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# Novel Reaction: Decarboxylative Ramberg-Bäcklund Rearrangement In Some α-Isopropyl Sulfonyl Carboxylic Esters.

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***Abstract:*** The reaction of some isopropylsulfonyl α-mono and disubstituted esters with KOH/t-BuOH/$CCl_4$ is reported. For the α,α-dialkyl and α-monoaryl substituted derivatives the key step of this reaction is proposed to be the decarboxylative 1,3-displacement in the chlorinated intermediates.

The Ramberg-Bäcklund rearrangement of halo sulfones, in the presence of base, leading to alkenes, has been extensively investigated,[1] as well as the Meyers modification,[2] in which sulfones are the starting materials and chlorination occurs *in situ*. This process has received an extensive attention not only because of its synthetic utility but also due to the mechanistic interest. Thus, it was reported that the step envolving 1,3-displacement of halide ion by carbanion with formation of episulfone is rate determining, and that the stereochemistry of the final alkene is established during this step.[3]

Our recent results of decarboxylative sulfenylation of some α-phenylsulfonyl carboxylic acids, occurring in the presence of base,[4] prompted us to investigate the Ramberg-Bäcklund rearrangement of some α-isopropylsulfonyl acetic esters, as it was of interest to verify whether 1,3-displacement could occur through the carbanion generated by decarboxylation.

In fact, when some α-isopropyl substituted carboxylic esters[5,6] **1-5** were submitted to reaction, under reflux, with KOH/t-BuOH/$CCl_4$, according to the Meyers procedure,[2] in all cases the hydrolysis and decarboxylation took place (Table 1). However, only in the case of the dialkyl substituted derivatives **1, 2** the corresponding alkenes[7] **6, 7** were the unique reaction products. It may be seen that for the monoaryl derivatives **3** and **4** the alkenes **8** and **9**, though in major proportion, were in admixture with the chloroalkenes **10** and **11** and in the case of the monobenzyl derivative **5** the chloroalkene **12** was isolated as the only reaction product.

**Table 1.** Reaction of some α-isopropylsulfonyl substituted acetic esters with KOH/t-BuOH/$CCl_4$.

| | Starting Materials i-$PrSO_2CR_1R_2CO_2Et$ | | | Reaction Products $Me_2C=CR_3R_4$ | |
|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | | $R_3$ | $R_4$ |
| **1** | Me | Ph | **6**[a] | Me | Ph |
| **2** | Bn | Bn | **7**[b] | Bn | Bn |
| **3** | Ph | H | **8**[c] | Ph | H |
| | | | **10**[c] | Ph | Cl |
| **4** | p-Tol | H | **9**[d] | p-Tol | H |
| | | | **11**[d] | p-Tol | Cl |
| **5** | Bn | H | **12**[e] | Bn | Cl |

[a] 61%; [b] 59%; [c] **8:10** = 3.0; [d] **9:11** = 1.5; [e] 61%

The first question, which should be clarified, in order to establish the sequence steps in these reactions, was to verify if under the reaction conditions the decarboxylation occurs initially. An evidence that no initial decarboxylation takes place was provided when neither α-isopropylsulfonyl dibenzyl **2** or monophenyl **3** acetic esters underwent decarboxylation but only hydrolysis when treated under reflux with KOH in t-BuOH (Scheme 1). This was an unexpected result, considering the fact that the corresponding α-phenylsulfonyl carboxylic acids loose $CO_2$ in basic media at temperatures under 100°C,[4,8,11] and may be attributed to the weaker withdrawing effect of the isopropylsulfonyl in comparison with the phenylsulfonyl group.

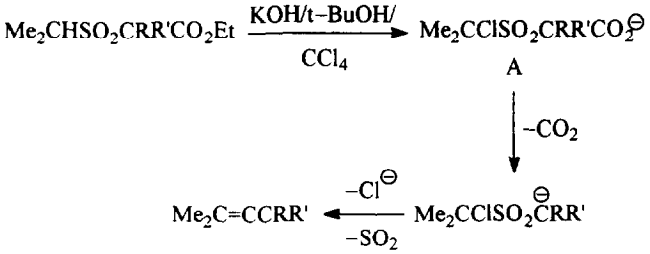
**SCHEME 1**

$$\underset{\mathbf{2}}{\text{i-PrSO}_2\text{CBn}_2\text{CO}_2\text{Et}} \xrightarrow[\text{refl.}]{\text{KOH/t-BuOH}} \text{i-PrSO}_2\text{CBn}_2\text{CO}_2\text{H}$$

$$\underset{\mathbf{3}}{\text{i-PrSO}_2\text{CHPhCO}_2\text{Et}} \xrightarrow[\text{refl.}]{\text{KOH/t-BuOH}} \text{i-PrSO}_2\text{CHPhCO}_2\text{H}$$

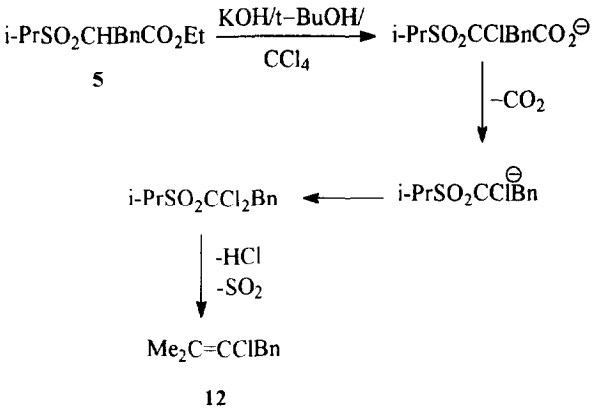
In the case of the disubstituted derivatives **1**, **2** it seems reasonable to suggest that the chlorination at the isopropyl group should occur initially. This is supported by the fact that di-isopropyl sulfone was reported to undergo easily the Ramberg-Bäcklund rearrangement[2] to give tetramethyl alkene. The intermediate **A** (Scheme 2) due to the withdrawing effect of the chloro substituted isopropyl group would undergo decarboxylation to give carbanion which would promote the 1,3-displacement of the chloride ion to give the corresponding episulfone, precursor of alkene.

**SCHEME 2**



Similar mechanism can be proposed to account for the formation of the alkenes **8** and **9**, which are the main reaction products in the case of the α-aryl substituted isopropylsulfonyl acetic esters **3** and **4**, in which the initial decarboxylation should be precluded. The formation of the choroalkenes **10** and **11** as the secondary products from the esters **3** and **4** and of chloroalkene **12** as the only product from the ester **5** may be rationalyzed by the mechanism proposed for the benzyl isopropyl sulfone[12] and butyl isopropyl sulfone[2] in which the benzyl or butyl instead of the isopropyl group, would be the chlorination site. It seems reasonable to suggest that the resulting α-chlorocarboxylate would undergo decarboxylative chlorination, followed by 1,3-elimination of chloride ion in the intermediate dichloro derivative (Scheme 3).

**SCHEME 3**



It seems reasonable to attribute the abnormal chlorination at the isopropyl group in the α-isopropylsulfonyl aryl acetic esters 3 and 4 to the increased stability of the benzylic carbanion due to the presence of the carboxylate.

In conclusion, a new 1,3-elimination, promoted by carbanion generated by decarboxylation, is proposed to occur in the course of the Ramberg-Bäcklund rearrangement of some isopropylsulfonyl α,α-dialkyl- and α-monoaryl acetic esters.

**Acknowledgements**

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5. Ester **3** was prepared by thiolation of the corresponding α-bromoester, followed by peracetic acid oxidation. Similar oxidation of the parent sulfide (Ogura, K., Itoh, H., Morita, T., Sanada, K. and Iida, H.; *Bull.Chem.Soc.Jpn.* **1982**, *55*, 1216) yielded sulfone **5**. Methylation of **3** by ion pair extraction under PTC afforded compound **1**. Benzylation of ethyl isopropylsulfonyl acetate in homogeneous medium (NaH/DMSO) gave ester **2**. Sulfonyl ester **4** was sintesized by treatment of p-methylbenzyl isopropyl sulfone[10] with $EtONa/(EtO)_2CO$.
6. Physical and spectroscopic data for compounds **1-5**. **1**: colorless oil. $^1H$ NMR (200MHz, $CDCl_3$) δ 0.66(3H,d), 1.32-1.40(6H,m), 2.08(3H,s), 4.00(1H,hept), 4.39(2H,q), 7.38-7.60(5H,m). Analysis: calculated, C 59.2, H 7.1, observed C 58.9, H 6.8. **2**: m.p. 111-112°C (MeOH). $^1H$ NMR (60MHz, $CDCl_3$) δ 1.10(6H,d), 1.34(3H,t), 2.66(1H,m), 3.30(4H,d), 4.19(2H,q), 7.00(10H,s). Analysis: calculated, C 67.4, H 7.0, observed C 67.5, H 7.0. **3**: m.p. 85-87°C (AcOEt/Hex) $^1H$ NMR (200MHz, $CDCl_3$) δ 1.28(6H,d), 1.36(3H,t), 3.35(1H,hept), 4.30(2H,m), 5.11(1H,s), 7.40-7.65(5H,m). Analysis: calculated, C 57.8, H 6.7, observed C 57.7, H 6.6. **4**: colorless oil, purified by column chromatography on silica-gel ($Me_2CO$/Hex).$^1H$ NMR (200MHz, $CDCl_3$) δ 1.28-1.38(9H,m), 2.37(3H,s), 3.34(1H,hept), 4.30(2H,m), 5.09(1H,s), 7.22(2H,d), 7.50(2H,d). Analysis: calculated, C 59.1, H 7.0, observed C 59.4, H 7.0. **5**: m.p. 65-67°C (AcOEt/Hex) $^1H$ NMR (200MHz, $CDCl_3$) δ 1.27-1.46(9H,m), 3.46(3H,m), 4.22(1H,m), 4.28(2H,q), 7.28(5H,m). Analysis: calculated, C 59.6, H 7.5, observed C 59.4, H 7.5.
7. $^1H$ NMR (200MHz, $CDCl_3$) δ for alkenes **6-12**. **6** : 1.58(3H,s), 1.80(3H,s), 1.96(3H,s), 7.10-7.33(5H,m). **7**: 1.27(6H,s), 3.40(4H,s), 7.79(10H,s). **8**: 1.84(3H,s), 1.89(3H,s), 6.27(1H,s), 7.12-7.36(5H,m). **9**: 1.84(3H,s), 1.88(3H,s), 2.33(3H,s), 6.21(1H,s), 7.09-7.23(4H,m). **10**: 1.73(3H,s), 2.00(3H,s), 7.12-7.36(5H,m). See ref. 12. **11**: 1,74(3H,s), 1.99(3H,s), 2.33(3H,s), 7.09-7.23(4H,m). See ref. 9. **12**: b.p. 95-96°C/16 mmHg. $^1H$ NMR (200MHz, $CDCl_3$) δ 1.88(6H,bs), 3.72(2H,s), 7.22(5H,m). MS: (70eV): m/z (%) 180(100,$M^+$), 182(30,$M^{2+}$), 145(99,$M^+$-Cl), 129(53), 117(20), 102(30), 91(42).
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