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RING OPENING AND RING ENLARGEMENT OF A CYCLOPROPENE CARBOXYLIC ACID

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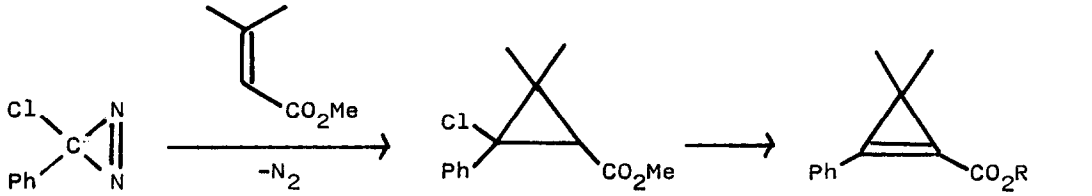
Abstract: 3,3-Dimethyl-2-phenyl-cyclopropenecarboxylic acid 4 is prepared, starting with chlorophenyldiazirine 1. With acids 4 yields the open chain carboxylic acids 5, 6 and 7. Thionylchloride leads to the cyclobutenone 10, DCC to the acid anhydrides 11 and 13.

The reaction of chlorocarbenes, obtained from chlorodiazirines, with olefins has been investigated intensively [1]; elimination of hydrogen chloride from the chlorocyclopropanes formed is possible, but has been used only sporadically [2].

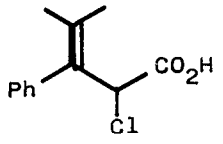
In connection with syntheses of pyrethroids we reacted chlorophenyldiazirine 1 with methyl 3,3-dimethyl-acrylate at 95°. From the E,Z-mixture of chlorocyclopropanecarboxylate 2, formed in 70% yield, 3 [3] was obtained with ^{t}BuOK. Action of powdered potassium hydroxide in toluene brought about both elimination of HCl and saponification to give 3,3-dimethyl-2-phenyl-cyclopropenecarboxylic acid 4 in 50% yield, m.p. 118-120°. ^{1}H-NMR (100 MHz, $CDCl_3$) δ 1.48 (s 6H); 7.4 (m 3H); 7.7 (m 2H). ^{13}C-NMR [4] δ 25.1 (2 CH_3); 25.5 (C-3); 116.4 (C-2); 127.4 (C-1); 128.9, 131.3, 131.5 (arom.C); 146.1 (C-ipso); 167.5 (CO_2H).



1 2 3: R = Me; 4: R = H

4 is stable at room temperature for several months.

Since attempted esterifications pointed to considerable sensitivity of 4 towards acid [5], we investigated the action of acid and obtained from 4 with HCl in toluene a mixture of unsaturated acids 5 and 6. Working at 40 - 80° favoured formation of 2-chloro-4-methyl-3-phenyl-pent-3-enoic acid 5 (ca. 4:1), isol. yield 60%, m.p. 107-113°; at 20° Z-4-chloro-4-methyl-3-phenyl-pent-2-enoic acid 6 predominated ca. 7:3.



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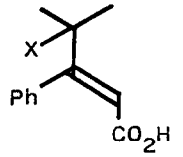
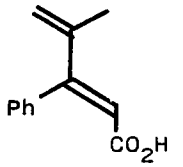


6: X = Cl

6a: X = OH



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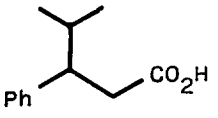

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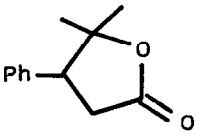

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4-Toluenesulfonic acid in boiling toluene transformed 4 into Z-4-methyl-3-phenyl-penta-2,4-dienoic acid 7, m.p. 112-114°. 5 as well as 7 could be hydrogenated over Pd on charcoal to the known [6] carboxylic acid 8. 6 was hydrolyzed at room temperature to the hydroxyacid 6a, m.p. 157°, yield 30%, which on hydrogenation yielded lactone 9 [7].

NMR-data of 5 - 7:

5: ^{1}H-NMR ($CDCl_3$) δ 1.56 (s 3H); 1.97 (s 3H); 5.6 (s 1H); 7.2 (m 5H).

6: " " δ 1.72 (s 6H); 6.34 (s 1H); 7.1 (m 2H); 7.3 (m 2H).

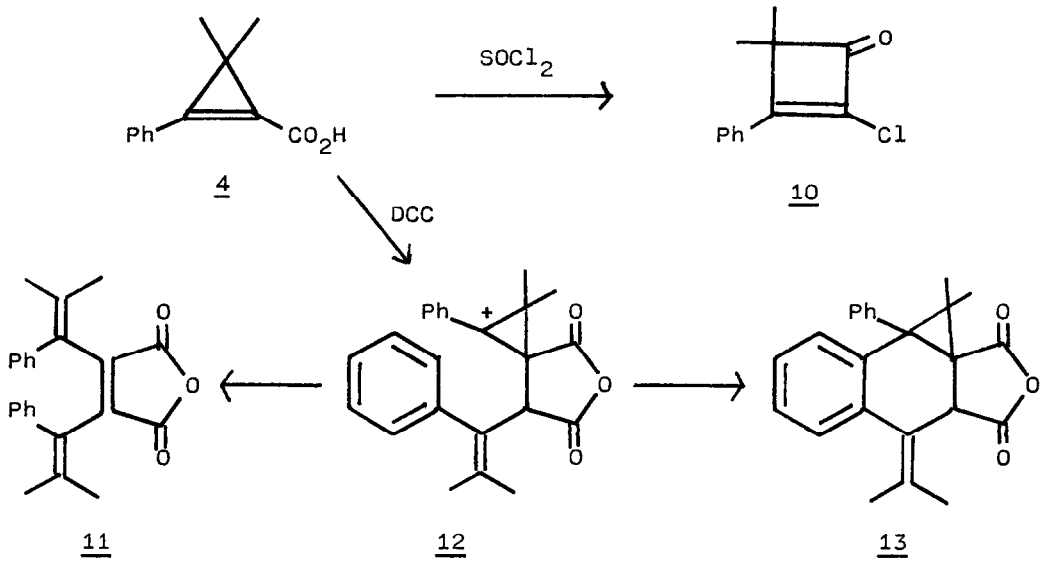
6a: " (CD_3CN) δ 1.26 (s 6H); 6.30 (s 1H); 7.1 (m 2H); 7.3 (m 2H).

7: " ($CDCl_3$) δ 2.02 (d 3H); 4.88 (m 1H); 5.38(m 1H); 6.04(s 1H); 7.1 (m 2H); 7.3 (m 3H).

^{13}C-NMR δ 20.5 (CH_3); 116.2 (C-5); 124.1 (C-2); 127.6, 128.5 (arom. C); 137.8 (C-ipso); 144.1 (C-4); 158.5 (C-3); 171.4 (CO_2H).

Attempts to prepare an acid chloride by the action of thionylchloride on 4 yielded a compound with melting point 66-67°, which in spite of fitting brutto formula, MS (206 (M^+); 143 (M^+ -Cl -CO)) and ^{1}H-NMR could not be an acid chloride due to its stability towards NaOMe in methanol, where it survived for more than a week at room temperature. ^{13}C-data (δ 20.8 (2 CH_3);

60.9 (quat. C); 118.7 (Ph-C=); 129.2 (o- and p-arom. C); 129.6 (C-ipso); 132.2 (m-arom. C); 173.7 (Cl-C=); 191.8 (CO)) indicated, that ring enlargement had occurred to give 2-chloro-4,4-dimethyl-3-phenyl-cyclobutenone 10. The four-membered ring structure 10 was proved by X-ray analysis.



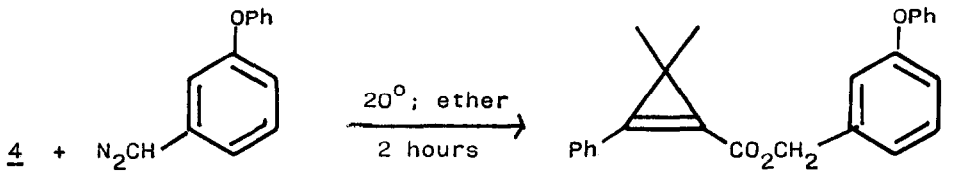
4 10 11 12 13

Attempted preparation of an acid anhydride from 4 by reaction with dicyclohexylcarbodiimide (DCC) in ether led to elimination of water and formation of two isomeric compounds $C_{24}H_{22}O_3$, isolable by flas h chromatography. The main product, yield 40%, m.p. 120°, was demonstrated to be a disubstituted maleic anhydride 11 by ^{1}H-NMR, ^{13}C-NMR and MS [8]; ^{1}H-NMR ($CDCl_3$) δ 1.7 (br. s 12 H); 6.7 (m 4H); 7.2 (m 6H). ^{13}C-NMR d 21.9 q (CH_3); 22.9 q (CH_3); 124.5 s (C=); 127.4 d, 128.2 d, 129.4 d (arom. C);138.6 s, 141.2 s, 144.4 s (C-ipso and 2 C=); 164.7 s ($-CO_2-$). MS 358 (100%, M^+); 343 (90%, $M^+ - CH_3$). IR 1820 cm^{-1} (CO).

13, yield 10%, m.p. 209-210°, showed ^{1}H-NMR-data for four different methyl groups: ($CDCl_3$) δ 1.1 s, 1.62 s, 2.03 s, 2.08 s, one aliphatic H at 4.16 s and only nine arom. H at 7.2 m. ^{13}C-NMR δ 19.6, 21.0, 21.4, 24.8 (4 CH_3); 37.7, 42.2 (2 quat. C); 45.4 (C-H); 46.2 q (quat. C); 123.7 (C=); 125.8-130.6 (arom.C); 134.0, 134.3, 137.2, 138.2 (3 C-ipso, C=); 170.9 ($-CO_2-$). MS (chem.ind.) 359 (M^+ +1); MS 285 (100%, $M^+ - 73$). $C_{24}H_{22}O_3$ calc. C 80.40, H 6.19; found C 79.91, H 5.94.

Cation 12 appears plausible as an intermediate in formation of both 11 and 13.

Preparation of a pyrethroid-like ester of 4 was finally accomplished using 3-phenoxy-phenyldiazomethane 14. 14 was made from 3-phenoxy-benzylamine by tosylation, nitrosation and alcaline cleavage [9]. 15 was isolated by flash chromatography from toluene and showed the molecular ion for $C_{25}H_{22}O_3$ at 370. ^{13}C-NMR indicated an intact cyclopropene ring: δ 25.3 (2 CH_3 and C-3); 116.8 (C-2); 127.4 (C-1).



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References and remarks:

1) For a review see: M.T.H.Liu, Chem.Soc.Reviews 11, 127 (1982).

2) A.Padwa and D.Eastman, J.Org.Chem.34, 2728 (1969); A.Padwa, M.J.Pulver and T.J.Blacklock, Org.Syntheses 60, 53 (1981).

3) V.Sander and P.Weyerstahl, Chem.Ber. 111, 3879 (1978).

4) All ^{13}C-spectra in $CDCl_3$ with a CFT-20 Varian HMDS.

5) 3 was reported to be extremely sensitive towards acids. The formation of an ester 6 with MeO in place of Cl from 3 in acidic methanol was described recently by A.Padwa and G.D.Kennedy, J.Org.Chem. 49, 4344 (1984).

6) D.J.Cram, H.L.Nyquist and F.A.Abd ELHAFEZ, J.Am.Chem.Soc. 79, 2876 (1957).

7) P.Kolsaker and A.S.Berg, Acta Chim.Scand.(B) 33, 755 (1979).

8) The dimethylester, formally derived from anhydride 11, was isolated after thermolysis of 3 at 175°, ref.[5].

9) In analogy to the preparation of phenyldiazomethane by C.G.Overberger and J.P.Anselme, J.Org.Chem. 28, 592 (1963).

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