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Novel Syntheses of Isomers of Damascenone from Ethyl 2,6,6-Trimethyl-4-oxo-2-cyclohexene-1-carboxylate

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Received July 20, 1990

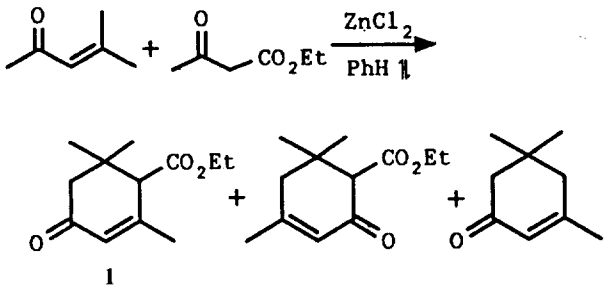
Three isomers of damascenone, odorous terpenic ketones, have been synthesized conveniently from a same starting material, ethyl 2,6,6-trimethyl-4-oxo-2-cyclohexene-1-carboxylate(**1**), which was easily available by the acid-catalyzed condensation of mesityl oxide or acetone with ethyl acetoacetate. α-Damascenone(**7**) was prepared by converting the enone ester **1** into the corresponding tosylhydrazone(**4**), followed by treating with 4 molar equiv of allyllithium. β-Damascenone(**12**) was synthesized by chemoselective reduction of **1** with sodium borohydride/cerium chloride to give corresponding allylic alcohol **8**, conversion of **8** into acetate **9**, and thermal decomposition of **9** with DBU to afford ethyl β-safranate(**10**), followed by reaction with an excess amount of allyllithium. γ-Damascenone(**15**) was obtained by dehydration of **8** with boric acid to furnish γ-safranate(**13**), followed by treatment with 2 molar equiv of allyllithium.

Introduction

β-Damascenone(**12**), a terpenic ketone first isolated from Bulgarian rose oil[1] (*Rosa damascena* Mill) and later found in the essential oils of other natural materials,[2,3] is a highly odoriferous compound important in the creation of modern fragrances. Because of its industrial importance, much effort has been devoted[1,4-16] to the synthesis of this enone as well as its structurally related isomers, α-damascenone(**7**) and γ-damascenone(**15**), which are of equal industrial interest. Existing syntheses proceed from β-cyclocitral,[1,7] ethyl β-safranate,[5] 5-acetyl-4,4-dimethylcyclohexene,[11] dimedone,[14] or from 2,2,6-trimethylcyclohexanone derivatives. However, these methods not only require starting materials which are not readily available, but also result in poor product selectivity and low total yield. In this paper we describe a full account of new and efficient syntheses of α-, β-, and γ-damascenones from a common starting material, ethyl 2,6,6-trimethyl-4-oxo-2-cyclohexene-1-carboxylate(**1**).

Results and Discussion

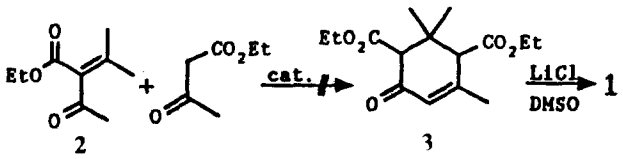
The enone ester **1** has been prepared by zinc chloride[17] or boron trifluoride[18] catalyzed condensation of mesityl oxide with ethyl acetoacetate or by boron trifluoride catalyzed condensation of ethyl acetoacetate with acetone.[18,19] In the preparation of **1** by the literature procedure of Surmatis *et al.*[17] (Scheme 1), we examined various catalysts such as chlorides



Scheme 1.

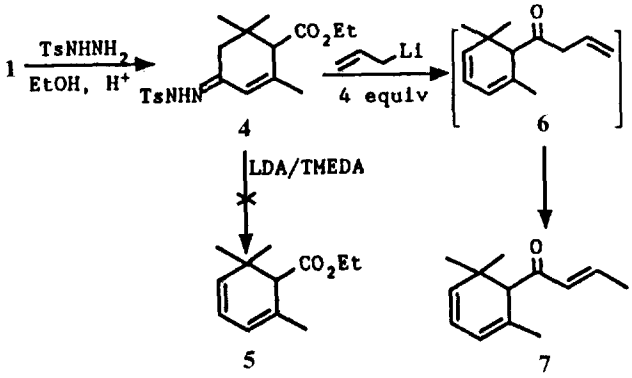
of antimony, cadmium, mercury, silver, tin and titanium, and formic acid and titanium dichlorodiisopropoxide, though the zinc chloride was found to be the best one.

This reaction must proceed *via* acid-catalyzed Michael addition of ethyl acetoacetate to mesityl oxide, followed by intramolecular aldol condensation of the addition product, to give a mixture product containing an enone ester **1** and the isomer. Because of lower yield and some troubles in separation of **1** from the other side products of this reaction, we tried a preparation of pure enone diester **3** by the analogous reaction using an enone ester **2**, for it could be expected to convert **3** into pure **1** by regioselective decarboethoxylation. In spite of structural advantage, the enone ester **2** did not react with ethyl acetoacetate even under various catalysts to give the anticipated enone diester **3**. Better preparation of the enone ester **1** has not been developed so far.

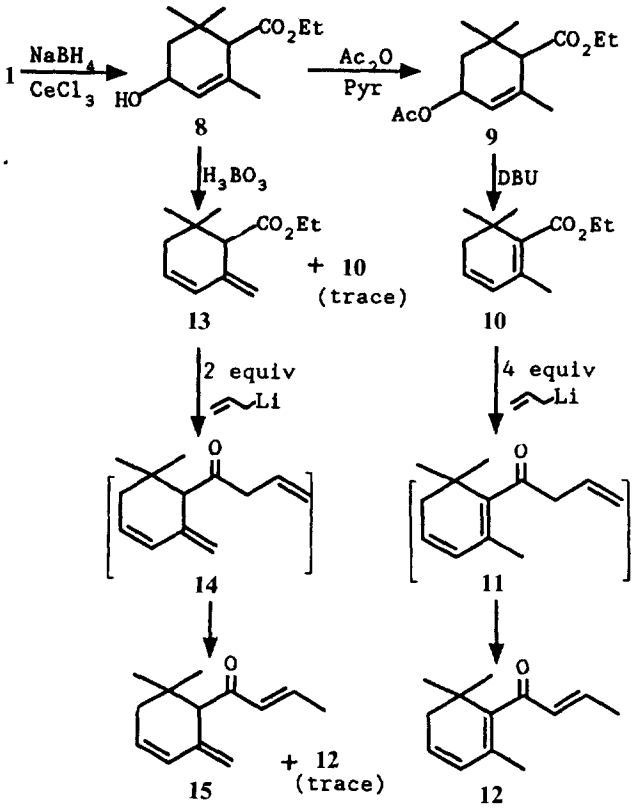


α-Damascenone(7) was first synthesized by Büchi and Wüest[5] by the action of allyllithium[20] on ethyl α-safranate(5), followed by isomerization of the primary condensation product 6 with t-BuOK. They prepared the synthetic precursor 5 in 60-69% yield by the Wittig condensation of α-isopropylideneacetoacetate with the ylide prepared from allyltriphenylphosphonium chloride and BuLi (or MeLi). This method, however, is not applicable in practical use, since the reactants are not easily available. So, we tried the synthesis of 5 by reducing the easily available enone ester 1 to the corresponding allylic alcohol 8, followed by dehydration. However, oddly enough, the dehydration product was not the anticipated 5, but a mixture of β- (10) and γ-isomer(13) (*vide infra*). Thus, application of the Shapiro olefination[21,22] was examined to the conversion of 1 into 5: The tosylhydrazone 4 was prepared by the reaction of tosylhydrazine with 1 in ethanol, to give colorless needles, mp. 140-141℃. Treatment of 4 with a strong base LDA in THF/TMEDA did not give Shapiro product, diene ester 5, but a complicated mixture, which was not identified.

Now, we examined the chemoselective reaction of butyllithium with 4 that has two functionalities, hydrazone and ester, since we expected, if any difference in reactivity between the two functional groups, the formation only of the Shapiro product 5 or a tertiary alcohol bearing hydrazone unit. Careful experiments were performed varying the reaction temperature(−78℃ to 0℃) and the amount of the metallic reagent. But, it was found that the reaction was not chemoselective, because the metallic reagent attacked both of the reaction sites simultaneously. Thus, the reaction of 4 with allyllithium was examined, expecting both Shapiro olefination at hydrazone and crotonation at ester functions, to give 6. With a small amount of allyllithium, the reaction product showed complicated spots on TLC. But, by increasing the metallic reagent the reaction became simpler, and use of an excess of this reagent resulted in the formation of 7 as a major product. The best result was obtained by treating 4 with 4 molar equiv of allyllithium, providing 67-70% isolated yield of 7(Scheme 2). The precursor 6 was not formed. In this novel reaction, allyllithium acted not only as



Scheme 2.



Scheme 3.

a base for Shapiro reaction to form a olefinic function, but also as an ordinary nucleophile for condensation with ester moiety. Allyl Grignard reagent can not take the place of allyllithium, not only because it gives tertiary alcohol upon reaction with ester group, but also it has no effect on the Shapiro reaction. The spectral data of 7 thus synthesized were well agreed in all respects(NMR, IR, MS) with those on the literature.[5]

In this synthesis, reaction product was not the expected trienone 6, but the isomer 7. The effect of excess allyllithium (4 equiv) used in this experiment could be accounted for by assuming that 2 equiv of this reagent was consumed by the Shapiro olefination, 1 equiv was used for attack on ester function to give 6, and the remaining base was utilized for abstraction of α-proton from 6 to form an enolate which might retard the formation of tertiary alcohol and/or for *in situ* isomerization of 6 by reaching the equilibrium which was in favor of the conjugated enone 7.

β-Damascenone(12) has been extensively investigated by many workers. One of the most important synthetic precursors of the enone 12 is ethyl β-safranate(10). Büchi and Wüest[5] prepared 10 by the acid(TsOH) catalyzed isomerization of α-safranate(5) in benzene. However, 5 could not be converted completely into the corresponding β-isomer 10, and they obtained a mixture of α-, β-, and γ-isomers in the ratio 20:58:22, from which 10 was separated by chromatography. But, this method is not recommendable because of the difficulty of separation of 10 from the other isomers. In 1979, Torii *et al.*[13] reported a new synthesis of methyl β-safranate (10′) to utilize in the synthesis of 7, instead of 10. Their synthesis of 10′ involves a base-catalyzed desulfination of 2,6,6-trimethyl-1-(methoxycarbonyl)-4-(phenylsulfonyl)cyclo-

hexene which was obtained from the acid-catalyzed cyclization of methyl 5-(phenylsulfonyl) geranate prepared from prenyl phenyl sulfone. Although the yield is reasonable, this method is also not appropriate in practical use, because the reagents used are not easily available and the procedure is long and annoying.

In this work we develped a new and convenient synthesis of **10** from the enone ester **1**, without any impurities or isomers: The regioselective 1,2-reduction of **1** to the corresponding allylic alcohol **8** could be carried out, in almost quantitative yield without any impurities, by treating **1** in methanol with sodium borohydride and cerium(III) chloride.[23] Treatment of **8** with acetic anhydride in pyridine gave the corresponding acetate **9** in excellent yield. Ethyl β-safranate(**10**) could be prepared, with the isolated yield of 95%, by thermal decomposition of the acetate **9** in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU)[14] for 20 sec(Scheme 3). But, the other bases such as 1,4-diazabicyclo[2.2.2]octane(Dabco), 2,6-lutidine, Et_3N, and t-BuOK cannot take the place of DBU.

β-Damascenone(**12**) was obtained by treating β-safranate (**10**) at 0℃ with an excess amount of allyllithium. However, the best result was obtained here by the reaction of **10** with 4 molar equiv of allyllithium to afford 70% isolated yield of **12**, Büchi *et al.*[5] carried out this reaction at −60℃ using 2 molar equiv of allyllithium to give a mixture of **11** and **12**, which was then isomerized with t-BuOK into **12**. In our experiment, however, the isomerization step was unnecessary, as the product was not the mixture of **11** and **12**, but the pure **12**. The spectral data of **12** prepared in this way were well agreed in all respects (NMR, IR, MS) with those on the literature.[5,14]

γ-Damascenone(**15**) is not a natural product and the synthetic study has never been done. In the beginning of this work, we were trying the preparation of **5** by dehydration of **8**, as a synthetic precursor of **7**. Though examined the various dehydration agents for this purpose, we were unable to convert **8** into **5**. The dehydration product was not the anticipated **5**, but a mixture of **10** and **13**. With some dehydration agents, **13** was the major product. For instance, use of phosphorus oxychloride[24] and anhydrous cupric sulfate[25] as dehydration agent gave 30-40% yield of a mixture of **13** and **10** in the ratio of about 3:1. Now, we investigated the efficient conversion of **8** into **13**. The dehydration of **8** by pyrolysis with boric acid[26] gave the best result. Strong heating of a mixture of **8** and boric acid in a sand bath furnished a reasonable yield of dehydration product **13**, though slightly contaminated[27] by **10**, which could be separated by ordinary chromatographic technique. The spectral data of **13** thus prepared were well agreed with those on the literature.[5] γ-Damascenone(**15**) could also be prepared in good yield by treating **13** with proper amount of allyllithium. But, in this case, different from those of α- and β-isomers, an excess of the metallic reagent must be avoided. Use of a large excess of the reagent did not give **15**, but exclusively **12** as a main product. This fact could be accounted for by assuming that the excess reagent not only isomerizes **14** to **15**, but also **15** to **12**. The best result was obtained by treating **13** in THF with 2 equiv of allyllithium, providing 60% yield of almost pure **15**.

In summary, we have shown that three isomers of damascenone could be conveniently synthesized from an easily available enone ester **1**. Herein, we note that: (1) the direct conversion of the tosylhydrazone **4** into α-damascenone is a novel reaction; (2) synthesis of pure β-safranate from **1** is a new synthetic procedure; (3) the conversion of allylic alcohol **8** into γ-safranate is a new method; (4) γ-damascenone can be completely converted with base into the β-isomer. The reaction of allyllithium in this work is of considerable interest, since desired products were selectively yielded depending upon the amount of the metallic reagent and substrates.

Experimental Section

General. All anhydrous reactions were conducted with the unusual precautions for rigorous exclusion of air and moisture. Diethyl ether and tetrahydrofuran were purified by refluxing for hours with sodium benzophenone ketyl under nitrogen, followed by distilling prior to use. Flash chromatography was carried out using silica gel 60 (E. M. Merck, particle size 0.040-0.063 mm, 230-400 mesh ASTM). proton NMR spectra were recorded on a Bruker AC-80, a Varian VXR-200, or a Varian EM-360A spectrometers to an internal standard of TMS. IR spectra were obtained on Perkin-Elmer Model 782 spectrometer. MS spectra were recorded on a Shimazu-LKB 9000 GC/MS system, or VG-7025 normal geometry. Melting points were uncorrected.

Ethyl 2,6,6-trimethyl-4-oxo-2-cyclohexene-1-carboxylate(1). This compound was prepared by the literature procedure reported by Surmatis *et al.*[17] In a 100-m*l* round-bottomed flask, fitted with a reflux condenser and a Dean-Stark trap, were placed mesityl oxide(9,8 g, 100 mmol), ethyl acetoacetate(13 g, 100 mmol), $ZnCl_2$(2 g, 15 mmol), and a mixed solvent of n-hexane/benzene(20 m*l*, 1:1, v/v), and the mixture was heated at reflux for 3 d. The reaction mixture was extracted with ether, washed with aq. $NaHCO_3$ and water successively, dried(anhyd. $MgSO_4$), and removed the solvent. The crude product was distilled *in vacuo* (2-3 torr), collecting the mixture of **1** and the isomer (4:1) at 130℃(lit. 77-78℃, 0.2 torr). The crude distillate was chromatographed (silica gel, n-hexane/ether, 7:3 v/v) to give **1** as an oil in 20-25% yield.

Allyllithium. This organometallic reagent was prepared by the literature procedure[20] which involves reaction of allyl phenyl ether in THF with sixfold excess of metallic lithium. The yield of this reaction was estimated to be 60% as determined by a double titration method in the literature.

Tosylhydrazone 4. To a hot solution of **1** (4.0 g, 19.0 mmol) in ethanol(95%, 10 m*l*) were added tosylhydrazine (3.9 g, 20.9 mmol) and conc. HCl(3 drops), and the mixture was boiled for 10 min and allowed to cool overnight in an ice bath. The solid product was collected by suction filtration and washed with a small amount of ether, to give a colorless crystal, mp. 140-141℃, in 78%(5.6 g) yield. ^{1}H-NMR($CDCl_3$/TMS, 80 MHz) δ 0.91(s, 3H, CH_3), 1.03(s, 3H, CH_3), 1.21(t, J=7 Hz, 3H, CH_2CH_3), 1.81(d, J=1 Hz, 3H, allylic CH_3), 2.08 and 2.43(J_{AB}=16 Hz, 2H, CH_2 in ring), 2.41(s, 3H, $ArCH_3$), 4.11(q, J=7 Hz, 2H, CH_2CH_3), 6.06(s, 1H, vinyl), 7.23-7.89(m, 4H, arom.), 7.68(s, 1H, NH). IR(KBr) 3200(N-H), 2990, 1740 (C=O), 1600, 1160 cm^{-1}.

α-Damascenone(7); 2,6,6-Trimethyl-trans-1-crotonyl-2,4-cyclohexadiene. To a solution of **4**(0.76 g, 2.0 mmol) in

THF(15 m*l*), cooled to −20℃, was added dropwise, during 30 min, allyllithium (8.4 mmol) prepared from allyl phenyl ether(1.9 g, 14 mmol) and metallic lithium(0.28 g, 40 mmol). The mixture was allowed to warm to room temperature, followed by stirring for 12 h. Water(50 m*l*) was added, extracted with ether, washed the organic layer with water, dried(anhyd. $MgSO_4$), and removed the solvent at a reduced pressure. The crude product was chromatographed on a silica gel column using n-hexane/dichloromethane(9:1, v/v) as an eluent, to give 67%(0.25 g) yield of **7** as an oil. ^{1}H-NMR($CDCl_3$/TMS, 200 MHz) δ 0.98(s, 3H, CH_3), 1.04(s, 3H, CH_3), 1.69(s, 3H, allylic CH_3), 1.81(dd, J=7, 2 Hz, 3H, crotonyl CH_3), 2.70(s, 1H, tert. CH), 5.42-5.48 and 5.80-5.88(m, 3H, vinyl in ring), 6.45(dq, J=16, 2 Hz, 1H, CO-CH=), 6.88(dq, J=16, 7 Hz, 1H, =CHMe). IR(neat, NaCl) 3020, 2980, 1680, 1620, 1595, 970 cm^{-1}. MS(*m/z*) 190(M^+), 121, 69.

Ethyl 2,6,6-trimethyl-4-hydroxy-2-cyclohexene-1-carboxylate(8). To a solution of enone ester **1**(0.9 g, 4.28 mmol) and $CeCl_3 \cdot 7H_2O$(1.6 g, 4.3 mmol) in methanol(10 m*l*) was added $NaBH_4$(0.17 g, 4.5 mmol) in portion and stirred for 5 min. The reaction mixture was neutralized with dilute HCl, and methanol was removed by evaporation under reduced pressure. The residue was extracted with ether, dried(anhyd. $MgSO_4$), and evaporated the solvent *in vacuo*. The crude product was chromatographed(silica gel/ether) to give **8** as an oil in 97%(0.88 g) yield ^{1}H-NMR($CDCl_3$/TMS, 80 MHz) δ 0.89(s, 6H, $2CH_3$), 1.24(t, J=7 Hz, 3H, CH_2CH_3), 1.62(s, 3H, allylic CH_3), 1.59-1.71(m, 2H, CH_2 in ring), 2.43(s, 1H, OH), 2.49(s, 1H, CH-C=O), 4.16(q, J=7 Hz, 3H, CH_2CH_3 and O-CH), 5.59(m, 1H, vinyl). IR(neat, NaCl) 3400(O-H, broad), 2980, 1735(C=O) cm^{-1}.

Ethyl 2,6,6-trimethyl-4-acetoxy-2-cyclohexene-1-carboxylate(9). A solution of **8**(2.1 g, 10 mmol) and acetic anhydride(7.0 g, 68 mmol) in pyridine(24 m*l*) was stirred at 0℃ for 30 min, and then at room temperature for 12 h. The reaction mixture was poured into 5% aq. tartaric acid (10 m*l*), extracted with ether, dried(anhyd. $MgSO_4$), and evaporated the solvent *in vacuo*. The crude product was chromatographed on silica gel using dichloromethane/ether (6:1, v/v) as an eluent, to give an oil in 95% (2.4 g) yield. ^{1}H-NMR($CDCl_3$ /TMS, 60 MHz) δ 1.1(s, 6H, $2CH_3$), 1.3(t, J=7 Hz, 3H, CH_2CH_3), 1.6-1.9(m, 2H, CH_2 in ring), 1.7(s, 3H, allylic CH_3), 2.1(s, 3H, CH_3C=O), 2.9(s, 1H, CHC=O), 4.2(q, J=7 Hz, 2H, CH_2CH_3), 5.5(m, 1H, AcO-CH), 5.9(m, 1H, vinyl). IR (neat, NaCl) 2990, 1745, 1680, 1245 cm^{-1}.

β-Safranate(10); Ethyl 2,6,6-trimethyl-1,3-cyclohexadiene-1-carboxylate. A mixture of **9**(2.0 g, 7.9 mmol) and DBU(2.4 g, 15.8 mmol) was heated at reflux for 20 sec and cooled to room temperature. The reaction was poured into water(20 m*l*), extracted with ether, washed with 0.1 M HCl and water successively, dried(anhyd. $MgSO_4$), and evaporated the solvent at a reduced pressure. The crude product was chromatographed(SiO_2/CH_2Cl_2), to give an oil in 95%(1.5 g) yield. ^{1}H-NMR($CDCl_3$/TMS, 80 MHz) δ 1.12(s, 6H, $2CH_3$), 1.35(t, J=7 Hz, 3H, CH_2CH_3), 1.81(s, 3H, allylic CH_3), 2.12(d, J=2 Hz, 2H, CH_2 in ring), 4.23(q, J=7 Hz, 2H, CH_2CH_3), 5.51-5.87(m, 2H, vinyl). IR(neat, NaCl) 3045, 2950, 1705, 1650, 1590 cm^{-1}. MS(*m/z*) 194(M^+), 121, 107.

β-Damascenone(12); 2,6,6-Trimethyl-trans-1-crotonyl-1,3-cyclohexadiene. To a solution of β-safranate **10** (0.39 g, 2.0 mmol) in THF(15 m*l*), cooled to 0℃ under nitrogen, was added allyllithium (4 mmol) prepared from allyl phenyl ether (1.8 g, 13.3 mmol) and lithium shavings (0.25 g, 35 mmol), during the course of 30 min. The mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was quenched with water, extracted with ether, washed with water, dried (anhyd. $MgSO_4$), and evaporated the solvent *in vacuo*. The crude product was chromatographed on silica gel using n-hexane/dichloromethane as an eluent, to give almost colorless oil in 70%(0.27 g) yield. ^{1}H-NMR($CDCl_3$/TMS, 200 MHz) δ 1.03(s, 6H, $2CH_3$), 1.63(s, 3H, CH_3), 1.93(dd, J=7, 2 Hz, 3H, crotonyl CH_3), 2.10(d, J=3 Hz, 2H, CH_2 in ring), 5.81-5.84(m, 2H, CH=CH in ring), 6.18 (dq, J=16, 2 Hz, 1H, CO-CH= in crotonyl), 6.84(dq, J=16, 7 Hz, 1H, =CH-Me in crotonyl). IR(neat, NaCl) 3040, 2950, 1665, 1630, 1610, 970 cm^{-1}. MS(*m/z*), 190(M^+), 121, 69.

γ-Safranate(13); Ethyl 6,6-dimethyl-2-methylene-3-cyclohexene-1-carboxylate. A mixture of **8** (5.0 g, 23.6 mmol) and boric acid (1.5 g, 24 mmol) was heated with stirring to 100-105℃, and then to 220℃ for 30 min, and cooled to room temperature. The reaction mixture was poured into water, extracted with ether, washed with 5% aq. $NaHCO_3$ and water successively, dried (anhyd. $MgSO_4$), and evaporated the solvent *in vacuo*. The crude product was chromatographed(SiO_2/CH_2Cl_2), to give **13** as an oil in 88%(4.0 g) yield. ^{1}H-NMR ($CDCl_3$/TMS, 80 MHz) δ 0.92(s, 3H, CH_3), 1.01(s, 3H, CH_3), 1.24(t, J=7 Hz, 3H, CH_2CH_3), 1.79(dd, J=14, 5 Hz, 1H, CH in ring), 2.42(d, J=14 Hz, 1H, CH in ring), 2.97(s, 1H, CH-C=O), 4.12(q, J=7 Hz, 2H, CH_2CH_3), 4.97(d, J=5 Hz, 2H, $=CH_2$), 5.70-6.22(m, 2H, CH=CH in ring). IR (neat, NaCl) 3010, 2980, 1725, 1640, 895 cm^{-1}. MS(*m/z*) 194 (M^+), 121, 105.

γ-Damascenone(15); 6,6-Dimethyl-2-methylene-trans-1-crotonyl-3-cyclohexene. To a solution of **13**(1.0 g, 5.0 mmol) in THF(10 m*l*), cooled to −78℃ under nitrogen, was added dropwise allyllithium (10 mmol), prepared from allyl phenyl ether (2.4 g, 18 mmol) and lithium shavings (0.15 g, 22 mmol), during the course of 30 min. The reaction mixture was allowed to warm to room tempeature, quenched with cold water, and extracted with ether. The organic layer was washed with water, dried(anhyd. $MgSO_4$), and evaporated the solvent under reduced pressure. The crude oil product was chromatographed(silica gel, n-hexane/dichloromethane), to give **15** as an oil in 60%(0.57 g) yield. ^{1}H-NMR ($CDCl_3$/TMS, 200 MHz) δ 0.91(s, 3H, CH_3), 0.95(s, 3H, CH_3), 1.77(dd, J=18, 1 Hz, 1H, CH in ring), 1.87(dd, J=7, 2 Hz, 3H, crotonyl CH_3), 2.40(d, J=18 Hz, 1H, CH in ring), 3.23(s, 1H, CH-C=O), 4.95(d, J_{AB}=26 Hz, 2H, $=CH_2$), 5.84-5.88(m, 2H, CH=CH in ring), 6.21(dq, J=16, 2 Hz, 1H, crotonyl CO-CH=), 6.87(dq, J=16, 7 Hz, 1H, =CHMe). IR(neat, NaCl) 3040, 3010, 1690, 1680, 1660, 1625, 1600, 1440, 890 cm^{-1}. MS(*m/z*) 190(M^+), 175, 162, 121, 69. HRMS, calcd for $C_{13}H_{18}O$ 190.1357; Found 190.1356.

Acknowledgment. We are indebted to the Korea Science and Engineering Foundation for grant, KOSEF 870306, that supported this work.

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Catalytic Activity of $Nd_{1-x}Sr_xCoO_{3-y}$ on the Oxidation of Carbon Monoxide

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The catalytic activity of $Nd_{1-x}Sr_xCoO_{3-y}$, $0 \leq x \leq 0.75$ and $0.001 \leq y \leq 0.103$, on the oxidation of carbon monoxide has been investigated from the structure analyses of the catalysts by X-ray diffraction and infrared spectroscopy and the measurements of the oxidation and adsorption rates of carbon monoxide. The catalytic activity is found to be correlated with Sr substitution (x) and nonstoichiometry (y). The oxidation power of carbon monoxide increases continuously with increasing Sr substitution without oxygen, but increases with Sr substitution up to $x=0.25$ and then is almost constant at larger x values up to $x=0.75$ with oxygen. This change of catalytic activity is explained by the oxidation-reduction properties of the catalyst due to the variation of nonstoichiometry.

Introduction

In metallic oxides the electronic factors are not dependent upon the type, but are closely linked to the properties of the metallic oxides. The catalytic activities of metallic oxides are therefore related to their nonstoichiometric composition and electronic properties. The catalytic oxidation of carbon monoxide on metallic oxide as a catalyst is useful to understand the physicochemical properties of metal oxide. A correlation between the catalytic activity and the d-electron configuration was found to exist in metallic oxide catalyst. Derouane[1] reported that the catalytic activity of metallic oxide on the oxidation of carbon monoxide increases with increase in the empty d-orbital of metal ion.

Perovskite-type mixed oxide $NdCoO_{3-y}$ is suitable catalyst for the basic investigation of the relationships between the physicochemical property of metal oxide and the catalytic activity, since its bulk structure has been well characterized and the number of oxygen vacancies are easily controlled by the incorporation of the foreign element without changing the fundamental structure[2]. The catalytic activities of perovskite oxides have been interpreted by Voorhoeve *et al.*[3,4] as the backbonding between d-orbital of metal ion and π^*-orbital of carbon monoxide on the oxidation of carbon monoxide.

In this work, we have investigated the catalytic activity of $Nd_{1-x}Sr_xCoO_{3-y}$ catalyst on the oxidation of carbon monoxide from the measurements of the oxidation rates of carbon monoxide and adsorptions of CO and O_2 under various CO