, J = 7.0 Hz, 1H), 3.98 (t, J = 6.6 Hz, 1H), 6.04 (d, J = 6.3 Hz, 1H), 7.35 (d, J = 8.7 Hz, 2H), 7.40−7.42 (m, 3H), 7.66−7.70 (m, 2H), 8.18 (d, J = 8.7 Hz, 2H); ^{13}C NMR δ 12.0, 19.9, 41.1, 45.5, 103.1, 124.0, 124.7, 128.6, 129.0, 129.5, 131.7, 145.7, 147.4. 151.1, 169.5. Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.25; H, 5.64; N, 4.31.

***trans*-3-Ethyl-4-benzoyl-6-phenyl-3,4-dihydropyran-2-one (6d):** pale-yellow microcrystals (72%), mp 74−76 °C (from hexanes); ^{1}H NMR δ 0.99 (t, J = 7.4 Hz, 3H), 1.51−1.64 (m, 1H), 1.77−1.87 (m, 1H), 2.71 (ddd, J = 8.5, 5.9, 2.6 Hz, 1H), 3.63 (t, J = 2.6 Hz, 1H), 5.46 (d, J = 2.5 Hz, 1H), 7.35−7.44 (m, 6H), 7.52−7.56 (m, 2H), 7.61−7.65 (m, 2H); ^{13}C NMR δ 12.0, 25.4, 49.2, 56.4, 98.3, 115.3, 125.1, 125.6, 128.5, 128.7, 129.0, 129.3, 129.4, 139.2, 155.4, 177.2. HRMS (EI) calcd for $C_{20}H_{18}O_3$ (M): 306.1256. Found: 306.1257.

3-Ethyl-4-phenyl-6-(*trans*-2-styryl)-3,4-dihydropyran-2-one (6e/7e): colorless oil (53%); ^{1}H NMR δ 1.00 (t, J = 7.4 Hz, 3H), 1.16−1.26 (m, 1H), 1.69−1.80 (m, 1H), 2.70 (dd, J = 12.8, 6.8 Hz, 1H (*cis*)), 2.80 (dd, J = 13.9, 6.9 Hz, 1H (*trans*)), 3.65 (dd, J = 6.9, 4.7 Hz, 1H (*cis*)), 3.78 (t, J = 6.7 Hz, 1H (*trans*)), 5.38 (d, J = 4.7 Hz, 1H (*cis*)), 5.59 (d, J = 6.3 Hz, 1H (*trans*)), 6.52 (d, J = 15.9 Hz, 1H), 7.08−7.14 (m, 3H), 7.18−7.36 (m, 6H), 7.44 (d, J = 7.6 Hz, 2H); ^{13}C NMR δ (only for the *trans*-isomer) 12.0, 19.8, 41.4, 46.0, 109.3, 119.9, 126.8, 127.6, 128.0, 128.2, 128.7, 128.8, 129.9, 136.1, 138.0, 149.4, 170.2. HRMS (FAB) calcd for $C_{21}H_{21}O_2$ (M + 1): 305.1542. Found: 305.1502.

***trans*-3-(*n*-Hexyl)-4,6-diphenyl-3,4-dihydropyran-2-one (6f):** white needles (79%), mp 81−82 °C (from hexanes); ^{1}H NMR δ 0.86 (t, J = 6.6 Hz, 3H), 1.15−1.38 (m, 7H), 1.39−1.44 (m, 2H), 1.66−1.77 (m, 1H), 2.93 (dd, J = 13.7, 7.0 Hz, 1H), 3.83 (pseudo-t, J = 6.4 Hz, 1H), 6.07 (d, J = 6.4 Hz, 1H), 7.15−7.18 (m, 2H), 7.23−7.43 (m, 6H), 7.66−7.70 (m, 2H); ^{13}C NMR δ 14.0, 22.5, 26.4, 27.2, 29.1, 31.6, 41.5, 44.2, 104.8, 124.6, 127.6, 128.1, 128.5, 128.9, 129.1, 132.2, 138.0, 150.1, 170.6. Anal. Calcd for $C_{23}H_{26}O_2$: C, 82.60; H, 7.84. Found: C, 82.88; H, 8.15.

3-Isopropyl-4,6-diphenyl-3,4-dihydropyran-2-one (6g/7g): white microcrystals (24%), mp 74−77 °C (from hexanes); ^{1}H NMR δ 0.90 (d, J = 6.7 Hz, 3H), 0.94 (d, J = 6.5 Hz, 3H), 1.84−1.92 (m, 1H), 2.55 (dd, J = 8.0, 3.4 Hz, 1H (*cis*)), 2.67 (dd, J = 8.6, 6.8 Hz, 1H (*trans*)), 3.79 (dd, J = 5.7, 3.3 Hz, 1H (*cis*)), 3.89 (pseudo-t, J = 6.6 Hz, 1H (*trans*)), 5.84 (d, J = 5.9 Hz, 1H (*cis*)), 6.01 (d, J = 6.6 Hz, 1H (*trans*)), 7.20−7.38 (m, 8H), 7.61−7.65 (m, 2H); ^{13}C NMR δ 20.6, 21.8, 25.9, 40.6, 50.5, 105.4, 124.5, 127.4, 127.9, 128.4, 128.8, 128.9, 132.1, 138.7, 149.5, 169.8. HRMS (EI) calcd for $C_{20}H_{20}O_2$ (M): 292.1463. Found: 292.1429.

1-Phenylhexa-1,3-diene (10a/11a): colorless liquid[16] (68%); ^{1}H NMR δ 1.03 (t, J = 7.5 Hz, 3H), 2.10−2.20 (m, 2H (*E*,*E*)), 2.22−2.36 (m, 2H (*E*,*Z*)), 5.51 (dt, J = 10.6, 7.6 Hz, 1H (*E*,*Z*)), 5.84 (dt, J = 15.1, 6.6 Hz, 1H (*E*,*E*)), 6.06−6.25 (m, 1H), 6.42 (d, J = 15.8 Hz, 1H (*E*,*E*)), 6.50 (d, J = 15.5 Hz, 1H (*E*,*Z*)), 6.74 (dd, J = 15.6, 10.3 Hz, 1H (*E*,*E*)), 7.06 (dd, J = 15.5, 11.1 Hz, 1H (*E*,*Z*)), 7.17 (dd, J = 13.5, 7.0 Hz, 1H), 7.24−7.41 (m, 4H); ^{13}C NMR δ 13.5 and 14.3, 21.3 and 25.8, 124.3, 126.1, 126.3, 127.0, 127.3, 128.1, 128.5, 128.6, 129.4, 129.5, 129.9, 131.9, 134.8, 137.3, 137.6, 137.7.

1-(2-Methoxyphenyl)hexa-1,3-diene (10b/11b): colorless oil (50%); ^{1}H NMR δ 1.04 (t, J = 7.5 Hz, 3H), 2.11−2.21 (m, 2H (*E*,*E*)), 2.27−2.33 (m, 2H (*E*,*Z*)), 3.83 (s, 3H), 5.49 (dt, J = 10.4, 7.6 Hz, 1H (*E*,*Z*)), 5.84 (dt, J = 15.1, 6.6 Hz, 1H (*E*,*E*)), 6.12−6.28 (m, 1H), 6.76−6.95 (m, 3H + H (*E*,*E*)), 7.08 (dd, J = 15.8, 11.1 Hz, 1H (*E*,*Z*)), 7.14−7.24 (m, 1H), 7.44 (d, J = 7.7 Hz, 1H (*E*,*E*)), 7.49 (d, J = 7.7 Hz, 1H (*E*,*Z*)); ^{13}C NMR δ 13.5 (*E*,*E*) and 14.3 (*E*,*Z*), 21.3 (*E*,*Z*) and 25.8 (*E*,*E*), 55.4, 110.8, 120.6, 124.7, 125.0, 126.2, 126.4, 126.6, 126.7, 128.0, 128.3, 128.8, 130.1, 130.3, 134.2, 136.7, 156.5. Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.19; H, 8.84.

1-(2-Furyl)hexa-1,3-diene (10c/11c): yellow unstable liquid (66%); ^{1}H NMR δ 1.03 (t, J = 7.4 Hz, 3H), 2.10−2.20 (m, 2H (*E*,*E*)), 2.24−2.34 (m, 2H (*E*,*Z*)), 5.51 (dt, J = 10.4, 7.7 Hz, 1H (*E*,*Z*)), 5.85 (dt, J = 15.1, 6.6 Hz, 1H (*E*,*E*)), 6.01−6.14 (m, 1H), 6.17−6.28 (m, 2H), 6.33−6.38 (m, 1H), 6.67 (dd, J = 15.6, 10.6 Hz, 1H (*E*,*E*)), 6.97 (dd, J = 15.4, 11.5 Hz, 1H (*E*,*Z*)), 7.33 (d, J = 6.6 Hz, 1H); ^{13}C NMR δ 13.5 and 14.3, 21.3 and 25.9, 107.3, 108.0, 111.4, 111.5, 117.8, 119.5, 123.1, 127.7, 128.2, 129.1, 135.1, 137.6, 141.6, 141.9, 153.5. HRMS (FAB) calcd for $C_{10}H_{13}O$ (M + 1): 149.0966. Found: 149.1064.

(*E*,*E*)-1-(4-*tert*-Butylphenyl)-2-methylhexa-1,3-diene (10d): colorless oil (25%); ^{1}H NMR δ 1.05 (t, J = 7.4 Hz, 3H), 1.32 (s, 3H), 1.99 (s, 2H), 2.10−2.22 (m, 2H), 5.80 (dt, J = 15.7, 6.5 Hz, 1H), 6.23 (d, J = 15.5 Hz, 1H), 6.40 (s, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ 13.9, 14.0, 26.0, 31.3, 34.5, 125.0, 128.9, 129.1, 131.5, 134.4, 135.3, 149.1. Anal. Calcd for $C_{17}H_{24}$: C, 89.40; H, 10.61. Found: C, 89.75; H, 11.02.

1-Phenyl-3-methylhexa-1,3-diene (10e/11e): colorless liquid[17] (82%); ^{1}H NMR δ 1.02 (t, J = 7.6 Hz, 3H (*E*,*E*)), 1.03 (t, J = 7.6 Hz, 3H (*E*,*Z*)), 1.84 (s, 3H (*E*,*E*)), 1.92 (s, 3H (*E*,*Z*)), 2.12−2.36 (m, 2H), 5.45 (t, J = 7.4 Hz, 1H (*E*,*Z*)), 5.62 (t, J = 7.3 Hz, 1H (*E*,*E*)), 6.44 (d, J = 16.1 Hz, 1H (*E*,*E*)), 6.54 (d, J = 16.1 Hz, 1H (*E*,*Z*)), 6.79 (d, J = 16.1 Hz, 1H (*E*,*E*)), 7.12−7.24 (m, 1H + 1H (*E*,*Z*)), 7.25−7.34 (m, 2H), 7.36−7.46 (m, 2H); ^{13}C NMR δ 12.2, 14.0, 14.5, 20.5, 20.9, 21.7, 125.5, 126.0, 126.1, 126.3, 126.8, 127.1, 128.1, 128.5, 128.6, 131.4, 133.2, 133.9, 134.0, 135.9, 138.0.

1-Phenyldeca-1,3-diene (10f/11f): colorless liquid[18] (66%); ^{1}H NMR δ 0.89 (t, J = 6.9 Hz, 3H), 1.29−1.42 (m, 8H), 2.14 (dd, J = 14.0, 6.9 Hz, 2H (*E*,*E*)), 2.28 (dd, J = 14.0, 6.9 Hz, 2H (*E*,Z)), 5.53 (dt, J = 10.7, 7.7 Hz, 1H (*E*,*Z*)), 5.82 (dt, J = 15.0, 7.0 Hz, 1H (*E*,*E*)), 6.11−6.25 (m, 1H), 6.43 (d, J = 15.7 Hz, 1H (*E*,*E*)), 6.52 (d, J = 15.7 Hz, 1H (*E*,*Z*)), 6.75 (dd, J = 15.7, 10.3 Hz, 1H (*E*,*E*)), 7.06 (dd, J = 15.5, 11.1 Hz, 1H (*E*,*Z*)), 7.15−7.43 (m, 5H); ^{13}C NMR δ 14.1, 22.6, 28.0, 28.9 and 29.0, 29.3 and 29.7, 31.7 and 32.9, 124.5, 126.1 and 126.3, 127.0 and 127.3, 128.5 and 128.6, 128.7 and 129.5, 129.9 and 130.4, 131.9 and 133.4, 136.1 and 137.7.

(*E*,*E*)-1-(4-*tert*-Butylphenyl)-2-methyldeca-1,3-diene (10g): colorless liquid (49%); ^{1}H NMR δ 0.89 (t, J = 6.6 Hz, 3H), 1.32 (s, 9H), 1.30−1.51 (m, 8H), 1.99 (s, 3H), 2.11−2.19 (m, 2H), 5.76 (dt, J = 15.5, 6.9 Hz, 1H), 6.23 (d, J = 15.5 Hz, 1H), 6.39 (s, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 14.0, 14.1, 22.6, 29.0, 29.6, 31.3, 31.8, 33.0, 34.5, 125.0, 128.9, 129.0, 130.1, 135.2, 135.3, 135.4, 149.1. Anal. Calcd for $C_{21}H_{32}$: C, 88.65; H, 11.36. Found: C, 88.73; H, 11.67.

1-Phenyl-3-methyldeca-1,3-diene (10h/11h): colorless liquid (58%); ^{1}H NMR δ 0.89 (t, J = 6.6 Hz, 3H), 1.29−1.43 (m, 8H), 1.86 (s, 3H (*E*,*E*)), 1.94 (s, 3H (*E*,*Z*)), 2.14−2.30 (m, 2H), 5.47 (t, J = 7.4 Hz, 1H (*E*,*Z*)), 5.64 (t, J = 7.4 Hz, 1H

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(*E*,*E*)), 6.44 (d, J = 16.0 Hz, 1H (*E*,*E*)), 6.54 (d, J = 16.1 Hz, 1H (*E*,*Z*)), 6.81 (d, J = 16.1 Hz, 1H (*E*,*E*)), 7.15−7.24 (m, 1H + 1H (*E*,*Z*)), 7.27−7.35 (m, 2H), 7.38−7.45 (m, 2H); ^{13}C NMR δ 12.4, 14.1, 20.5, 22.6 (*E*,*Z*), 27.6 and 28.5, 29.0 and 29.1, 29.6 and 29.9, 31.8 (*E*,*E*), 125.4, 126.1, 126.3, 126.8, 127.1, 128.0, 128.5 and 128.6, 131.8, 132.5, 133.6, 134.1, 134.6, 138.0 and 138.1. HRMS (FAB) calcd for $C_{17}H_{24}$ (M): 228.1878. Found: 228.1853.

1-Phenyl-5-methylhexa-1,3-diene (10i): colorless liquid[19] (8%); ^{1}H NMR δ 1.05 (d, J = 6.7 Hz, 6H), 2.36−2.44 (m, 1H), 5.81 (dd, J = 15.2, 6.7 Hz, 1H), 6.17 (dd, J = 15.1, 10.3 Hz, 1H), 6.46 (d, J = 15.8 Hz, 1H), 6.75 (dd, J = 15.7, 10.3 Hz, 1H), 7.19 (t, J = 7.1 Hz, 1H), 7.26−7.32 (m, 2H), 7.37 (d, J = 7.4 Hz, 2H); ^{13}C NMR δ 22.3, 31.3, 126.1, 127.0, 127.5, 128.5, 129.6, 130.1, 137.7, 142.7.

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