similar to those observed in neutral compounds.[17,34]

Experimental Section

NMR Spectra. ^{13}C NMR spectra were recorded at −70° to −10 °C on a JEOL FX-100 spectrometer with a 6000-Hz spectral width, 8192 data points, and a 45° pulse angle. In the case of solutions of cations, field stabilization was provided by acetone-d_6 held in a 3-mm (o.d.) capillary together with Me_4Si as a reference. Chemical shifts are ±0.1 ppm from external Me_4Si. Assignments were made on the basis of fully coupled and off-resonance decoupled spectra, ^{13}C–^{19}F coupling constants, and previously reported assignments for benzylic[2,10] and 1,1-diaryl-1-ethyl cations (see above). Equivocal assignments have been indicated in Table I (supplementary material).

Carbocations. The ions were prepared by the slow addition of the appropriate alcohol, either as a solution in SO_2ClF or as a solid to a solution of FSO_3H/SbF_5 (1 mol/1 mol)/SO_2ClF or FSO_3H/SO_2ClF (**11**, Z = 3,4-CH_2CH_2O, Z = 4-OCH_3, Z = 4-CH_3; Z = H; **12**) at −78 °C with rapid vortex mixing. The resulting highly colored (orange to brown) solutions (~0.5 M) were transferred under nitrogen to 10-mm NMR tubes.

Alcohols. The aryl(3,4-ethyleneoxyphenyl)methanols **17** were prepared by Grignard reactions by using the appropriate reactants, including 5-lithio-2,3-dihydrobenzo[*b*]furan[35] and 5-formyl-2,3-dihydrobenzo[*b*]furan.[36] Alcohols **18**–**22** were prepared in a similar fashion by using the appropriate benzaldehydes and bromobenzenes. In the case of the symmetrically substituted compounds **18** (4-OCH_3), **20** (4-F), **21** (4-CF_3), and **22** (3,5-$(CF_3)_2$), two mol of Grignard reagent were treated with ethyl formate. All of the above alcohols gave ^{13}C spectra and mass spectra in accordance with the assigned structures. All new compounds also gave satisfactory elemental (C, H ±0.3% F ±0.4%) or high-resolution mass spectral analysis.

5-Formyl-2,3-dihydrobenzo[*b*]furan. 2,3-Dihydrobenzo[*b*]furan (10.8 g) was formylated with dichloromethyl ether (8.63 g) and $TiCl_4$ (16.5 cm^3) according to the method of Rieche et al.[37] Distillation afforded 6.1 g (55%) of 5-formyl-2,3-dihydrobenzo[*b*]furan: bp 110–112 °C (1.5 mm) [lit.[35] bp 140–142 °C (8 mm)]; IR $\nu_{C=O}$ 1680 cm^{-1}; ^{13}C NMR δ ($CDCl_3$) 190.5, 165.6, 132.9, 130.4, 128.5, 125.9, 109.5, 72.4, 28.7.

Acknowledgment. We thank K. Koutsomitis for assistance with the preparation of some of the precursors, and Dr. R. T. C. Brownlee for obtaining the DSP analysis. The work was supported by the Australian Research Grants Scheme. M.J.J. gratefully acknowledges a Commonwealth Postgraduate Award.

Registry No. **11** (Z = 3,4-CH_2CH_2O), 87901-52-8; **11** (Z = 4-OCH_3), 87901-53-9; **11** (Z = 4-CH_3), 87901-54-0; **11** (Z = 4-F), 87901-55-1; **11** (Z = 4-H), 81390-58-1; **11** (Z = 4-CF_3), 87901-64-2; **11** (Z = 3,5-$(CF_3)_2$), 87901-65-3; **12** (Z = 4-OCH_3), 13948-07-7; **12** (Z = 4-CH_3), 42289-58-7; **12** (Z = 4-F), 39769-54-5; **12** (Z = 4-CF_3), 87901-56-2; **12** (Z = 3,5-$(CH_3)_2$), 87901-57-3; **13** (Z = 4-CH_3), 58493-75-7; **13** (Z = 4-F), 39769-57-8; **13** (Z = 4-CF_3), 87901-58-4; **13** (Z = 3,5-$(CF_3)_2$), 87901-59-5; **14** (Z = 4-F), 39769-55-6; **15** (Z = 4-F), 39769-58-9; **15** (Z = 4-CF_3), 87901-60-8; **15** (Z = 3,5-$(CF_3)_2$), 87901-61-9; **16** (Z = 4-F), 87901-62-0; **16** (Z = 3,5-$(CF_3)_2$), 87901-63-1; **17** (Z = 3,4-CH_2CH_2O), 87901-66-4; **17** (Z = 4-OCH_3), 87901-67-5; **17** (Z = 4-CH_3), 87901-68-6; **17** (Z = 4-F), 87921-90-2; **17** (Z = 4-H), 81390-92-3; **17** (Z = 4-CF_3), 87901-69-7; **17** (Z = 3,5-$(CF_3)_2$), 87901-70-0; **18** (Z = 4-OCH_3), 728-87-0; **18** (Z = 4-CH_3), 838-22-2; **18** (Z = 4-F), 1426-55-7; **18** (Z = 4-CF_3), 87901-71-1; **18** (Z = 3,5-$(CH_3)_2$), 87901-72-2; **19** (Z = 4-CH_3), 885-77-8; **19** (Z = 4-F), 345-91-5; **19** (Z = 4-CF_3), 33757-36-7; **19** (Z = 3,5-$(CF_3)_2$), 87901-73-3; **20** (Z = 4-F), 365-24-2; **21** (Z = 4-F), 39768-86-0; **21** (Z = 4-CF_3), 22543-52-8; **21** (Z = 3,5-$(CF_3)_2$), 87901-74-4; **22** (Z = 4-F), 87901-75-5; **22** (Z = 3,5-$(CF_3)_2$), 87901-76-6; 5-lithio-2,3-dihydrobenzo[*b*]furan, 68151-00-8; 5-formyl-2,3-dihydrobenzo[*b*]furan, 55745-70-5; 2,3-dihydrobenzo[*b*]furan, 496-16-2; dichloromethyl ether, 542-88-1.

Supplementary Material Available: Tables of ^{13}C NMR data of carbocations **1** and **11**–**16** and of precursor alcohols **17**–**22** (4 pages). Ordering information is given on any current masthead page.

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A Spectrophotometric Study of 4-Nitro-, 2,4-Dinitro- and 2,4,6-Trinitrobenzyl Carbanions. Decarboxylation of (Nitrophenyl)acetate Anions[1]

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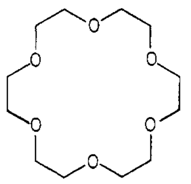
A spectrophotometric study of the reactions of the potassium salts of (2,4,6-trinitrophenyl)acetic acid (**3**), (2,4-dinitrophenyl)acetic acid (**4**), and (4-nitrophenyl)acetic acid (**5**) in Me_2SO, THF, and DME is reported, including the effect of catalysis by crown ether **1**. These processes are believed to give rise to the corresponding carbanions resulting from decarboxylation. The UV–visible spectrum of the species obtained from reaction of **3** agrees well with literature data for the expected carbanion **6**, but there is some discrepancy regarding the species derived from **4** and **5**. From the decay of the absorption spectra with time, the stabilities of the benzyl carbanions in these systems correspond to 2,4,6-trinitrobenzyl > 2,4-dinitrobenzyl > 4-nitrobenzyl.

Decarboxylation reactions are important in a variety of biological processes as well as in synthesis.[2,3] Mechanistic studies of decarboxylation have proceeded in parallel and various criteria have been used to shed light on transi-

Table I. Spectral Data in Reaction of Potassium (2,4,6-Trinitrophenyl)acetate (3) in Me_2SO and THF at Room Temperature: Formation of 6 and, on Addition of CH_3OK/CH_3OH, Formation of 7

expt no.	$10^3[3]$, M	$10^3[1]$, M	solvent	$10^3[CH_3OK]$, M	λ_{max}, nm	A	ϵ^{520} (species 6)	ϵ^{552} (species 7)
1	0.604		Me_2SO		376, 522, 630	0.64, 0.96, 0.58	15 900	
2	0.809		Me_2SO		376, 522, 630	0.84, 1.29, 0.80	15 900	
3a	0.404		THF		372, 520, 630	0.32, 0.50, 0.28	12 400	
3b	0.404	0.499	THF		372, 520, 630	0.43, 0.64, 0.32	15 800	
4a	0.647		THF		372, 520, 630	0.56, 0.82, 0.44	12 700	
4b	0.647	0.702	THF		372, 520, 630	0.66, 0.98, 0.50	15 100	
5a	0.501		Me_2SO		376, 522, 630	0.58, 0.82, 0.52	16 400	
5b	0.501		Me_2SO	4.58	460, 552	0.68, 0.92		18 300
6a	0.935		Me_2SO		376, 522, 630	0.93, 1.45, 0.92	15 500	
6b	0.935		Me_2SO	9.20	460, 522	1.14, 1.58		16 900

tion-state structure, including medium[4] and kinetic isotope effects.[5] Recent studies[6–10] have focused on model enzyme systems and the effect of catalysis by micelles and by crown ether type macrocyclics, monomeric 1 or polymeric 2.



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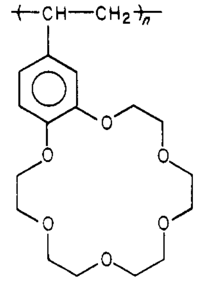

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In an extensive investigation, Hunter et al.[10] correlated reactivities in the decarboxylation of metal carboxylate salts with stabilities of the resulting carbanions (eq 1), with

$$RCO_2^-M^+ \rightarrow R^-M^+ + CO_2 \qquad (1)$$

particular reference to the effect of crown ether catalysis. It was found that in tetrahydrofuran (THF) solvent, the crown ether 1 caused an increase in the rate of decarboxylation by 13- to 500-fold and there was a correlation between the decarboxylation rate and the pK_a of the resulting hydrocarbon acid for a series of fluorenyl and arylmethyl carboxylic acid sodium salts.

It appeared to us that decarboxylation of nitro-substituted arylmethyl carboxylate salts in aprotic media such as THF, dimethoxyethane (DME), and dimethyl sulfoxide (Me_2SO) could offer an attractive method for the preparation and spectroscopic study of (nitroaryl)methyl carbanions. Literature data on these species are sparse and, in part, conflicting (vide infra). We report here the results of our studies on the reactions of the potassium salts of (2,4,6-trinitrophenyl)acetic acid (3), (2,4-dinitrophenyl)acetic acid (4), and (4-nitrophenyl)acetic acid (5), including

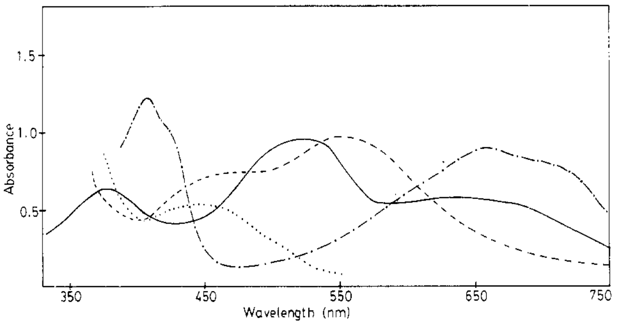
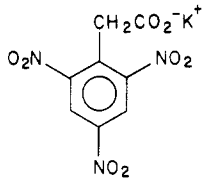


Figure 1. Spectra of the nitroaryl carbanions obtained in the decarboxylation of the corresponding carboxylates in Me_2SO solution: (–) 2,4,6-trinitrobenzyl anion (6), (–··–) 2,4-dinitrobenzyl anion (8), (···) 4-nitrobenzyl anion (9). (- -) Spectrum corresponds to the dianionic species 7 resulting from addition of methoxide ion to the 2,4,6-trinitrobenzyl anion.



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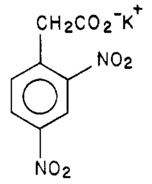

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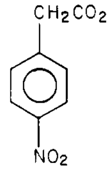

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the effect of catalysis by crown ether 1. This study is a continuation of our spectroscopic investigations of arylmethyl carbanions.[1b,11–16]

Results and Discussion

Potassium (2,4,6-Trinitrophenyl)acetate (3). Addition of 3 to Me_2SO at room temperature gives rise to a purple solution, immediately on mixing. The purple solution has absorption maxima at 376, 522, and 630 nm (experiments 1 and 2 in Table I, Figure 1), with an extinction coefficient at 522 nm of 15 900 L mol^{-1} cm^{-1}. The spectrum is stable for several hours.

When the reaction was performed in THF solvent, a purple solution was again formed instantly, with a closely

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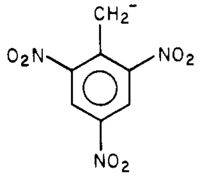
Table II. Spectral Data in Reaction of Potassium (2,4-Dinitrophenyl)acetate (4) in Me_2SO and THF

expt no.	$10^3[4]$, M	$10^3[1]$, M	solvent	λ_{max}, nm	A	ϵ^{408}
1	1.11		Me_2SO^a	408, 660, 710	1.64, 1.14, 0.98	14 100
2	1.28		Me_2SO^a	408, 660, 710	1.87, 1.18, 1.02	14 500
3a	1.08		THF	406, 640, 700	0.13, 0.12, 0.10	1 200
3b	1.08	1.47	THF^a	406, 640, 700	1.51, 1.14, 0.92	14 000
4	0.800	0.882	THF^b	406, 640, 700	0.96, 0.70, 0.59	12 000

[a] Room temperature. [b] Mixed at −50 °C and allowed to warm up to room temperature.

similar spectrum as in Me_2SO but an extinction coefficient ~20% smaller (experiments 3a, 4a). However, addition of crown ether 1 caused the absorbance to increase to the value observed in Me_2SO (experiments 3b, 4b). Simultaneously, there was a slight separation of the peak at 520 nm into a broader peak having a shallow minimum. In our work with the triphenylmethyl and diphenylmethyl carbanions,[11-13] it was found that crown ether caused the conversion of contact or solvent separated ion pairs into complexed ion pairs, and a similar situation may hold in the present case. The purple color of these solutions was immediately discharged on addition of trifluoroacetic acid.

The purple solution obtained in this reaction can be identified with the 2,4,6-trinitrobenzyl anion 6, formed on decarboxylation of 3, on the following grounds. Firstly, the carbanion is the expected species by analogy with work reported on the decarboxylation of carboxylate ions of various structural types, in particular the decarboxylation of arylacetate salts in THF as recently studied by Hunter.[10] Furthermore, direct evidence concerning the identity of the purple species can be adduced in this case, since the 2,4,6-trinitrobenzyl anion had previously been obtained by Buncel et al.[15,16] in the deprotonation of 2,4,6-trinitrotoluene (TNT) by alkoxide ions in the respective alcohols (see also ref 17–19). The spectral characteristics of that species coincides closely with the present, minor differences being accounted for by the different solvents used in the respective studies. This was further proven by Fyfe and Norris[20] who generated 6 in methanolic Me_2SO media.



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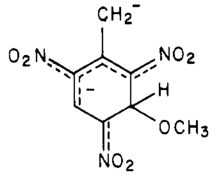

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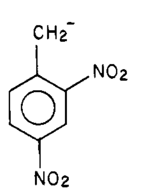
It was shown by Fyfe et al.[20] using the flow NMR technique that TNT in the presence of excess methoxide ion, in Me_2SO-rich methanolic media, gave rise to the dianion 7, which was characterized by NMR as well as UV–visible spectroscopy. Therefore, we performed runs (experiments 5b, 6b) in which methanolic methoxide was added to the purple solution obtained in the reaction of 3 in Me_2SO (experiments 5a, 6a). The spectrum recorded immediately on addition of base is shown as the accompanying spectrum in Figure 1; it was found to be stable for several hours. This spectrum coincides almost exactly with that ascribed by Fyfe et al. to the dianionic species 7. These and the previously described results[15-20] provide conclusive evidence concerning the course of the reaction of 3 in these solvent systems and the identity of the purple species obtained in this decarboxylation.

Potassium (2,4-Dinitrophenyl)acetate (4). An immediate reaction occurred on addition of 4 to Me_2SO, as evidenced by the formation of a bluish-green solution with absorptions at 408, 660, and 710 nm (experiments 1 and 2 in Table II, Figure 1). On monitoring the spectrum with time, a gradual decrease in the absorption maxima was found to occur (~25% in 1 h). The spectrum was instantly discharged on the addition of trifluoroacetic acid. By analogy with the discussion in the last section, it is concluded that the blue-green species with the characteristic spectrum shown in Figure 1 is due to the 2,4-dinitrobenzyl anion 8.



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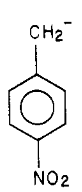

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When the reaction of 4 was performed in THF medium, the absorptions due to 8 developed only very weakly (experiment 3a in Table II). However, addition of crown ether 1 to the reaction solution caused the absorptions due to 8 to develop immediately (experiment 3b); on standing the absorptions began to decrease (70% in 2 h). Performing the experiment at low temperature (ca. −30 °C, see Experimental Section) led also to the immediate formation of this species (experiment 4). Heating the solution but in the absence of crown ether did not yield significant improvement over the result indicated in experiment 3a.

In an investigation of the ionization of 2,4-dinitrotoluene in ethylenediamine–water mixtures, Schaal[24] reported a species with λ_{max} at 410 and 660 nm (shoulder 710 nm) and assigned it as 8. More recently Terrier and co-workers[25] obtained a very similar spectrum on treatment of 2,4-dinitrotoluene with sodium methoxide in Me_2SO–methanol (80/20, v/v) and showed that this reverted completely to the parent 2,4-dinitrotoluene on treatment with acid. The results obtained by Schaal and Terrier are in close agreement with the work here reported.

However, Margerum et al.[21,22] reported on the photochemical decarboxylation of 4 in aqueous solution, which was also stated to give rise to the carbanion 8, but the spectral characteristics of the transient species, viz., λ_{max} 530 nm (extrapolated from multiple photolyses), were found to differ substantially from those observed in the present work. These results will be considered further subsequently.

Potassium (4-Nitrophenyl)acetate (5). Preliminary experiments with this substrate pointed to a behavior that was different, on two accounts, from that found with 3 and

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Table III. Spectral Data in Reaction of Potassium (4-Nitrophenyl)acetate (5) in Me$_2$SO, THF, and DME

expt no.	10^3[5], M	10^3[18-crown-6], M	solvent	λ_{max}, nm	A
1	7.93	9.19	THF[a]		
2	9.79	10.9	THF	430	0.14
3	8.57	9.38	THF	430	0.10
4	9.00	9.51	THF[b]	430	0.18
5	8.86	9.69	DME	430	0.08
6	12.5	12.2	DME[b]	430	0.10
7	9.82		Me$_2$SO	442	0.30
8	7.55		Me$_2$SO[b]	442	0.46[c]

[a] Molecular sieve absent; in all other experiments molecular sieve present. [b] Experiments performed at 45 °C; all other experiments were performed at room temperature. [c] Corresponds to 4% reaction assuming an extinction coefficient of 15 000 M^{-1} cm^{-1} for the species produced.

4. Firstly, the reaction of **5** was found to be sensitive to traces of moisture introduced as water of crystallization in the sample of **5** used (OH absorption in IR); this could be corrected by carrying out the experiments in the presence of molecular sieves. Secondly, it soon became apparent that reaction, when successful, proceeded to a small extent only, in contrast to the situation with **3** and **4** where reaction could apparently be carried practically to completion.

The first experiment in Table III shows the absence of a spectral absorption when THF was used as the solvent and in the presence of crown ether **1**. A similar result was obtained on varying the concentration of **5** over the range 1 to 55 × 10^{-3} M. The following two experiments show that, in the presence of molecular sieves and under otherwise similar conditions, some reaction does indeed occur as seen by the gradual ($\sim$20 min) development of a pale yellow color (λ_{max} 430 nm). Raising the temperature of the reaction mixture to 45 °C for a few minutes (experiment 4) caused an increase in the rate of development of color, but the final absorbance was only slightly greater, while the ensuing decomposition also increased in rate. Reactions carried out in DME as solvent (experiments 5, 6) yielded comparable results.

Me$_2$SO was found to be the optimum solvent for the reaction of **5**, the final (10 min) absorbance value reached (Figure 1) exceeding that in THF or DME, even though crown ether was not added (experiment 7). Wen the solution was heated to 45 °C for a few minutes, a further increase in rate and also in the final absorbance occurred (experiment 8). In these experiments as well, the color of the solution slowly faded after its initial development, the absorbance at 430 nm diminishing to approximately zero within 1 h, a colorless solution resulting.

The photochemical decarboxylation of **5** was reported by Margerum et al.[21,22] to yield the carbanion **9**, but, again, the spectral characteristics of this species were reported to be different than those observed in the present work. Thus Margerum et al. report a λ_{max} of 358 nm, contrasting with the value of 430 nm shown in the spectrum in Figure 1. On the other hand, Margerum et al. point out the agreement in the spectral characteristics of the species they report and the initial species observed by Miller and Pobiner[23] in the deprotonation of 4-nitrotoluene with *t*-BuOK/*t*-BuOH (362 nm).

However, more recently the deprotonation of *p*-nitrotoluene was examined by Chatrousse et al.[26] as part of a kinetic and equilibrium study of a series of *p*-nitrobenzyl derivatives. They observed a spectral species with λ_{max} at 440 nm in Me$_2$SO–methanol containing methoxide and assigned it to **9**. We have reported on the interaction of *p*-nitrotoluene with a variety of bases including potassium hydride, dimsylpotassium, and (triphenylmethyl)potassium in THF, DME, and Me$_2$SO and have observed both proton-transfer and electron-transfer processes.[14] The initially formed spectrum (λ_{max} 430 nm in THF or DME and 450 nm in Me$_2$SO) was assigned to the *p*-nitrobenzyl anion formed as a result of proton transfer. This absorption, however, diminished in time and was replaced by shorter wavelength absorption with λ_{max} 330 nm (THF and DME), which was assigned to the *p*-nitrotoluene radical anion formed as a result of electron transfer. The final species formed in these systems was the 4,4′-dinitrostilbene radical anion (λ_{max} 582, 626 nm) formed by a coupling process. It was further suggested[14] that the initial spectral species with λ_{max} 362 nm in the *p*-nitrotoluene–*t*-BuOK/*t*-BuOH system[23] was a charge-transfer complex between *p*-nitrobenzyl anion and *p*-nitrotoluene, as proposed earlier by Russell and Janzen.[27]

One can make a prediction concerning the absorption of the *p*-nitrobenzyl anion on the basis of literature data, noting that benzylsodium in THF absorbs at 355 nm.[28] Comparison of the spectra of tris(4-nitrophenyl)methyl carbanion and bis(4-nitrophenyl)methyl carbanion[29,30] with the unsubstituted triphenylmethyl and diphenylmethyl carbanions,[11-13] respectively, indicates that the *p*-nitro substituent causes a bathochromic shift of 80–85 nm in these systems. This increment when added to λ_{max} for the benzyl carbanion would give λ_{max} for the *p*-nitrobenzyl carbanion in the region of $\sim$440 nm, in good agreement with the present observations. Finally, semiempirical calculations using the CNDO method[31] for the *p*-nitrobenzyl carbanion yield a λ_{max} of 412 nm for the principal absorption ($\pi \rightarrow \pi^*$).

Conclusions

It is concluded from the results of the present study that the decarboxylation of the (nitrophenyl)acetate potassium salts **3**–**5** in solvents THF, DME, and Me$_2$SO result in formation of the nitrobenzyl anions **6**, **8**, and **9**, respectively. The reaction in THF and DME is aided by the presence of crown ether **1**. For decarboxylation of **3**–**5** there is good agreement between the spectral characteristics of the species thereby produced and those observed previously in the alkoxide ion deprotonation of TNT,[15-20] 2,4-dinitrotoluene,[25] and 4-nitrotoluene[26] (cf. ref 14, 23). However, the photochemical decarboxylation of **4** as well as **5** studied by Margerum et al.[21,22] was believed to give rise to the nitrobenzyl carbanions **8** and **9** as transient

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species, but the spectral absorptions assigned to these species differ from the present work.

We have no ready explanation for this variance apart from noting that the photochemical decarboxylation was carried out in aqueous medium and that there could be an unusually large medium effect associated with these absorptions, as has been observed in the case of the anion derived from (*p*-nitrophenyl)acetonitrile.[32] However it is perhaps conceivable that the photochemical decarboxylation could occur by a radical process as has been postulated for phenylacetate ion[33] (eq 2). There would then

$$\mathrm{ArCH_2CO_2^-} \xrightarrow[\mathrm{H_2O}]{h\nu} \mathrm{ArCH_2\cdot} + \mathrm{CO_2} + \mathrm{e^-_{aq}} \tag{2}$$

be the further possibility that the nitrobenzyl radical would combine with the solvated electron to yield the nitrobenzyl anion, and the sequence of transient spectral transformations could be difficult to resolve with this technique. In contrast, in the thermal decarboxylations of the present work, the spectra are relatively stable, while the carbanion mechanism has been thoroughly documented in analogous studies of arylmethyl carboxylate salts and related systems.[2–10]

Experimental Section

Materials. (4-Nitrophenyl)acetic acid (Eastman) was recrystallized from ethanol, mp 153–154 °C. (2,4-Dinitrophenyl)acetic acid (Eastman) was recrystallized from ethanol, mp 180–181 °C. (2,4,6-Trinitrophenyl)acetic acid was prepared according to published procedure,[34] mp 159–160 °C. 18-Crown-6 ether was recrystallized from hexane. THF and DME were dried and stored as described previously.[11] $\mathrm{Me_2SO}$ was distilled from calcium hydride and stored in evacuated vessels.

Potassium (4-nitrophenyl)acetate (**5**) was prepared by reaction of (4-nitrophenyl)acetic acid with an aqueous solution of potassium hydroxide short of equivalence point, filtration of the excess acid, and lyophilization. The salts **3** and **4** were prepared from the corresponding acids and aqueous potassium bicarbonate solution, followed by lyophilization, in similar manner.

Procedure. Reactions were performed in a cylindrical vessel (~120 mL) fitted with a 1-mm quartz cuvette and a greaseless Rotaflo stopcock.[11] Solvent (10–20 mL) was transferred into the reaction vessel under vacuum and a known weight of the appropriate potassium (nitroaryl)acetate (2–20 mg) was introduced through the side arm under vacuum. In the experiments with THF as solvent, this was followed by the addition of a known weight of 18-crown-6 (4–20 mg) through the side arm. The contents of the reaction vessel were shaken and the spectra monitored on a Unicam SP800B spectrophotometer. In some experiments, the reaction vessel containing THF was cooled to −50 °C prior to addition of potassium (nitroaryl)acetate and the crown ether, and the reaction mixture was then allowed to warm to room temperature while the spectra were being recorded.

The spectra in Figure 1 were obtained by the above procedure. The concentrations of the starting carboxylate salts were as follows: for reaction of potassium (2,4,6-trinitrophenyl)acetate, 0.604×10^{-3} M; for reaction of potassium (2,4-dinitrophenyl)acetate, 0.794×10^{-3} M; for reaction of potassium (4-nitrophenyl)acetate, 7.55×10^{-3} M. Formation of **7** was effected by the addition of 5 μL of 1.2 M potassium methoxide solution to 13 mL of potassium (2,4,6-trinitrophenyl)acetate in $\mathrm{Me_2SO}$ (0.501×10^{-3} M).

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Regio- and Stereochemistry of Acid-Catalyzed Opening of (1,2-Epoxyalkyne)dicobalt Hexacarbonyls

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The highly reactive (1,2-epoxyalkyne)dicobalt hexacarbonyls **5** and **6** have been generated in situ, and the regio- and stereochemistry of their acid-catalyzed reactions with various nucleophiles have been studied. Epoxide **5** when treated with $\mathrm{HBF\cdot Me_2O}$ in the presence of methanol, anisole, allyltrimethylsilane, and isopropenyl acetate undergoes regiospecific ring opening, producing the corresponding β-hydroxy-α-substituted derivatives in fair to excellent yields. The cyclohexene oxide **6** reacts with $\mathrm{CH_3OH}$, $\mathrm{H_2O}$, and $\mathrm{Cl_3CCO_2H}$ under acidic conditions to produce 50:50, 59:41, and >95:5 cis/trans ratios, respectively, of the 1-substituted-2-hydroxy products. These results are contrasted with the corresponding reactions of the free ligand, which give 1:99, 2:98, and 42:58 cis/trans ratios. These data are interpreted in terms of the powerful electron-releasing capability of the (alkyne)$\mathrm{Co_2(CO)_6}$ moiety.

Introduction

In earlier reports we established the remarkable ability of the (alkyne)$\mathrm{Co_2(CO)_6}$ moiety to dramatically stabilize an adjacent carbonium ion center.[1,2] More recently, we have examined synthetic applications taking advantage of this effect by developing facile, *regiospecific* propargyl/nucleophile coupling reactions (eq 1, Nu = aromatics,[3] β-dicarbonyls,[4] enol derivatives,[5,6] allylsilanes,[7] and organoaluminums.[8,9]

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