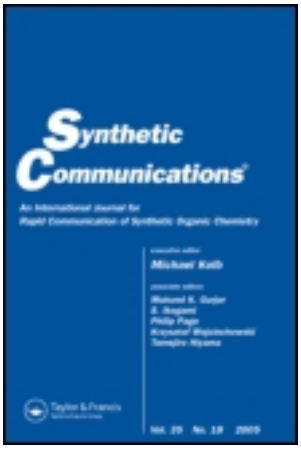

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Efficient Synthesis of Tetrahydrobenzo[b]pyrans under Solvent-Free Conditions at Room Temperature

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Efficient Synthesis of Tetrahydrobenzo[*b*]pyrans under Solvent-Free Conditions at Room Temperature

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Abstract: A range of tetrahydrobenzo[*b*]pyrans have been synthesized in very good yields under solvent-free conditions by grinding α-cyanocinnamonitrils or β-cyano-β-carbethoxy styrene and 5,5-dimethyl-1,3-cyclohexanedione in the presence of TEBA as catalyst. The short reaction time, cleaner reaction, and easy workup make this protocol practical and economically attractive.

Keywords: α-Cyanocinnamonitrils, β-cyano-β-carbethoxy styrene, solvent-free conditions, tetrahydrobenzo[*b*]pyrans

The increasing attention during the past decades on environmental protection has influenced both modern academic and industrial groups to develop

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chemical processes with maximum yield and minimum cost while using nontoxic reagents, catalysts, and solvents, or even better, no solvents. In recent years, solid-state organic reactions have caused great interest. They have many advantanges such as high efficiency and selectivity, easy separation and purification, and mild reaction conditions and benefit industry as well as the environment.[1] Many articles about solid-state reactions with grinding have been reported, such as such as the Grignard reaction,[2] Reformatsky reaction,[3] aldol condensations,[4] Dieckmann condensations,[5] phenol coupling reaction,[6] reduction reaction,[7] and other reactions.[8]

Pyrans and their derivatives are versatile intermediates[9] in the fields of pharmaceuticals, cosmetics, and perfumes. Pyran derivatives also act as modulators of potassium channels, influencing the activity of the heart and blood pressure.[10] Further, tetrahydrobenzo[*b*]pyrans are important derivatives of pyrans, which have received considerable attention in recent years because of their wide range of biological activities.[11] Compounds with these ring systems have diverse pharmacological activities such as anticoagulant, anticancer, spasmolytic, diuretic, and activities anti-ancaphylactia.[12] Tetrahydrobenzo[*b*]pyrans also constitute the structural unit of a series of natural products.[13] A number of 2-amino-4*H*-pyrans are useful as photoactive materials.[14] Several methods have been reported for the synthesis of this compounds; for example, Kamaljit et al.[15] reported that ethyl 2-amino-5,6,7,8-tetrahydro-5-oxo-4-aryl-7,7-dime-thyl-4*H*-benzo-[*b*]-pyran-3-carboxylates were prepared by the reaction of β-cyano-β-carbethoxy styrene with 1,3-cyclohexanedione in refluxing acetonitrile–acetic acid (10 : 1, V/V). Wang et al.[16] reported synthesis of these compounds in DMF using piperidine as catalyst. They both used organic solvents, made the workup procedure complicated, and led to poor yields of the products besides polluting the environment. Kaupp et al.[17] reported a novel method for the synthesis of benzo[*b*]pyrans utilizing the reactants in solid or molten state. This reaction has some limitations: the two-step reaction was performed at very high temperature and required a longer period of time. Moreover, the reaction was applied for the synthesis of only a few compounds. Ipsita et al.[18] and Tu et al.[19] have reported synthesis of 4*H*-benzo[*b*]pyrans under microwave irradiation conditions, but it has only been carried out in laboratory and is difficult to apply in the industrial process until now. Shi et al.[20] has also reported synthesis of those compounds in water, but used high reaction temperatures and long reaction times. Herein, we describe an efficient, green, and convenient procedure for the synthesis of tetrahydrobenzo[*b*]pyrans under solvent-free conditions at room temperature.

Recently, in our research, we found phase-transfer catalysis (such as triethylbenzylammonium chloride, TEBA) could be efficiently used in solid-state organic reactions.[21] To extend our research, we chose TEBA as a catalyst and tried to use in the synthesis of tetrahydrobenzo[*b*]pyrans from the reaction of 5,5-dimethyl-1,3-cyclohexanedione with α-cyanocinnamonitrils; to our surprise, we found the reaction could be completed with high

yields in a very short time. When we chose β-cyano-β-carbethoxy styrene instead of α-cyanocinnamonitrils, it reacted with 5,5-dimethyl-1,3-cyclohexanedione in similar conditions, and the outcomes of reaction were good also.

The experimental procedure was very simple. A mixture of α-cyanocinnamonitrils or β-cyano-β-carbethoxy styrene 1 (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione 2 (1 mmol), and TEBA (2 mmol) was ground at room temperature with the agate mortar and pestle under solvent-free conditions. Within a few minutes, the reactions could be completed with high yields (Scheme 1). The results are summarized in Table 1.

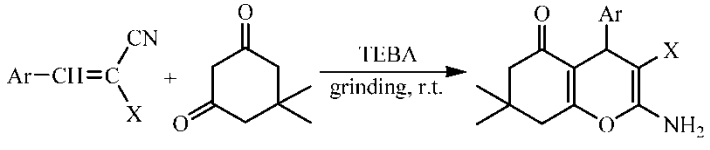
In conclusion, we have developed a new protocol for synthesizing tetrahydrobenzo[*b*]pyrans. To our knowledge, TEBA is first used as a catalyst in solvent-free reactions. The present method describes an efficient and practical alternative to the preparation of tetrahydrobenzo[*b*]pyrans that, in contrast to most of the existing protocols, does not require any solvent and consequently minimizes the generation of toxic waste. We believe that the present methodology addresses the current trend toward green chemistry.

EXPERIMENTAL

Melting points were uncorrected. ^{1}H NMR spectra were obtained for solutions in $CDCl_3$ with Me_4Si as internal standard using an Inova-400 spectrometer. Microanalyses were carried out using a Perkin-Elmer 2400 II analyzer. IR spectra were recorded on an FTIR-8101 spectrometer in KBr.

General Procedure

α-Cyanocinnamonitrils or β-cyano-β-carbe-thoxy styrene **1** (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione **2** (1 mmol), and TEBA (2 mmol) were added to a mortar. The mixture was ground with a pestle at room temperature. The reaction was completed within a few minutes (monitored by TLC) and poured into water. The product was filtered, dried, and recrystallized from 95% ethanol. All the products were characterized by comparison of their spectroscopic and physical data with authentic samples synthesized by reported procedures.[20]



1 **2** **3**

Scheme 1.

Table 1. Synthesis of tetrahydrobenzo[*b*]pyrans under mild and solvent-free conditions

Entry	Ar	X	Reaction time (min)	Yield (%)
3a	C_6H_5	CN	10	92
3b	4-ClC_6H_4	CN	5	95
3c	4-FC_6H_4	CN	5	94
3d	4-$CH_3C_6H_4$	CN	10	90
3e	4-$CH_3OC_6H_4$	CN	10	85
3f	2-ClC_6H_4	CN	5	93
3g	3,4-$OCH_2OC_6H_4$	CN	8	95
3h	4-BrC_6H_4	CN	5	91
3i	2,4-$Cl_2C_6H_4$	CN	4	96
3j	C_6H_5	$COOC_2H_5$	15	88
3k	4-ClC_6H_4	$COOC_2H_5$	8	93
3l	4-FC_6H_4	$COOC_2H_5$	8	94
3m	2,4-$Cl_2C_6H_4$	$COOC_2H_5$	5	97
3n	4-$CH_3C_6H_4$	$COOC_2H_5$	15	90
3o	4-$CH_3OC_6H_4$	$COOC_2H_5$	15	90
3p	3,4-$OCH_2OC_6H_4$	$COOC_2H_5$	10	94
3q	C_6H_5	$COOCH_3$	10	92
3r	4-ClC_6H_4	$COOCH_3$	8	95
3s	4-$CH_3C_6H_4$	$COOCH_3$	10	90
3t	2,4-$Cl_2C_6H_4$	$COOCH_3$	8	96

Spectral and Analytical Data of Some Selected Compounds

Compound **3a**: mp: 232–234°C. IR (KBr) ν: 3397, 3213, 3034, 2961, 2199, 1681, 1661, 1598, 1443, 1414, 1370, 1251, 1214, 1150, 1036, 843, 812, 745, 695 cm^{-1}. ^1H NMR (DMSO-d6) δ: 0.95 (3H, s, CH_3), 1.04 (3H, s, CH_3), 2.10 (1H, d, $J = 16.0$ Hz, C8-H), 2.25 (1H, d, $J = 16.0$ Hz, C^8-H), 2.47–2.55 (2H, m, C^6-H), 4.16 (1H, s, C^4-H), 6.99 (2H, s, NH_2), 7.12–7.30 (5H, m, ArH). Anal. calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.20; H, 6.43; N, 9.61%.

Compound **3b**: mp 237–249°C. IR (KBr) ν: 3375, 3181, 2958, 2188, 1664, 1596, 1490, 1495, 1398, 1364, 1234, 1215, 1132, 1087, 1032, 854, 825, 770, 685 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.94 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 2.10 (d, $J = 16.0$ Hz, 1H, C^8-H), 2.24 (d, $J = 16.0$ Hz, 1H, C^8-H), 2.46–2.55 (m, 2H, C^6-H), 4.19 (s, 1H, C^4-H), 7.05 (s, 2H, NH_2), 7.16 (d, $J = 7.2$ Hz, 2H, ArH), 7.34 (d, $J = 7.2$ Hz, 2H, ArH). Anal. calcd. for $C_{18}H_{17}ClN_2O_2$: C, 65.75; H, 5.21; N, 8.52. Found: C, 65.50; H, 5.40; N, 8.65%.

Compound **3c**: mp 192–194°C. IR (KBr) ν: 3367, 3179, 2960, 2190, 1675, 1628, 1593, 1506, 1406, 1367, 1253, 1216, 1156, 1131, 1033, 975, 859,

838, 775, 706 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.94 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 2.10 (d, $J = 16.0$ Hz, 1H, C^8-H), 2.24 (d, $J = 16.0$ Hz, 1H, C^8-H), 2.45–2.57 (m, 2H, C^6-H), 4.19 (s, 1H, C^4-H), 7.02 (s, 2H, NH_2), 7.07–7.19 (m, 4H, ArH). Anal. calcd. for $C_{18}H_{17}FN_2O_2$: C, 69.22; H, 5.49; N, 8.97. Found: C, 69.17; H, 5.34; N, 9.10%.

Compound **3d**: mp 220–222°C. IR (KBr) ν: 3426, 3331, 2957, 2192, 1676, 1640, 1601, 1510, 1459, 1404, 1369, 1318, 1242, 1205, 1157, 1136, 1033, 971, 909, 842, 765 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.95 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.09 (d, $J = 16.0$ Hz, 1H, C^8-H), 2.24 (d, $J = 16.0$ Hz, 1H, C^8-H), 2.25 (s, 3H, CH_3), 2.45–2.56 (m, 2H, C^6-H), 4.12 (s, 1H, C^4-H), 6.96 (s, 2H, NH_2), 7.02 (d, $J = 8.0$ Hz, 2H, ArH), 7.08 (d, $J = 8.0$ Hz, 2H, ArH); Anal. calcd. for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N 9.08. Found C, 74.30; H, 6.77; N, 9.31%.

Compound **3e**: mp 196–198°C. IR (KBr) ν: 3377, 3186, 2964, 2198, 1681, 1655, 1596, 1509, 1456, 1406, 1369, 1249, 1209, 1171, 1157, 1137, 1037, 1034, 968, 843, 768 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.95 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 2.09 (d, $J = 16.0$ Hz, 1H, C^8-H), 2.24 (d, $J = 16.0$ Hz, 1H, C^8-H), 2.46–2.56 (m, 2H, C^6-H), 3.71 (s, 3H, OCH_3), 4.12 (s, 1H, C^4-H), 6.84 (d, $J = 8.0$ Hz, 2H, ArH), 6.95 (s, 2H, NH_2), 7.05 (d, $J = 8.0$ Hz, 2H, ArH). Anal. calcd. for $C_{19}H_{20}N_2O_3$: C, 74.35; H, 6.21; N, 8.64. Found: C, 74.25; H, 6.77; N, 8.31%.

Compound **3j**: mp: 151–153°C. IR (KBr) ν: 3403, 3290, 3027, 2956, 1693, 1655, 1606, 1524, 1475, 1453, 1371, 1288, 1202, 1165, 1081, 1039, 835, 796, 725, 697 cm^{-1}. ^1H NMR (DMSO-d6) δ: 0.89 (3H, s, CH_3), 1.04 (3H, s, CH_3), 1.09 (3H, t, $J = 7.2$ Hz CH_3), 2.06 (1H, d, $J = 16.0$ Hz, C^8-H), 2.26 (1H, d, $J = 16.0$ Hz, C^8-H), 2.46 (1H, d, $J = 17.6$ Hz, C^6-H), 2.55 (1H, d, $J = 17.6$ Hz, C^6-H), 3.94 (2H, q, $J = 7.2$ Hz, CH_2O), 4.50 (1H, s, C^4-H), 7.02–7.22 (5H, m, ArH), 7.54 (2H, s NH_2). Anal. calcd. for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79; N, 4.10. Found: C, 70.53; H, 6.63; N, 3.97%.

Compound **3k**: mp: 153–154°C. IR (KBr) ν: 3480, 3327, 2976, 1681, 1665, 1524, 1485, 1371, 1302, 1298, 1202, 1165, 1081, 1039, 915, 835 cm^{-1}. ^1H NMR (DMSO-d6) δ: 0.89 (3H, s, CH_3), 1.04 (3H, s, CH_3), 1.09 (3H, t, $J = 7.2$ Hz CH_3), 2.06 (1H, d, $J = 16.0$ Hz, C^8-H), 2.26 (1H, d, $J = 16.0$ Hz, C^8-H), 2.46 (1H, d, $J = 17.6$ Hz, C^6-H), 2.55 (1H, d, $J = 17.6$ Hz, C^6-H), 3.94 (2H, q, $J = 7.2$ Hz, CH_2O), 4.50 (1H, s, C^4-H), 7.12–7.22 (5H, m, ArH), 7.56 (2H, s NH_2). Anal. calcd. for $C_{20}H_{22}ClNO_4$: C, 63.91; H, 5.90; N, 3.73. Found: C, 64.08; H, 5.71; N, 3.58%.

Compound **3n**: mp: 165–166°C. IR (KBr) ν: 3408, 3289, 2976, 1692, 1665, 1625, 1520, 1485, 1370, 1298, 1202, 1081, 1039, 835, 789 cm^{-1}. ^1H NMR (DMSO-d6) δ: 0.89 (3H, s, CH_3), 1.04 (3H, s, CH_3), 1.09 (3H, t, $J = 7.2$ Hz

CH_3), 2.06 (1H, d, $J = 16.0$ Hz, C^8-H), 2.20 (3H, s, CH_3), 2.26 (1H, d, $J = 16.0$ Hz, C^8-H), 2.46 (1H, d, $J = 17.6$ Hz, C^6-H), 2.55 (1H, d, $J = 17.6$ Hz, C^6-H), 2.53 (1H, d, $J = 17.6$ Hz, C^6-H), 3.94 (2H, q, $J = 7.2$ Hz, CH_2O), 4.50 (1H, s, C^4-H), 6.92–7.02 (4H, m, ArH), 7.50 (2H, s NH_2). Anal. calcd. for $C_{21}H_{25}NO_4$: C, 70.96; H, 7.09; N, 3.94. Found: C, 70.41; H, 6.83; N, 3.94%.

Compound **3q**: mp: 144–146°C. IR (KBr) ν: 3405, 3304, 2955, 1693, 1655, 1536, 1438, 1370, 1286, 1204, 1164, 1075, 1036, 838, 792, 766, 728, 704 cm^{-1}. ^{1}H NMR (DMSO-d6) δ: 0.88 (3H, s, CH_3), 1.03 (3H, s, CH_3), 2.06 (1H, d, $J = 16.0$ Hz, C^8-H), 2.26 (1H, d, $J = 16.0$ Hz, C^8-H), 2.45 (1H, d, $J = 16.0$ Hz, C^6-H), 2.53 (1H, d, $J = 16.0$ Hz, C^6-H), 3.50 (3H, s, CH_2O), 4.52 (1H, s, C^4-H), 7.06–7.22 (5H, m, ArH), 7.52 (2H, s NH_2). Anal. calcd. for $C_{19}H_{21}NO_4$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.77; H, 6.34; N, 4.66%.

Compound **3r**: mp: 160–161°C. IR (KBr) ν: 3478, 3319, 2960, 1693, 1655, 1536, 1488, 1370, 1286, 1204, 1164, 1075, 1036, 838, 792, 766, 728, 704 cm^{-1}. ^{1}H NMR (DMSO-d6) δ: 0.88 (3H, s, CH_3), 1.03 (3H, s, CH_3), 2.06 (1H, d, $J = 16.0$ Hz, C^8-H), 2.26 (1H, d, $J = 16.0$ Hz, C^8-H), 2.45 (1H, d, $J = 16.0$ Hz, C^6-H), 2.53 (1H, d, $J = 16.0$ Hz, C^6-H), 3.50 (3H, s, CH_2O), 4.52 (1H, s, C^4-H), 7.15 (2H, $J = 8.0$ Hz, ArH), 7.25 (2H, $J = 8.0$ Hz), 7.58 (5H, m, ArH), 7.55 (2H, s NH_2). Anal. calcd. for $C_{19}H_{20}ClNO_4$: C, 63.07; H, 5.57; N, 3.87. Found: C, 63.28; H, 5.46; N, 3.88%.

Compound **3s**: mp: 190–192°C. IR (KBr) ν: 3412, 3309, 2960, 1693, 1655, 1653, 1520, 1438, 1370, 1286, 1204, 1164, 1081, 1036, 907, 845, 792, 766, 740, 704 cm^{-1}. ^{1}H NMR (DMSO-d6) δ: 0.88 (3H, s, CH_3), 1.03 (3H, s, CH_3), 2.06 (1H, d, $J = 16.0$ Hz, C^8-H), 2.26 (1H, d, $J = 16.0$ Hz, C^8-H), 2.45 (1H, d, $J = 16.0$ Hz, C^6-H), 2.53 (1H, d, $J = 16.0$ Hz, C^6-H), 3.50 (3H, s, CH_2O), 4.52 (1H, s, C^4-H), 6.98–7.03 (4H, m, ArH), 7.48 (2H, s NH_2). Anal. calcd. for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79; N, 4.10. Found: C, 70.65; H, 6.52; N, 3.95%.

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