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VICINAL DIESTER DIANIONS. ANNELATION WITH ALLYLIC AND BENZYLIC α,ω-DIHALIDES. SYNTHESIS OF TRICYCLOBUTA[1,2:3,4:6,7]NAPHTHALENE

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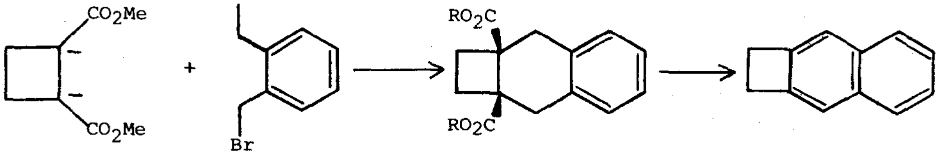
Abstract: A new method of annelation utilizing the reaciton of vicinal diester dianions with allylic and benzylic α,ω-dihalides is described. The synthesis of tricyclobuta-[1,2:3,4:6,7]naphthalene is reported.

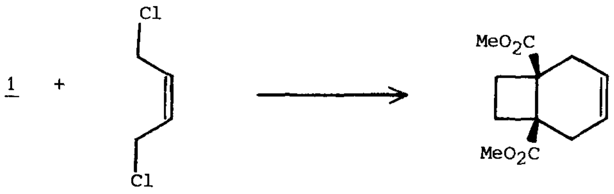
We have previously described the preparation[1] and some reactions[2] of the dimethyl cyclobutane-1,2-dicarboxylate dianion (1). We now wish to report the preparation of the dimethyl cyclohexane-1,2-dicarboxylate dianion (7) and describe a new method of annelation utilizing the reactions of 1 and 7 with allylic and benzylic α,ω-dihalides.

The dianion 1, prepared in THF by addition of the diester to 2 mole equivalents of lithium diisopropylamide at -75 °,[1] was reacted with 1 mole equivalent of α,α'-dibromo-o-xylene (2) at -98 ° and stirred for 1 h. The reaction mixture was then warmed to -75 ° and after 1 h quenched with aqueous acetic acid to yield the annelated product 3a (48 %).[3,4,5] Base hydrolysis of 3a gave 3b (79 %), which was decarboxylated with Pb(OAc)$_4$ in DMSO to give cyclobuta[b]naphthalene (4), 28 %.[6] In addition, the dianion 1 reacted at -75 °C with cis-1,4-dichloro-2-butene (5) to give the annelated compound 6 (37 %).[5,7]

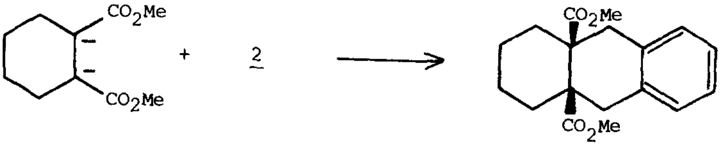
The dianion 7 was prepared at -75 ° by dropwise addition of the diester to a THF solution of LDA (2.0 mole equivalents) containing HMPA (2.8 mole equivalents). Reaction of dianion 7 with 1 mole equivalent of α,α'-dibromo-o-xylene at 20 ° for 18 h produced the annelated product 8 in 48 % yield.[3,4,8] The dianion 7 in THF-HMPA reacted at 20 °C with 5 to give 9 (61 %).[5,9]



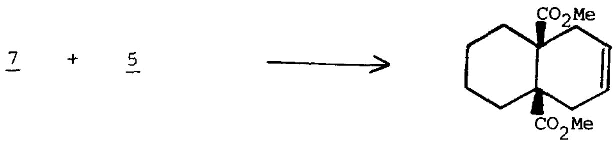
1   2   3a R = Me
b R = H   4



5 6



7 8



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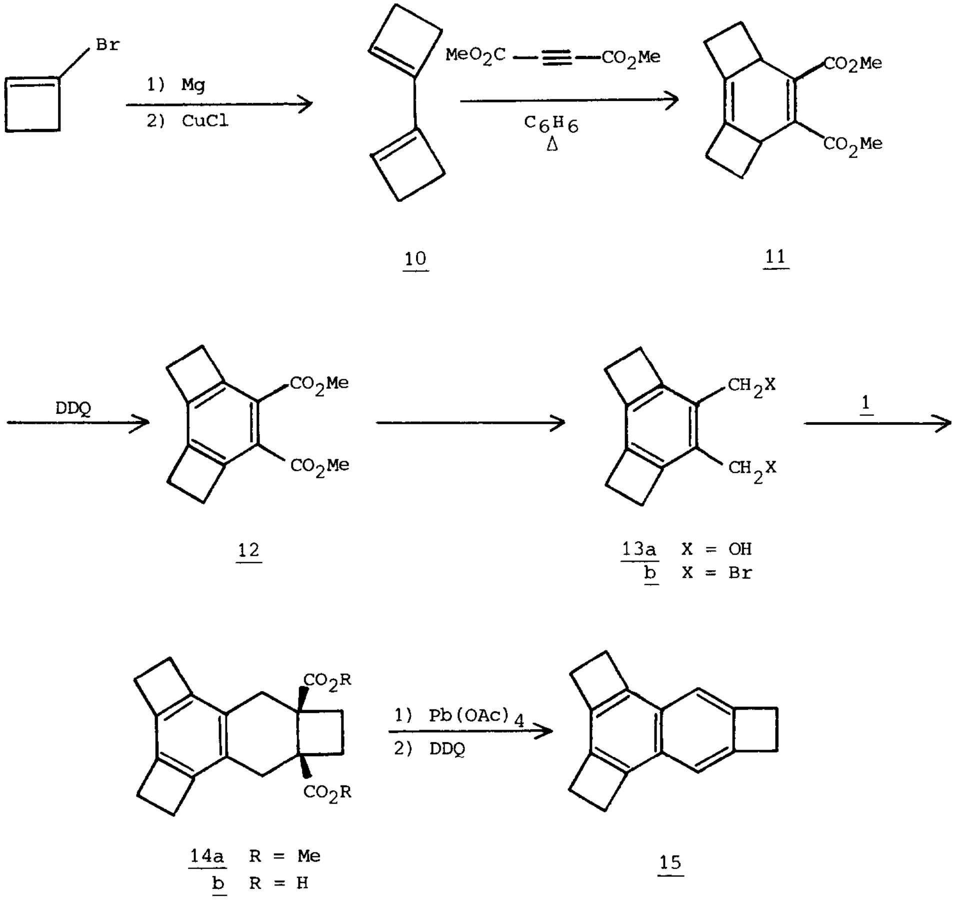
As an example of the synthetic utility of this annelation process, we have completed the preparation of tricyclobuta[1,2:3,4:6,7]naphthalene (15) as shown in the Scheme. 1-Bromocyclobutene[10] was treated with magnesium and then copper (I) chloride to give 10, 60 %,[4,11] which on reaction with dimethylacetylene dicarboxylate gave the adduct 11, 100 %.[3,4] Dehydrogenation of 11 with DDQ in benzene gave 12, mp 112-114 °, 38 %,[3,4] which was reduced with $LiAlH_4$ to the diol 13a, mp 121-124 °, 82 %.[3,4] Treatment of 13a with PBr_3 gave the dibromide 13b, 74 %,[3,4] which on reaction with 1.25 mole equivalents of 1 gave 14a, 61 %.[3,4] Hydrolysis (KOH, MeOH, H_2O) gave the diacid 14b, 100 %, which on treatment with $Pb(OAC)_4$ followed by DDQ gave 15, mp 171-173 °C, 10 %.[3] The ^1H NMR spectrum (CCl_4) of 15 showed signals at δ7.21 (s, 2H), 3.31 (s, 4H), 3.31 (m, 4H), 3.25 (m, 4H), and the ^{13}C NMR spectrum ($CDCl_3$, ppm) had signals at 143.6, 141.0, 136.5 (C1, C2, C6), 128.6 (C9), 115.5 (C5), 29.2, 28.8, 28.5 (C-α1, C-α2, C-α6). The electronic spectrum (pentane) had absorption maxima at 240 (ε=48,000), 244 (48,000), 289 (4400), 301 (4600) and 326 nm (700), typical of an alkyl substituted naphthalene.[12]



The reaction of α,ω-dihalides with these vicinal diester dianions provides an alternative synthetic method to the Diels-Alder reaction.[5] We are currently studying the limitations of this reaction and are exploring further the chemistry of vicinal dianions.

ACKNOWLEDGMENTS

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REFERENCES AND FOOTNOTES

1. P.J. Garratt and R. Zahler, *J. Amer. Chem. Soc.*, **100**, 7753 (1978).
2. P.J. Garratt and R. Zahler, *Tetrahedron Letters*, 73 (1979).
3. Satisfactory analytical and/or high resolution mass spectral data have been obtained for this compound.
4. ^{1}H NMR, δ: **3a** ($CDCl_3$), 7.22 (m, 4H), 3.71 (s, 6H), 2.92 (d of d, 4H), 2.33 (m, 2H), 1.34 (m, 2H); **8** (CCl_4), 7.04 (br s, 4H), 3.66 (s, 6H), 3.13 (br d, 4H), 2.41-1.11 (m, 8H); **10** ($CDCl_3$), 5.83 (br s, 2H), 2.54 (m, 8H); **11** ($CDCl_3$) 3.80 (s, 6H), 3.70 (m, 2H), 2.88-1.79 (m, 8H); **12** (CCl_4) 3.78 (s, 6H), 3.17 (m, 8H); **13a** ($CDCl_3$) 4.62 (s, 4H), 3.15 (br s, 8H), 2.48 (br s, 2H); **13b** ($CDCl_3$) 4.53 (s, 4H), 3.13 (br s, 8H); **14a** ($CDCl_3$) 3.69 (s, 6H), 3.07 (m, 10H), 2.70 (br d, 2H), 2.36 (m, 2H), 1.35 (m, 2H).
5. The *cis*-configuration of the annelated compounds **6** and **9** was assigned by comparison with the authentic compounds prepared by the appropriate Diels-Alder route.[7,9] The stereochemistry of the annelated products **3**, **8**, and **14** was assigned by analogy.
6. M.P. Cava and R.L. Shirley, *J. Amer. Chem. Soc.*, **82**, 654 (1960); R.P. Thummel, W.E. Cravey, and W. Nutakul, *J. Org. Chem.*, **43**, 2473 (1978).
7. E. Vogel, O. Roos, and K.H. Disch, *Ann. Chem.*, **653**, 55 (1962); R.P. Thummel and W. Nutakul, *J. Org. Chem.*, **42**, 300 (1977).
8. Alkylation of dianion **7** is considerably slower than alkylation of dianion **1**. The presence of HMPA in solutions of **7** resulted in enhanced yields of annelated products **8** and **9**.
9. K. Alder and K.H. Backendorf, *Ber.*, **71**, 2199 (1938); P. Brigl and R. Herrmann, *Ber*, **71**, 2280 (1938).
10. R. Willstätter and W. von Schmaedel, *Ber.*, **38**, 1992 (1905).
11. Since the completion of this synthesis of **10**, a similar reaction sequence using copper(II) chloride has been reported by F. Heinrich and W. Lüttke, *Ann. Chem.*, **1978**, 1880.
12. See R.P. Thummel and W. Nutakul, *J. Amer. Chem. Soc.*, **100**, 6171 (1978).

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