Tetrahedron Letters,Vol.23,No.36,pp 3657-3660,1982 0040-4039/82/363657-04$03.00/0
Printed in Great Britain

SYNTHESIS AND DIRECT PHOTOLYSIS OF CIS-1,2-DI-TERT.-BUTYL-CYCLOHEPTENE

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Summary 1,2-Di-tert -butyl-cycloheptene 6 was obtained from pimelic acid 1 in a three step sequence via intramolecular reductive coupling of the diketone 5 Direct photolysis of 6 gave endo-1,7-di-tert -butyl-norcarane 7

Numerous attempts to prepare a stable compound containing a trans-cycloheptene moiety have been unsuccessful [1] However, stabilization has been achieved [2] by complexation with Cu(I)- and Ag(I)-triflate and it is possible to trap compounds that are even more strained by reason of bond-shortening [3]

We speculated that the isolation of a free trans-cycloheptene might be possible if bulky substituents are placed at the double bond and thereby provide kinetic and (relative) thermodynamic stabilization of the trans isomer

Very recently Inoue [4] determined $\Delta H^{\ddagger}$ for the trans→cis-isomerization of trans-cycloheptene to be 18 2 kcal/mol by low temperature trapping experiments The cis isomer of di-tert -butylethylene is 9 6 kcal/mol higher in energy than the trans isomer, as determined by heats of hydrogenation [5], and the $\Delta H^{\ddagger}$ for trans→cis-isomerization is exceptionally high (57 42 kcal/mol) according to force field calculations of Ermer [6]

Direct photolysis, as well as singlet- and triplet- sensitization, have been used to affect cis→trans-isomerization of various cycloalkene systems - direct photolyses giving the best results [7] We decided to synthesize cis-1,2-di-tert -butyl-cycloheptene 6 and to examine its direct photolysis (scheme)

Several attempts to substitute OH or Cl in 1 or 2 with tert -butyl-lithium of tert -butyl-magnesium-bromide gave unsatisfactory results However, the diketone 5 was obtained in 68% isolated yield by the organo-copper-variant [8,9] Intramolecular reductive cyclization was achieved by dropwise addition of 5 (38g) to a suspension of "low valent titanium compounds" formed by refluxing the suspension of $TiCl_4$ (176ml) and $LiAlH_4$ (31 4g) in tetrahydrofuran (1 61) [9] 3 3g [10] of 6 were obtained after column chromatographie (1m x 2 5cm Kieselgel 60, n-pentane), subsequent bulb to bulb distillation and glc purification (6m 20% OV210, 130°C) Irradiation of 625mg of 6 in 300ml of n-pentane [9] with a low pressure mercury lamp (Hanau TNN 15/32, quartz) at 0°C for 18h resulted in the production of one major photoproduct and the gradual disappearance of 6 (capillary glc) Removal of the solvent and bulb to bulb distillation afforded 620mg of an oil that consisted of endo-1,7-di-tert -butyl-norcarane 7 (76%), 6 (4%), and three minor photoproducts 7 was isolated (glc) and identified spectroscopically The presence of cyclopropyl hydrogen was suggested by ir (2998cm^{-1}) and corroborated by ^{1}H-nmr (δ=0 43ppm, d, J=10 4Hz) and ^{13}C-nmr(δ=15 86, d) The appearance of only one strongly shielded hydrogen requires both tert -butyl groups being located at the cyclopropane, and the large coupling constant establishes the exo-configuration of 7-H

^{1}H-nmr spectra of a similarly (10°C) irradiated solution of 6 in cyclohexane-d_{12} contained in a degassed, sealed quartz-nmr-tube showed three sharp sing lets that coincided the tert -butyl resonances of 6 and 7 thus excluding the intermediacy of a stable trans olefine 8 down to a limit of 5% Low temperature photolyses, trapping experiments as well as variations of the alkyl substituent are planned

Satisfactory elemental analyses were obtained for all new compounds Physical and spectral data (^{1}H-nmr 90mHz, CCl_4, δ vs int TMS ir in CCl_4, cm^{-1} ms 70eV)

2 bp 93-97°C/0 2torr ^{1}H-nmr 2 94(t,J=6 9Hz,4H), 1 25-1 95(m,6H) ir 1800(C=O)

3 mp 52°C (n-hexane) ^{1}H-nmr 11 50(s,1H), 2 50(t,J=6 8Hz,2H), 2 36(t,J=6 8Hz,2H), 1 20-1 85 (m,6H), 1 15(s,9H) ir 3400-2500(CO_2H), 1710(C=O) ms 200(m^+), 143, 125, 91, 69, 51

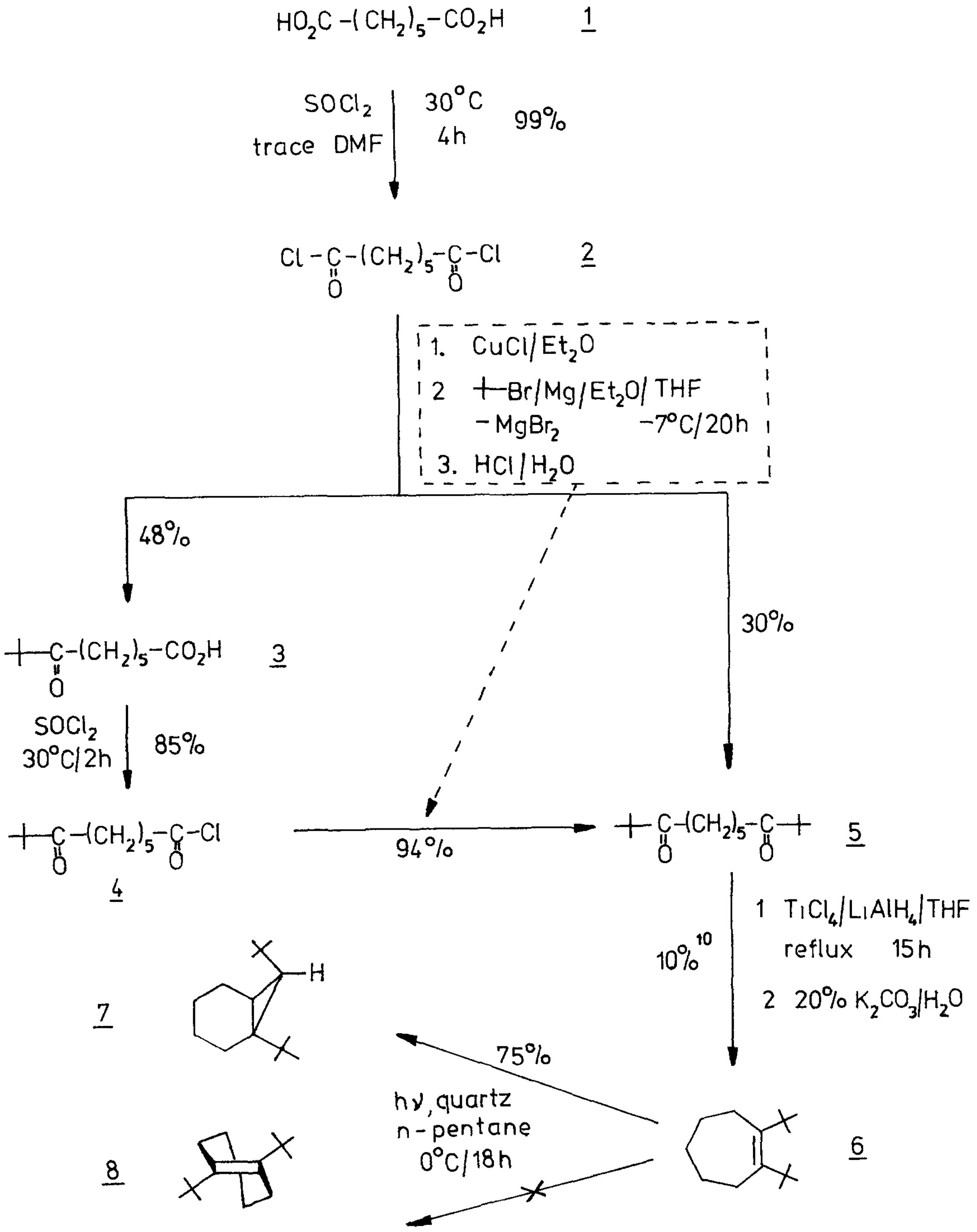
4 mp 28 5°C (n-pentane) ^{1}H-nmr 2 86(t,J=7 0Hz,2H), 2 41(t,J=6 3Hz,2H),1 15-1 90(m,6H), 1 09(s,9H) ir 1800(C=O), 1708(C=O)

5 bp 114°C/0 1torr ^{1}H-nmr 2 42(t,J=7 1Hz,4H), 1 15-1 75(m,6H), 1 09(s,18H) ^{13}C-nmr(80mHz, C_6D_6) 213 28(C=O), 43 75, 35 98, 29 07, 26 42(CH_3), 23 96 ir 1708(C=O) ms 240 20888 (m^+, calc 240 20894), 183(m^+ - $C(CH_3)_3$), 127, 57

6 bp 82°C/0 1torr ^{1}H-nmr 2 22-2 42(m,4H), 0 9(?)-1 65(m,6H,strongly disturbed by tert -butyl spinning-side-bands), 1 25(s,18H) ^{13}C-nmr (80mHz, $CDCl_3$) 144 87(C=C), 37 37, 33 85, 32 61 (CH_3), 30 20, 27 81 ir 2950, 2920, 1484, 1473, 1465, 1441, 1390, 1360, 1186 Raman (neat) 1557 (C=C) ms 208 (m^+), 151, 95, 83, 81, 69, 57

7 ^{1}H-nmr(250mHz) 1 73-1 87(m,2-,5-,5'-H, 1 30-1 53(m,3-,3'-,4-,4'-H), 0 91-1 23(m,2'-H), 1 05 (s,9H), 0 75-0,91(m,6-H), 0 80(s,9H), 0 43(d,$J_{1,7}$=10 4Hz,7-H) ^{13}C-nmr (250mHz,C_6D_6) 34 94(s), 32 85(d), 32 36(q), 32 06(s), 26 99(q), 23 14(t), 20 62(t), 19 84(t), 15 86(d) ir 2998, 2956, 2868, 1478, 1466, 1391, 1362, 1228 ms 208 (0 5%, m^+), 151, 95, 83, 81, 69, 57

I gratefully acknowledge support of this work by the Deutsche Forschungsgemeinschaft


HO2C-(CH2)5-CO2H
1
SOCl2
trace DMF
30°C
4h
99%
Cl-C-(CH2)5-C-Cl
O
O
2
1. CuCl/Et2O
2 Br/Mg/Et2O/THF
-MgBr2
-7°C/20h
3. HCl/H2O
48%
30%
C-(CH2)5-CO2H
O
3
SOCl2
30°C/2h
85%
C-(CH2)5-C-Cl
O
O
4
94%
C-(CH2)5-C
O
O
5
1 TiCl4/LiAlH4/THF
reflux 15h
2 20% K2CO3/H2O
10%10
H
7
8
75%
hν, quartz
n-pentane
0°C/18h
6

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9. Conducted in rigorously dried, degassed solvents under prepurified nitrogen.

10. A better yield may probably be obtained, when optimized reaction parameters are taken into account: R.Dams, M.Malinowski, I Westdorp, H Y.Geise, *J Org Chem* , *47*, 248 (1982)

(Received in Germany 26 May 1982)