

- Braekman, *ibid.*, **32**, 1171 (1976); (d) E. Ayanoglu, T. Gebreyesus, C. M. Beecham, C. Djerassi, and M. Kaisin, *Tetrahedron Lett.*, 1671 (1978); (e) D. G. Martin, G. Slomp, S. Mizak, D. J. Duchamp, and C. G. Chidester, *ibid.*, 4901 (1970); (f) H. Seto, T. Sasaki, J. Uzawa, S. Takeuchi, and H. Yonehara, *ibid.*, 4411 (1978); (g) J. D. Connolly, A. E. Harding, and I. M. S. Thornton, *J. Chem. Soc., Perkin Trans. I.*, 2478 (1974).
- (a) M. C. Pirrung, *J. Am. Chem. Soc.*, **101**, 7130 (1979); (b) M. Dermuth, S. Chandrasekhar, K. Nakano, P. R. Raghavan, and K. Schaffner, *Helv. Chim. Acta.*, **63**, 2440 (1980); (c) W. Oppolzer and V. Snieckus, *Angew. Chem., Int. Ed. Engl.*, **17**, 476 (1978); (d) B. M. Trost and M. J. Bogdanowicz, *J. Am. Chem. Soc.*, **95**, 298, 5331 (1973); (e) B. M. Trost and D. E. Keeley, *ibid.*, **98**, 248 (1976); (f) T. Hudlicky, T. M. Kutchan, S. R. Wilson, and D. T. Mao, *ibid.*, **102**, 6451 (1980).
  - B. M. Trost and P. H. Lee, *J. Am. Chem. Soc.*, **113**, 5076 (1991).
  - (a) J. Tsuji, Y. Kobayashi, H. Kataoka, and T. Takahashi, *Tetrahedron Lett.*, **21**, 1475 (1980); (b) B. M. Trost, T. A. Runge, and L. N. Jungheim, *J. Am. Chem. Soc.*, **102**, 2840 (1980); (c) B. M. Trost and T. A. Runge, *ibid.*, **103**, 2485, 7750, 7759 (1981).
  - (a) B. M. Trost and G. A. Molander, *J. Am. Chem. Soc.*, **103**, 5969 (1981); (b) J. Tsuji, H. Kataoka, and Y. Kobayashi, *Tetrahedron Lett.*, 2575 (1981); (c) J. Tsuji, *Tetrahedron.*, **42**, 4361 (1986).
  - J. Tsuji, K. Sato, and H. Okumoto, *J. Org. Chem.*, **49**, 1341 (1984).

## A New Synthesis of Solanone

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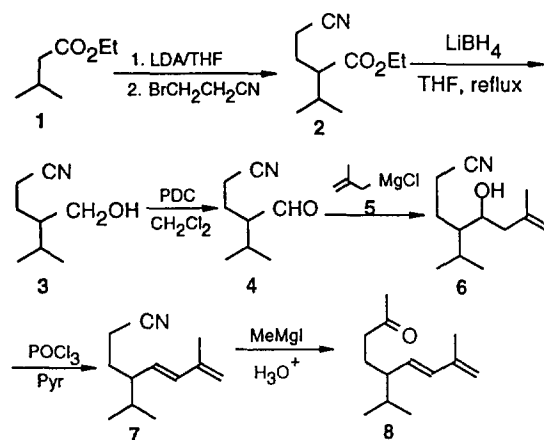
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Solanone (**8**), a colorless oil with a faint aroma reminiscent of carrots, has been detected in the Burley,<sup>1</sup> Greek tobacco<sup>2</sup> and marijuana.<sup>3</sup> The synthesis of solanone has been worked out by a few workers. In 1965, Johnson and Nicholson<sup>4</sup> isolated it from tobacco and elucidated the structure, confirming by synthesis. They carried out a relatively short synthesis of solanone starting from isovaleraldehyde. An optically active (S)-(+)-solanone has been also synthesized by Kohda and Sato<sup>5</sup> starting from optically active (R)-(+)-*p*-menthene.

Although it seems relatively short and convenient, Johnson's synthesis is not suitable for practical purpose, since the starting material (isovaleraldehyde) stinks, seriously con-



Scheme 1.

taminating the air for a long time. The Kohda's method, though significant as an asymmetric synthesis, is also inapplicable to perfumery industry. The present paper describes a new synthesis of solanone starting from ethyl isovalerate and/or diethyl malonate, which are inexpensive and smell good.

Treatment of ethyl isovalerate (**1**) with lithium diisopropylamide (LDA) at  $-78^{\circ}\text{C}$ , and reaction of the resultant ester enolate with 3-bromopropanenitrile in THF/HMPA, for 5 h at  $-78^{\circ}\text{C}$  and for additional 2 h at room temperature, gave ethyl 2-(2'-cyanoethyl)-3-methylbutanoate (**2**) in 69% yield (Scheme 1).

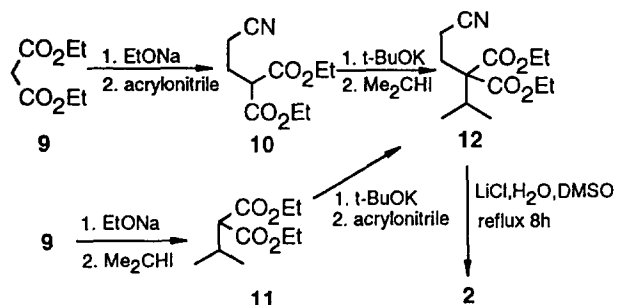
The chemoselective reduction of ester carbonyl<sup>6</sup> of the cyanoester **2**, without attack of nitrile function, could be effectively conducted. Treatment of **2** with lithium borohydride in refluxing THF for 2 days gave the corresponding cyanoalcohol **3** in 78% yield.<sup>7</sup> Oxidation of cyanoalcohol **3** for 18 h with PDC in dichloromethane gave 93% yield of 4-formyl-5-methylhexanenitrile (**4**). Direct conversion of cyanoester **2** to cyanoaldehyde **4** was also attempted using reported reagents, such as diisopropylaluminum hydride (DIBAL),<sup>8</sup> lithium aluminum hydride (LAH),<sup>9</sup> and diaminoaluminum hydride,<sup>10</sup> which were known to be effective for the conversion of ester to aldehyde. However, the chemoselective, direct reduction of **2** to **4** was not successful with these reagents, presumably because of the presence of cyano group in **2**.

Treatment of cyanoaldehyde **4** with methylmagnesium chloride (**5**)<sup>11</sup> at  $-78^{\circ}\text{C}$  under nitrogen, followed by stirring overnight, gave rise to a chemoselective Grignard condensation product, hydroxynitrile **6**, in 67% yield.

Dehydration of **6** with phosphorus oxychloride (POCl<sub>3</sub>) in refluxing pyridine afforded dienenitrile **7** in 78% yield. Although direct conversion of **4** to **7** can be also possible by Wittig olefination of **4**,<sup>4</sup> it may be less convenient and less economical, since it requires more steps, involving preparation of methyl Wittig salt, followed by treatment with base to give the ylide, and olefination with **4**.

Treatment of a solution of dienenitrile **7** in dry benzene with methylmagnesium iodide, followed by refluxing for 20 hours, and hydrolysis of the resulting ketimine with 6 N HCl furnished solanone (**8**) in the yield of 70%.

An alternative route to ester nitrile **2**, which begins with dialkylation of malonate ester, is shown in Scheme 2. Treat-



Scheme 2.

ment of diethyl malonate (**9**) with sodium ethoxide in ethanol, and addition of acrylonitrile, followed by stirring for 2 h, gave 51% yield of cyanoethyl malonate **10** as a Michael addition product. Successive alkylation of **10** by treating with potassium *t*-butoxide and then addition of isopropyl iodide, followed by heating at 70°C for 12 h, afforded diethyl (2-cyanoethyl) isopropylmalonate (**12**) in 88% yield. Decarbomethoxylation<sup>12</sup> of **12** can be conducted by refluxing for 6 h with lithium chloride in DMSO containing a small amount of water, to give cyanoester **2** in 65% yield. The reverse dialkylation of malonate ester **9** also gave similar results. Isopropylation of **9** first with isopropyl iodide in the presence of sodium ethoxide gave 75% of isopropyl malonate **11**, and Michael addition of **11** to acrylonitrile in the presence of potassium *t*-butoxide gave **12** in 91% yield. Since malonic ester **9** is much cheaper than valerate **1**, the preparation of **2** via dialkylation of ester **9** is a recommendable alternative.

In summary, our new synthetic route has the advantage of permitting a more practical synthesis of solanone, since it starts from readily available esters, such as ethyl isovalerate or diethyl malonate, which are inexpensive and do not stink.

## Experimental Part

All anhydrous reactions were conducted with precautions for rigorous exclusion of air and moisture. Flash chromatography was carried out using silica gel 60 (E. M. Merck, particle size 0.040-0.063 mm, 230-400 mesh ASTM). <sup>1</sup>H-NMR spectra were recorded on a Bruker AC-80 NMR spectrometer to an internal standard of tetramethylsilane. All chemical shifts ( $\delta$ ) are reported in parts per million, and *J*-values are in Hz. IR spectra were obtained on a perkin-Elmer Model 782 spectrometer. Mass spectra were recorded on a VG-7025 normal geometry. Following data were used for identification of the products in each step.

**Ethyl 2-(2'-cyanoethyl)-3-methylbutanoate (2).** IR (neat, NaCl window) 2900, 2250 (C≡N), 1750 (C=O), 1200 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  4.12 (q, 2H, OCH<sub>2</sub>Me), 2.5-2.0 (m, 3H, CH<sub>2</sub>CN, CHCO<sub>2</sub>Et), 1.8-1.6 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CN), 1.2 (m, 4H, OCH<sub>2</sub>CH<sub>3</sub>, CHMe<sub>2</sub>), 0.93 (d, 6H, 2CH<sub>3</sub> in *i*-Pr); EIMS (m/z), 184 (M<sup>+</sup>+1), 168, 138, 130, 115, 110.

**4-Hydroxymethyl-5-methylhexanenitrile (3).** IR (neat, NaCl window) 3450 (strong, broad, OH), 2975, 2258 cm<sup>-1</sup> (C≡N); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  3.55 (d, 2H, CH<sub>2</sub>O), 2.48 (t, 2H, CH<sub>2</sub>CN), 1.8-1.1 (m, 4H CHMe<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>OH, CH<sub>2</sub>CH<sub>2</sub>CN), 0.9 (d, 6H, 2 CH<sub>3</sub>); EIMS (m/z) 123 (M<sup>+</sup>-H<sub>2</sub>O).

**4-Formyl-5-methylhexanenitrile (4).** IR (neat, NaCl

window) 2900, 2750 (CHO), 2260 (C≡N), 1740 (C=O), 1390, 1370 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  9.8 (s, 1H, CHO), 2.45 (m, 3H, CH<sub>2</sub>CN, CH-CHO), 1.8-1.2 (m, 3H CHMe<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>CN), 0.9 (d, 6H, 2 CH<sub>3</sub> in *i*-Pr); EIMS (m/z) 139 (M<sup>+</sup>), 110, 97, 96.

### 4-Isopropyl-5-hydroxy-7-methyl-7-octenenitrile (6).

IR (neat, NaCl window) 3600, 2270 (C≡N), 1660 cm<sup>-1</sup> (C=C); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  4.9 (d, 2H, C=CH<sub>2</sub>), 3.8 (m, 1H, CHOH), 2.45 (m, 2H, CH<sub>2</sub>CN), 1.8-1.6 (m, 8H, C=C-CH<sub>2</sub>, C=C-CH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>CN, CH-C-OH), 1.2 (m, 1H, CHMe<sub>2</sub>), 0.9 (d, 6H, 2 CH<sub>3</sub> in *i*-Pr); EIMS (m/z) 196 (M<sup>+</sup>+1), 178, 140, 122, 98.

### 4-Isopropyl-7-methyl-5,7-octadienenitrile (7).

IR (neat, NaCl window) 2270 (C≡N), 1660 (C=C), 1380, 960 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  6.2 (d, 1H, C=CH, *trans*, *J*=14 Hz), 5.4 (q, 1H, C=CH, *trans*, *J*=14 Hz), 4.9 (d, 2H, C=CH<sub>2</sub>), 2.75 (d, 1H, C=C-CHMe<sub>2</sub>), 2.45 (t, 2H, CH<sub>2</sub>CN), 1.8-1.7 (m, 5H, CH<sub>2</sub>CHCN, C=C-CH<sub>3</sub>), 1.2 (m, 1H, CHMe<sub>2</sub>), 0.9 (d, 6H, 2 CH<sub>3</sub> in *i*-Pr); EIMS (m/z) 177 (M<sup>+</sup>), 162, 134, 121, 90.

### Solanone; 5-Isopropyl-8-methyl-6,8-nonadien-2-one (8).

IR (neat, NaCl window) 3080, 2980, 1720 (C=O), 1655 (CH=CH), 1610 (C=CH<sub>2</sub>), 1465, 1360, 890 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  6.05 (d, 1H, C=CH, *trans*, *J*=14 Hz), 5.27 (q, 1H, C=CH, *trans*, *J*=14 Hz), 4.9 (d, 2H, C=CH<sub>2</sub>), 2.75 (d, 1H, C=C-C), 2.45 (t, 2H, CH<sub>2</sub>C=O), 2.07 (s, 3H, CH<sub>3</sub>C=O), 1.8-1.5 (m, 6H C=C-C-CHMe<sub>2</sub>, CH<sub>2</sub>CHC=O, C=C-CH<sub>3</sub>), 0.97 (d, 6H, 2 CH<sub>3</sub> in *i*-Pr); EIMS (m/z) 194 (M<sup>+</sup>), 151, 136, 121, 93.

**Diethyl (2-Cyanoethyl)malonate (10).** IR (neat, NaCl window) 2900, 2250 (C≡N), 1750 (C=O), 1200 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  4.25 (q, 4H, 2 OCH<sub>2</sub>Me), 3.60 (t, 1H CHCO<sub>2</sub>Et), 2.7-2.0 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CN), 1.20 (t, 6H, 2 OCH<sub>2</sub>CH<sub>3</sub>); EIMS (m/z) 213 (M<sup>+</sup>), 198, 168.

**Diethyl Isopropylmalonate (11).** IR (neat, NaCl window) 2980, 1745 (C=O), 1470, 1100-1200 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  4.25 (q, 4H, 2 OCH<sub>2</sub>Me), 3.2 (d, 1H, CHCO<sub>2</sub>Et), 2.30 (m, 1H, CHMe<sub>2</sub>), 1.25 (t, 6H, 2 OCH<sub>2</sub>CH<sub>3</sub>), 1.0 (d, 6H, 2 CH<sub>3</sub> in *i*-Pr); EIMS (m/z) 202 (M<sup>+</sup>), 187, 160, 115, 87.

**Diethyl (2-Cyanoethyl)isopropylmalonate (12).** IR (neat, NaCl window) 2900, 2250 (C≡N), 1750 (C=O), 1200 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  4.25 (q, 4H, 2 OCH<sub>2</sub>Me), 2.6-1.6 (m, 5H, CHMe<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>CN), 1.20 (t, 6H, 2 OCH<sub>2</sub>CH<sub>3</sub>), 0.98 (d, 6H, 2 CH<sub>3</sub> in *i*-Pr); EIMS (m/z) 256 (M<sup>+</sup>+1), 210, 202, 182, 173.

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## References

- (a) E. Demole, C. Demole, and D. Berthet, *Helv. Chim. Acta*, **56**, 265 (1973); (b) E. Demole and C. Demole, *Helv. Chim. Acta*, **58**, 1867 (1975); (c) E. Demole and C. Berthet, *Helv. Chim. Acta*, **55**, 1886 (1972).
- I. Wahlberg, D. Behr, A. Eklund, T. Nishida, and C. R. Enzell, *Acta Chemica Scandinavica B*, **34**, 675 (1980).
- M. Novothy, F. Merli, D. Wiesler, M. Fencl, and T. Saeed, *J. Chromat.*, **238**, 141 (1982).
- R. R. Johnson and J. A. Nicholson, *J. Org. Chem.*, **30**, 2918 (1965).

5. A. Kohda and T. Sato, *J. C. S. Chem. Comm.*, 951 (1981).
6. (a) H. C. Brown, S. Narasimhan, and Y. M. Choi, *J. Org. Chem.*, **47**, 4072 (1982); (b) H. C. Brown and S. Narasimhan, *J. Org. Chem.*, **47**, 1604 (1982); (c) R. E. Ireland, R. H. Müller, and A. K. Willard, *J. Org. Chem.*, **41**, 986 (1975).
7. Lithium borohydride was freshly prepared prior to use by refluxing a mixture of sodium borohydride and one molar equiv of anhydrous lithium bromide in dry THF for 8 h: H. C. Brown, Y. M. Choi, and S. Narasimhan, *Inorg. Chem.*, **20**, 4454 (1981).
8. (a) C. Szantay, L. Töeke, and P. Kolonits, *J. Org. Chem.*, **31**, 1447 (1976).
9. J. S. Pizey, "Synthetic Reagents", Vol. 1., p. 178, John Wiley and Sons, Inc., New York (1974).
10. M. Muraki and T. Mukaiyama, *Chem. Lett.*, 215 (1975).
11. Methallyl Grignard **5** was prepared by dropwise addition, with vigorous stirring, of a solution of methallyl chloride in dry THF to a suspension of activated metallic magnesium, which was freshly prepared by refluxing a mixture of magnesium chloride and metallic potassium in dry THF: (a) R. D. Rieke, S. J. Uhm, and P. M. Hudnall, *J. Chem. Soc. Chem. Commun.*, 270 (1973); (b) R. D. Rieke and S. E. Bales, *J. Am. Chem. Soc.*, **96**, 1775 (1974); (c) Y. H. Lai, *Synthesis*, 585 (1981); (d) R. D. Rieke and P. M. Hudnall, *J. Am. Chem. Soc.*, **94**, 7178 (1972).
12. (a) A. P. Krapcho, J. F. Weimaster, J. M. Eldridge, E. G. E. Jahngen, Jr., A. J. Lovey, and W. P. Stephens, *J. Org. Chem.*, **43**, 138 (1978); (b) A. P. Krapcho, *Synthesis*, **805**, 893 (1981).

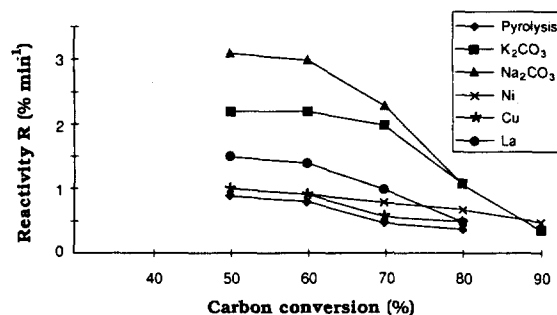
### In situ Diffuse Reflection FT-IR Spectroscopic Study of Lignite Gasification

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Among various spectroscopic techniques, infrared spectroscopy has been utilized as the most important tool in the characterization of coal because most of its organic and mineral components absorb in the infrared region.<sup>1</sup> However, infrared spectra of coals has been traditionally obtained by the transmission method after dispersing the sample in an infrared transparent medium (usually KBr) and then pressing into a glassy pellet.<sup>2</sup> Owing to its inherent disadvantage requiring mechanical mixing with other matrix, the infrared spectroscopic method has thus been regarded inappropriate for *in situ* studies. This changed with the pioneering work of Fuller and Griffiths,<sup>3</sup> who successfully developed diffuse reflectance technique for infrared spectroscopy and demonstrated its usefulness in coal characterization studies. In this NOTE, we wish to report the usefulness of diffuse reflectance infrared Fourier transform (DRIFT) technique for *in*



**Figure 1.** Reactivity vs. weight loss in steam gasification of lignite at 1073 K. See text. When preparing the Ni, Cu, and La incorporated samples, nitrate salts were used due to their solubilities in water.

*situ* studies of coal by interfacing the DRIFT optics with a reaction chamber. In this regard, the gasification of lignite has been investigated by recording the infrared spectra at various temperature.

Diffuse reflectance infrared spectra were measured with a vacuum-purged Bruker model IFS 113v FT-IR spectrometer. The source was a water-cooled Globar and a liquid nitrogen cooled mercury-cadmium-telluride detector was used. The diffuse reflection attachment (Harrick Model DRA-2CO) designed to use the 6 : 1, 90° off-axis ellipsoidal mirrors subtending 20% of the 4 $\pi$  solid angles was fitted to the sampling compartment of the FT-IR spectrometer. A reaction chamber made of stainless steel (Harrick Model HVC-DR2) was located inside the reflection attachment. The position of sampling cup was adjusted to match with the focal point of incident radiation. CaF<sub>2</sub> crystals were used as the infrared transparent windows. The temperature of sampling cup was regulated by a home-made temperature controller, and the chamber was flushed continuously with a wet nitrogen (*ca.* 100 ml/min) prepared by bubbling through a water trap.

Impregnation method has been used to incorporate the metallic species to lignite sample. After drying at 373 K overnight, its infrared spectra were measured at a nominal resolution of 4 cm<sup>-1</sup> by co-adding 128 scans. The temperature of sampling cup was raised at a rate of 3°C/min and kept for 4 min at each specified temperature to take the spectra. Diffuse reflectance spectra at infinite depth were calculated by taking ratio of the single-beam spectrum of the sample to that of the KBr reference placed in the same cup at room temperature. The spectrum was then converted to the Kubelka-Munk (K-M) function.<sup>4</sup> The triangular squared function was used in the apodization of measured interferograms. The proximate and ultimate analyses of the lignite sample have been reported previously.<sup>5</sup>

Prior to taking the *in situ* infrared spectra, the relative catalytic effectiveness of several metals in the steam gasification has been tested in a separate reactor. In this experiment, the weight % of metal was kept constant at below 10%. It was found that at below 773 K the weight loss of lignite occurred mainly by pyrolysis rather than by catalytic gasification. At higher temperatures above 873 K, the latter reaction seemed, however, to be more favorably to occur. Letting the amount of lignite, remaining after reaction at a higher temperature, be *W* based on the dry-ash-free state, the relative catalytic effect may then be comparatively stu-