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DOUBLY-DESTABILIZED CARBOCATIONS. DETECTION AND TRAPPING OF ARYL-BISCARBOETHOXYCARBOCATIONS

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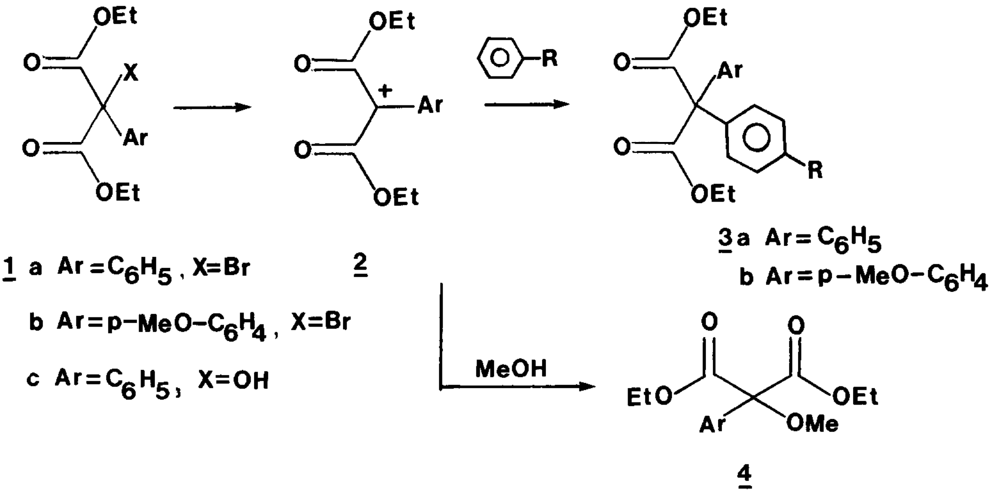
Summary: Diethyl bromo(aryl)malonates undergo ionization in superacids at -78°C to give the corresponding cations. These doubly destabilized cations can be trapped with benzene or toluene to give the corresponding Friedel-Crafts adducts.

The observation that certain electron-withdrawing substituents are less destabilizing than expected in carbocations has led to several studies of the chemistry and structure of these species[1-5]. We have observed diaryl- α -carbonylcarbocations under stable ion conditions by nmr and uv/visible spectroscopy and reported some of their chemical transformations[4]. As an extension to the studies and to test the limit for destabilizing carbocations we were interested in the possibility of preparing carbocations with two directly bonded carbonyl substituents. We report in this communication evidence for the existence of such species in the ionization of 2-bromo-2-aryl-malonic ester derivatives in strong acids.

The precursors to the carbocations were the diethyl esters of 2-phenyl-2-bromomalonic and 2-(p-anisyl)-2-bromomalonic acids 1a and 1b which were prepared from the 2-arylmalonates by NBS bromination. Diethyl 2-(p-anisyl)-malonate was prepared by thermal decarbonylation (175°C, 10 mm pressure) of the Claisen condensation product derived from ethyl p-anisylacetate and diethyloxalate[6].



1 a Ar $=C_6H_5$, X=Br

b Ar=p-MeO-C_6H_4, X=Br

c Ar=C_6H_5, X=OH

2

3a Ar=C_6H_5

b Ar=p-MeO-C_6H_4

4

Attempted observation of the carbocations 2a and 2b by the reaction of the bromide precursors (1a and 1b) with SbF_5 at low temperature in CD_2Cl_2 solution was unsatisfactory. This result was not very surprising due to the poor ion-solvating characteristics of this relatively non-polar solvent. Carbon disulfide could not be used as a solvent since it formed an unreactive complex with the Lewis acid, but satisfactory results occurred when SO_2 (bp -10°C) was used.

Mixing a solution of bromide 1a (0.05M) in SO_2 with SbF_5 at -65°C produced a slight colour change from clear to pale violet. The ^{13}C NMR spectrum showed one low field carbon at 181 ppm[7] attributable to the carbonyl carbon signal. No other low field signals were observed. Quenching of this solution at -65°C with methanol resulted in the quantitative recovery of only starting bromide. This result suggests that the bromide was not ionized under the reaction conditions and the small shifts in the NMR peaks when compared with the spectrum in the absence of SbF_5 could be attributed to Lewis acid complexation effects of the substrate. However when benzene was added to the mixture at -65°C and the solution warmed to room temperature, diethyl 2-phenylmalonate was obtained in 13% yield along with oligomeric products derived from benzene (which were not further identified). Similarly, quenching of the mixture with toluene gave 29% of adduct 3a ($R=CH_3$), and 28% of diethyl 2-phenylmalonate as well as oligomeric products derived from toluene.

In contrast, when a solution of bromide 1b in SO_2 (0.04M) was mixed with SbF_5 at -78°C a deep orange-red solution resulted. The ^{13}C NMR spectrum exhibited three low field signals at 195, 180 and 174 ppm which are assigned to the benzylic, carbonyl and p-methoxyaryl carbon of the anisyl group, respectively. The ^{13}C NMR spectrum was complicated by additional less intense peaks which we attributed to condensation products and/or Lewis acid complexation effects of the products; however, dilution experiments and comparison of peaks with the same relative intensities enabled us to assign the signals associated with carbocation 2b[8]. Quenching of this solution with methanol gave ether 4b as the major product. Quenching the carbocation with benzene or toluene gave the adducts 3b (R=H)[9] and 3b ($R=CH_3$) in 50 and 52% yields respectively with some condensation product (30%) which was not identified, but in the case of this carbocation (2b) no oligomeric products derived from benzene or toluene were detected or isolated. Additional evidence for the ease of ionization of bromide 1b relative to 1a is the observation of methanolysis of 1b taking place readily at ambient temperature to form ether 4b, while no observable reaction occurred for 1a even under more vigorous methanolysis conditions.

When the colourless alcohol 1c (in SO_2 (0.07 M) was mixed with SbF_5 at -65°C, an orange solution resulted. The ^{13}C NMR spectrum was similar to that which resulted from the attempted ionization of the bromide 1a in that there was no low field carbon signal which could be attributed to the formation of the carbocation 2a, and the small shifts in the carbon signals that were observed could be attributed merely to complexation of 1c with the Lewis acid. The unreacted alcohol could be recovered from the solution after warming to room temperature, and further attempts to trap any carbocation derived from 1c with either benzene or toluene were unsuccessful with the alcohol being inert to reaction under these conditions.

The above observations point to the formation of the p-anisyl-bis-carboethoxymethyl cation as a distinct intermediate under stable ion conditions. To our knowledge this represents the first example of a long-lived carbocation with two destabilizing carbonyl substituents. The possibility that bromide 1a also undergoes ionization to 2a is indicated by the observation of adducts 3a ($R=CH_3$) and of diethyl 2-phenylmalonate upon quenching with toluene and benzene. The formation of diethyl 2-phenylmalonate can be rationalized in terms of hydride abstraction by carbocation 2a[10]. In light of this result it is surprising that no methanol adduct is formed from quenching of the SbF_5/SO_2 solution of 1a. The latter observation along with the ^{13}C NMR data suggest that 1a does not completely ionize and that an intimate ion pair or complex may be present in the SbF_5/SO_2 solution. Quenching of this complex or ion pair with methanol gives rise only to reaction products derived from methanolysis of SbF_5. Reaction of the ion pair derived from 1a with benzene or toluene may likely occur since these compounds would not interact with SbF_5 in a solvolysis reaction, thus destroying the Lewis acid, at least to the extent that methanol would. On the other hand the ^{13}C NMR data and the observation of the methanol, benzene and toluene adducts of 2b suggest that this species exists as a free ion rather than an intimate ion pair as in 2a. The difficulty in ionization of 1a as compared with 1b is consistent with the enhanced stabilization of ion 2b due to the larger positive charge delocalization effect of the anisyl group. Further studies on the chemistry of these carbocations are in progress.

The ^{13}C NMR sample was prepared by layering a solution of SbF_5 in SO_2 (ca. 5 M) on top of a frozen solution of the bromide in SO_2 at -78°C. The solutions were thawed and mixed together at -63°C and the spectrum recorded.

The alkylation adducts were obtained by layering a solution of SbF_5 in SO_2 on top of a frozen solution of the bromide and toluene in SO_2. The solution was thawed and mixed and allowed to warm slowly to ca. -25°C when 2N hydrochloric acid was added cautiously. The resultant aqueous mixture was extracted with dichloromethane and the products isolated by column chromatography.

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6. P.A. Levene and G.M. Meyer, Org. Synth. Coll. Vol. II 288 (1943).
7. The ^{13}C NMR spectra were obtained on a Bruker AM-300 instrument operating at 75 MHz using external CD_2Cl_2 or $CDCl_3$ as D-lock as well as ^{13}C reference signal for chemical shift assignments.

8. Chemical shift assignments for carbocation 2b: δ (ppm ref. to CD_2Cl_2): 195 (C^+), 180 (C=O), 174 (quat. C of benzene bonded to CH_3O), 149 (quat. aryl C), 144, 134 (methine aryl C's), 84 ($O\underline{C}H_3$), 69 (methylene C), 14 (methyl C). ^{13}C spectrum for 1b: 167 (C=O), 160 (aryl C attached to OMe), 130, 113 (methine aryl C's), 127 (aryl quat. C), 63 ($\underline{C}H_2$), 63.1 ($\underline{C}$-Br), 55 ($O\underline{C}H_3$), 13 ($\underline{C}H_3$).
9. R.P. Kopinsky, J.T. Pinhey, B.A. Rowe, Aust. J. Chem. 37, 1245 (1984). Although the spectral data were identical to those reported our compound was obtained as crystals mp 108-109°C (EtOH) while the authors report this compound as an oil.
10. Hydride abstraction by α-carbonylaryl methyl cations have been observed by Charpentier-Morize; S.P. Begue, M. Charpentier-Morize, Acc. Chem. Res. 13, 207 (1980).

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