2,3-DICARBOMETHOXY-1,3-BUTADIENE AND ITS REACTIONS

Bongkoch Tarnchompoo, Chachanat Thebtaranonth, Yodhathai Thebtaranonth*

Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand.

Abstract : The preparation of 2,3-dicarbomethoxy-1,3-butadiene from flash vacuum pyrolysis of 3 (itself obtained from methylenation of 2) is described. The diene's reactions with nucleophiles and dienophiles are also reported.

In contrast to 1,3-butadiene-1,4-dicarboxylic acid (Muconic acid) and esters thereof, the 2,3dicarboxylic acid isomer <u>1</u> is neither easily accessible nor commercially available, despite its long recognized potential as a versatile starting block in organic synthesis.¹ It comes as no surprise, therefore, to find that much research has been focussed on the synthesis of <u>1</u>, the many approaches including elimination reactions of the corresponding diacetate¹ and dibromide,² bismethylenation of the succinic ester phosphonate,³ nickel (0) catalized coupling reaction of α -halomethyl acrylate,⁴ cycloreversion of 1,2-dicarbomethoxycyclohexene,⁵ and, evidently the most successful, ground state electrocyclic ring opening of 1,2-dicarbomethoxycyclobutene.⁶ On our part we present, in this and the accompanying paper, an extremely efficient method for the preparation of the title compound and results from a study of its rather interesting and useful reactions.

Anthracene adduct <u>3</u> obtained (65% overall yield) via Stobbe condensation⁷ in a straightforward manner from the known dimethyl itaconate-anthracene adduct <u>2</u> is here conveniently employed as the precursor of diene <u>1</u>. Flash vacuum pyrolysis of <u>3</u> gives, directly, an almost quantitative yield of <u>1</u>. Subsequent purification by direct vacuum distillation of the pyrolytic condensate readily delivers analytically pure <u>1</u>⁸ in high yield (Scheme 1).

SCHEME I



SCHEME II



Yields indicated are isolated yields.

Contrary to expectations, pure <u>1</u> is reasonably stable and quite easily handled, hence its chemical reactions could be studied without special manipulations. Thus <u>1</u> dimerized via a [2+4]-cycloaddition reaction when heated neat at 80° for 4 hr. under nitrogen. However, reaction with dienophile competed successfully with the self-dimerization when an excess (1.5-2 equivalents) of dienophile was heated with <u>1</u> at 80° without solvent. Interestingly, although <u>1</u> has been predicted⁶ to react with electron-rich alkenes, yet the few examples reported^{1,2} have been reactions of <u>1</u> with electron-defficient dienophiles. Our study has now shown that <u>1</u> reacts with both electron rich and poor dienophiles, examples of which are listed in Scheme II.

Particularly interesting is the reaction of <u>1</u> with benzyne to give <u>15</u>, a convenient precursor of the naphthalene derivative <u>16</u>. The unusual $C_6 + C_4$ (benzyne nucleus + diene <u>1</u>) assembly mode offers a useful alternative to the conventional $C_8 + C_2$ (<u>o</u>-quinodimethane + dienophile e.g. dimethylacetylene dicarboxylate) method of constructing the naphthalene nucleus. Another reaction with potential in synthesis is the addition of <u>1</u> to quinones to finally yield <u>12</u> and <u>14</u>, which could well play an important role in future anthracyclinone chemistry.

Additions of ester enolates $(-78^{\circ}, \text{THF})$ take place in a conjugate fashion. Thus addition of the enolate to <u>1</u> yielded product <u>17</u>, while reaction of the nucleophile with monoepoxide <u>18</u> (prepared either from <u>m</u>-CPBA oxidation of <u>1</u> or from epoxidation of <u>3</u> and subsequent pyrolysis) gave a single isomer of <u>20</u>. Attempted generation of the succinate dianion <u>21</u> with the ester enolates used was, however, unsuccessful and the only product obtained from the reaction of <u>1</u> with excess nucleophile was <u>17</u>.



In a previous report⁹ we had demonstrated that, although not easily available by other methods, 8-alkoxy-1-tetralones were readily prepared via a tandem Michael addition - Dieckmann condensation reaction of an acrylic ester and a toluate anion (e.g. 22).¹⁰ Application of this reaction to diene <u>1</u> was, however, not successful, the treatment of <u>1</u> with <u>22</u> always resulting in a complex mixture. Nevertheless, by treating, instead, the diene precursor <u>3</u> with anion <u>22</u> at -78° in THF solution and leaving the mixture to stir overnight, the reaction proceeded smoothly according to that shown in Scheme IV and yielded <u>23</u> as a mixture of two separable isomers. Flash vacuum pyrolysis of 23 afforded the highly functionalized tetralone <u>24</u> in high yield.

SCHEME IV



The work described above reports the synthesis and reactions of diene <u>1</u>. From the results of the study it can be seen that compound <u>1</u> and its precursor <u>3</u> could well prove to be valuable building blocks in organic synthesis.

REFERENCES

- 1. W.J. Bailey, R.L. Hudson, E.T. Yates, <u>J. Org. Chem.</u>, 1963, <u>28</u>, 828.
- 2. D.P.G. Hamon, P.R. Spurr, Synthesis, 1981, 873.
- 3. R.M. Davidson, G.L. Kenyon, J. Org. Chem., 1977, 42, 1030.
- M.F. Semmelhack, P. Helquist, L.D. Jones, L. Keller, L. Mendelson, L.S. Ryono, J.G. Smith, R.D. Stauffer, J. Am. Chem. Soc., 1981, 103, 6460.
- 5. R.L. Cobb, J.E. Mahan, J. Org. Chem., 1977, 42, 2829.
- D. Bellus, C.D. Weis, <u>Tetrahedron Lett.</u>, 1973, 999 : D. Bellus, K. von Bredow, H. Sauter, C.D. Weis, Helv. Chim. Acta, 1973, 56, 3004.
- 7. M. Kodpinid, Y. Thebtaranonth, Tetrahedron Lett., 1984, 25, 2509.
- 8. Elemental analysis were performed by Scientific and Technological Research Equipment Center, Chulalongkorn University, Bangkok. All compounds described are properly characterized.
- 9. B. Tarnchompoo, C. Thebtaranonth, Y. Thebtaranonth, Synthesis, 1986, 785.
- T.A. Carpenter, G.E. Evans, F.J. Leeper, J. Staunton, M.R. Wilkinson, <u>J. Chem. Soc. Perkin</u> <u>Trans. 1</u>, 1984, 1043.

(Received in UK 21 August 1987)