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G. R. Jurch, Jr.,
M. D. Johnston, Jr.,
J. W. Perry,
and T. E. Detty

University of South Florida
Tampa, FL 33620

The Synthesis and Proton NMR Spectrum of Methyl 7-Cycloheptatrienylacetate

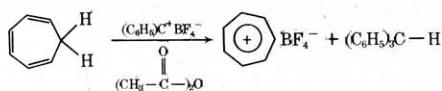
An advanced undergraduate laboratory experiment

During their senior year, the BS chemistry majors in our department take a 3-quarter sequential laboratory course. The objective of this sequence is to acquaint (or reacquaint) the student with methods and techniques for the investigation of chemical systems and then to apply these methods to the examination of an actual chemical problem. The first two quarters and the first two weeks of the third quarter are devoted to the discussion (lecture) and mastering (laboratory) of techniques such as spectroscopy (ultraviolet, infrared, NMR), statistical analysis of data (including the use of a computer), polarography, potentiometric titrations, mass spectrometry, chromatography (TLC, column, gas-liquid, liquid, gel), fractional distillation, and other methods of purification. The remainder of the third quarter is then used for the application of as many of these techniques as possible to an actual chemical problem. A wide variety of projects are available to the student, and they try to simulate as much as possible actual problems which may be encountered later when the student has become a practicing professional chemist.

One such problem which has met with success is the synthesis and proton NMR study of the title compound, methyl 7-cycloheptatrienylacetate (1, 2). This problem gives the student an opportunity to apply several synthetic and purification techniques and then provides several possibilities for the application of NMR spectroscopy. The project is excellent in that it can be done in its entirety, as shown here, or can be done only partially. In the latter case, it is still very profitable to the student's training.

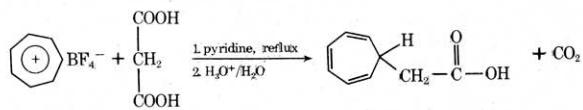
Synthetic Methods

The first step of the synthetic part of the project involves the synthesis of an organic salt, tropenium fluoroborate, from 1, 3, 5-cycloheptatriene.



This reaction provides experience in handling hydroscopic materials, and in spectroscopic examination of the product. The students are required to take NMR, infrared, or ultraviolet spectra after each step in a synthetic procedure. The spectra are used to confirm the structure and purity of each product.

The next synthetic step involves formation of the cycloheptatrienylacetic acid from the organic salt.



This reaction provides experience in handling and purifying a product whose melting point is near room temperature.

The next reaction gives the student experience in running a reaction where some of the products are gases which should not be allowed to escape into the atmosphere. This reaction involves the conversion of the acid into the acid halide via thionyl chloride. **This reaction can also be done using oxalyl chloride, but precautions must be used to contain the carbon monoxide produced.** This reaction should be done in a hood, or the gases can be removed by aspiration or can be trapped in a basic solution.

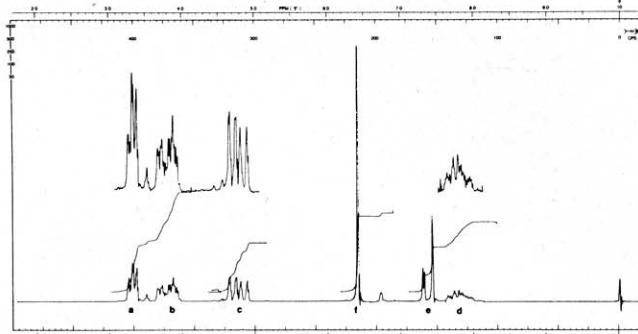
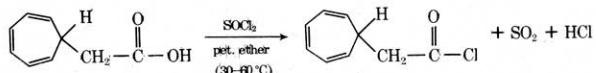


Figure 1. The NMR spectrum of methyl 7-cycloheptatrienylacetate (neat) at 60 MHz. The spectrum shown was obtained on a Varian A-60 spectrometer.

Table 1. NMR Spectral Parameters of Methyl 7-Cycloheptatrienylacetate in CCl₄

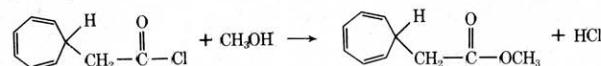
Chemical Shifts (ppm) ^a	Coupling Constants (Hz) ^b
$\delta_a = 6.50$	$J_{ab} = 3.3$
$\delta_b = 6.02$	$J_{ab'} = 3.3$
$\delta_c = 5.10$	$J_{bc} = 9.2$
$\delta_d = 2.16^c$	$J_{ac} \sim 0$
$\delta_e = 2.52$	$J_{cd} = 5.6$
$\delta_f = 3.58$	$J_{de} = 7.4$

^a Accurate to ± 0.01 ppm unless otherwise indicated.

^b Accurate to ± 0.2 Hz.

^c Accurate to ± 0.03 ppm.

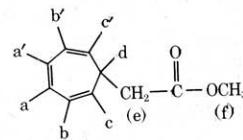
The final step in the preparation involves the formation of the ester.



The product is purified by vacuum distillation. The purity of the ester is checked by mass spectrometry and a carbon-hydrogen analysis; the former method is also used to check the product structure. At this point, the student is ready to proceed with the NMR part of the project.

The Basic NMR Spectrum

The NMR spectrum of the ester is shown in Figure 1 and the chemical shifts and discernible coupling constants are listed in Table 1. The spectrum is of intermediate character between first and second order. All six resonances are far enough apart to enable their integrals to be separated. To facilitate further discussion the protons are labeled by the letters *a-f*, as given in the structure below.



Preliminary assignments are relatively easy from the spectrum itself; however, confirmation must follow from further experiments. First, the olefinic resonances lie between 5 and 7 δ -units and the shapes of the splitting patterns allow one to distinguish *a* from *b* and *c*. However, the identities of *b* and *c* are only tentatively identifiable at this point—some extra information is needed to nail down which

¹ Author to whom correspondence should be addressed.

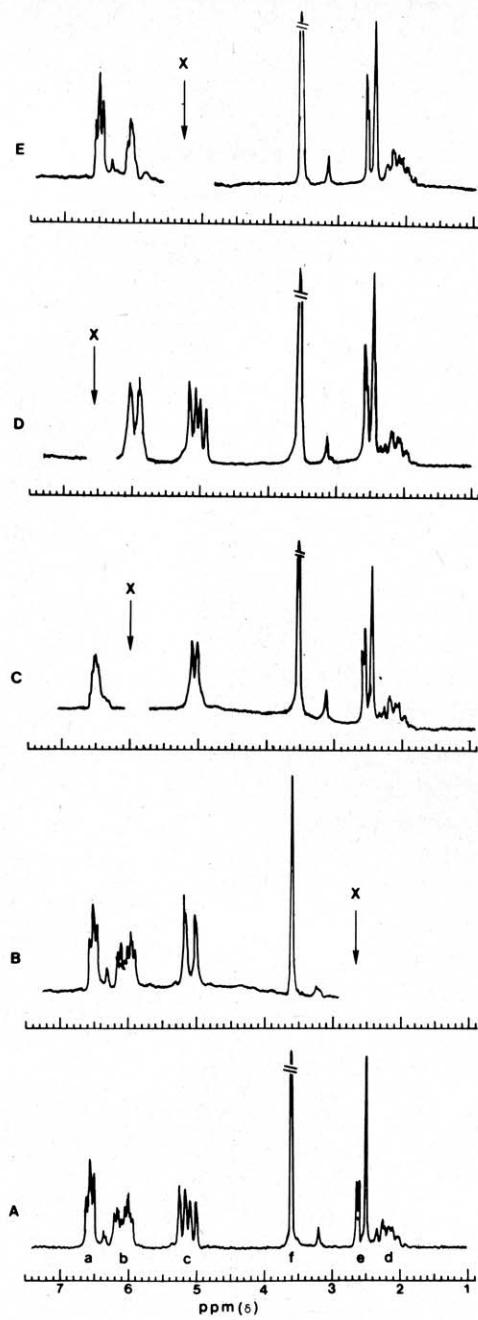


Figure 2. Spin decouplings (single irradiations), x on the title compound, A-unirradiated spectrum in CCl_4 ; B-spectrum irradiated at e; C-spectrum irradiated at b; D-spectrum irradiated at a; E-spectrum irradiated at c. The spectrum shown were obtained on a Varian EM-360 spectrometer.

is which. It is easy to see, in addition, from both the integrals and the coupling patterns which parts of the spectrum belong to d, e, and f. The methyl resonance, f, is a sharp singlet, e is nearly a clean doublet, and d is a more complex multiplet (almost a quintet). The small singlet at $3.3\ \delta$ is from an impurity. Care must be taken during the synthesis to avoid temperatures above 100°C , since it is reported that 7-substituted cycloheptatrienes can undergo thermal rearrangements (*3a, b*). The impurity in Figure 1 at $3.28\ \delta$ is probably one of these isomers, since it behaves similarly to the 7-substituted cycloheptatriene in shift reagent studies. A special feature we note in the spectrum, *in passim*, is the fine doublet in the downfield portion of the e resonance. This coupling is not long-range; rather, it is a second-order splitting. As will be shown later, upon addition of shift reagents the splitting vanishes.

So, as it stands, the only possible ambiguity lies in the assignments of b and c. Additional ferreting out of the coupling constants can probably reduce this ambiguity. That is, the magnitudes and types of couplings (geminal, vicinal, allylic, etc.) should serve to confirm assignments. However, as we shall presently see, this spectrum con-

tains at least one "surprise." It turns out that decoupling and/or shift reagent experiments are the easiest way to confirm the assignments and, hence, the identity of the final product. An attractive feature of this project is that either or both of these additional types of experiments can be performed. Thus, the experiment can be adapted readily to the particular aptitude of the students and to the equipment available.

Spin Decoupling Experiments

Decoupled spectra are shown in Figure 2; the presentation used is adapted from that of Egger and Moser (4). What is done is, simply, to successively irradiate each resonance and watch what happens to the others (Fig. 2A is the unirradiated spectrum). We shall concentrate on the high points here. First, irradiation in the region of e (Fig. 2B) causes the quartet tentatively assigned to c to collapse to a doublet. This occurrence immediately confirms the identity of the latter resonance and hence, by inference, of b. Irradiation of c (Fig. 2E) causes b to collapse to a fine multiplet—much more like a broad singlet than a clearly discernible doublet. Thus, we have confirmed b being coupled to c. It is of equal importance to note that this irradiation of c does not affect a, which should be the case if a and c are not coupled.

This latter finding is moderately surprising since a and c are allylically disposed toward each other. The fact that they are not strongly coupled is confirmed by subsequent irradiation of a (Fig. 2D) leaving the resonance of c totally unaffected. However, b collapses to a simple doublet upon this irradiation. Also, irradiation of b (Fig. 2E) is the only thing which has any effect on the a peaks. Yet a appears as a triplet in the original spectrum; i.e., it must be coupled to two protons rather than one. The answer to this riddle lies in the fact that a is coupled to both the other b protons. In one case, the coupling is vicinal (three-bond) and in the other case allylic. The two coupling constants are nearly equal and thus cause a to appear as a triplet rather than a pair of doublets. Thus, spin decoupling has allowed us to resolve what would probably, otherwise, have resulted in an error in assigning splittings if these measurements had not been performed.

Further irradiations are straightforward but give little additional information. No irradiation has any effect on the methyl (f) resonance, as expected. It is of particular importance to note that d and e are too close together for the coupling between them to be decoupled effectively, at least at 60 MHz. The latter fact should be pointed out to the student as one of the shortcomings and difficulties often encountered in decoupling experiments.

Shift Reagent NMR Experiments

It often happens that suitable decoupling equipment is not available even though the basic NMR spectrometer is readily accessible. Before the advent of lanthanide shift reagents (LSR) the experiment would thus have stopped after the basic spectrum was obtained. However, with LSRs much additional information is immediately at hand with a minimum of effort. Details of the mechanism of binding of LSRs and substrates and the methods used to analyze the shifts are discussed in several excellent reviews (5) and have been discussed earlier in *this Journal* (6). We shall not delve into these in too much detail. Rather, for this experiment it is sufficient to know that the lanthanide-induced shifts (LIS) follow, roughly, a $1/r^3$ dependence (where r is the distance between the LSR metal atom and the proton observed).

Two LSRs were used in this project: $\text{Pr}(\text{fod})_3$ and $\text{Eu}(\text{fod})_3$. In all experiments, the substrate concentration was kept constant at $\approx 0.2\ M$ and small amounts of LSR were added to obtain the shifted spectra. Successive additions were employed in both cases (Eu and Pr LSRs) and changes in the spectra monitored with each addition. These two reagents were chosen to allow the student to compare the advantages and disadvantages of each. It should be emphasized here that *either* LSR gives sufficient information to allow the assignments given earlier to be confirmed. However, there are distinct advantages in having the student use both LSRs to reach his own conclusions as to their relative effectiveness.

Using LIS as an aid in spectral analysis has one immediate, obvious advantage: the spectra are simplified. How this occurs in the case of the compound at hand is shown in Figures 3 and 4. In both cases, the spectra are much easier to interpret. It should be noted here that $\text{Pr}(\text{fod})_3$, Figure 4, does a better job in resolving the olefinic part of the spectrum whereas $\text{Eu}(\text{fod})_3$, Figure 3, is better at aiding the analysis of the other portions. $\text{Pr}(\text{fod})_3$ induces upfield shifts whereas $\text{Eu}(\text{fod})_3$ shifts in a downfield direction.

However, of more importance here, are the relative sizes of the shifts. There are two ways of comparing these: (1) plots of LIS versus relative LSR concentration and (2) plots of shift versus shift. It is

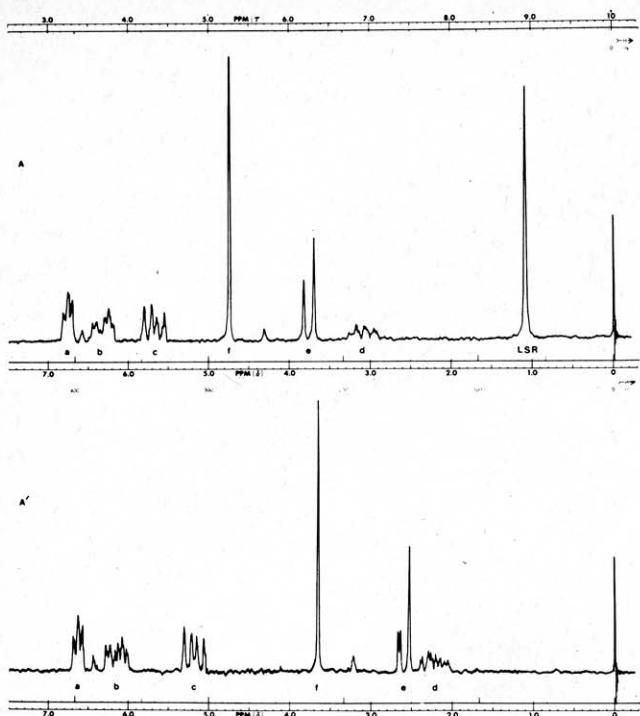


Figure 3. Typical LIS spectrum using Eu(fod)₃, (A). The undoped spectrum (no LSR added) is A'.

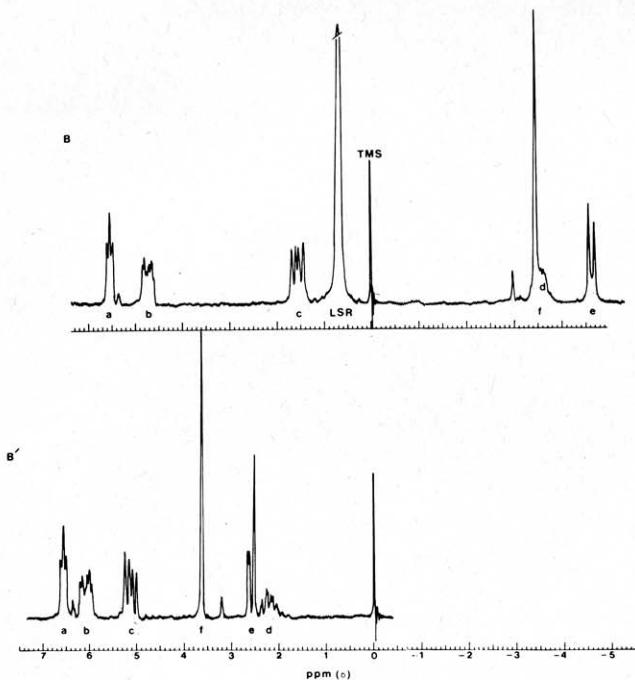


Figure 4. Typical LIS spectrum using Pr(fod)₃, B. The undoped spectrum (no LSR is added B').

well-known that the LIS of a given proton is linear *versus* ρ (the ratio of moles of LSR to moles of substrate) up to $\rho \sim 0.4$ (5). However, concentrations are not very easy to determine accurately in experiments of the type used here. Fortunately, shifts can be measured quite accurately and, at doping levels of the order used here ($0 \leq \rho \leq 0.25$), shifts are perfectly linear *versus* each other. Ideally, one should have one resonance easily discernible and "moving rapidly." This ideal is the case for the methyl (*f*) resonance of the ester. Plots of the observed shifts of all the protons *versus* the shift change in the *f* resonance are shown in Figure 5 [for Pr(fod)₃] and Figure 6 [Eu(fod)₃] data. The data and results of the relevant linear regressions are given in Tables 2 and 3.

Upon examination of the results we see that the LIS for both LSRs

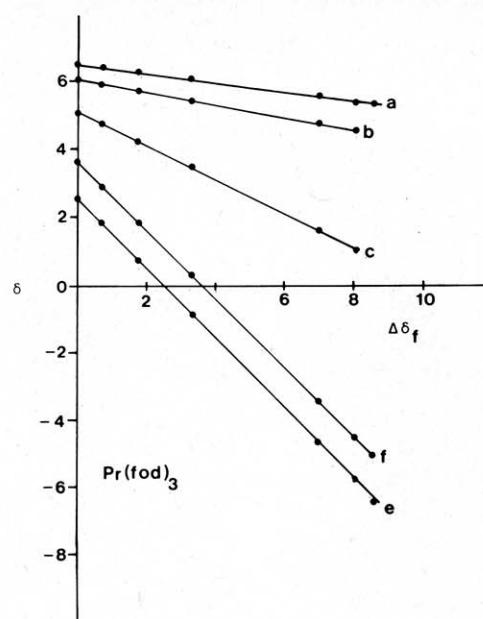


Figure 5. Pr(fod)₃ LIS plotted versus the shift change observed for the methyl resonance.

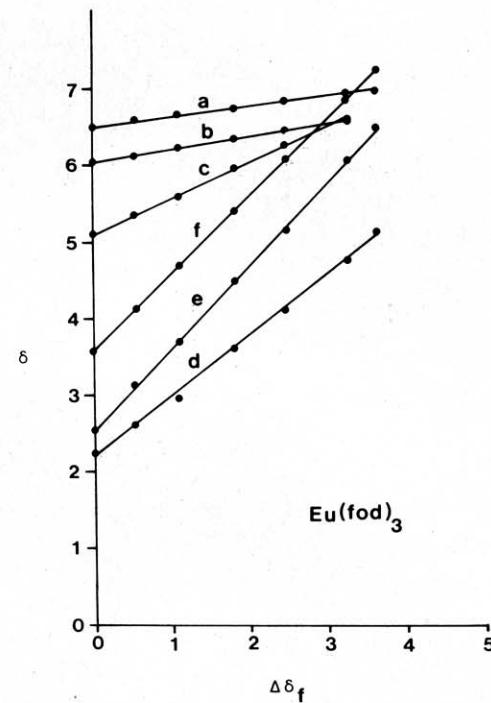


Figure 6. Eu(fod)₃ LIS plotted versus the shift change observed for the methyl resonance.

go in the order $e > f > d > c > b > a$. In the case of Pr(fod)₃ the *d* resonance was obscured too much of the time to be of more than qualitative use. However, this poses no difficulties in nailing down the required assignments. It can be seen that the ambiguity in the *b* and *c* assignments is immediately resolved and that the other assignments are confirmed just as readily. All this follows from the simple rule of "what is closest to the carbonyl is shifted the most."

Plots of shift *versus* shift are extremely easy to do and give gratifying straight lines. It should be noted that δ_0 -values (values of the shifts in the absence of LSR) are also obtained. In this case, it allows a check of the values in Table 1. In other cases, δ_0 's can be obtained even if the shift is obscured in the regular spectrum. Students should, however, weigh all their samples and have a good idea of their reagent concentrations. At high doping levels, the simple straight line relationship can break down.

If the time allows, both shift reagents should be used. If however,

Table 2. Results of Pr(fod)₃ Experiments

Raw Shifts (ppm): ^a							
ρ^b	δ_a	δ_b	δ_c	δ_d^c	δ_e	δ_f	$ \Delta\delta_f $
0.0	6.50	6.02	5.09	—	2.54	3.58	0.0
0.029	6.42 ₅	5.92	4.75	—	1.82	2.88	0.70
0.064	6.27	5.72	4.23	—	0.77	1.83	1.75
0.107	6.06	5.43	3.47	—	-0.82	0.31	3.27
0.204	5.55	4.74	1.58	—	-4.62	-3.43 ₅	7.01 ₅
0.236	5.37 ₅	4.52	1.04	—	-5.68	-4.47	8.05
0.254	5.31	—	—	—	-6.39	-4.97 ₅	8.55 ₅

Linear regression results: ^d							
Proton	δ_0	Relative shift slopes					
a	6.51 ± 0.01	-0.140 ± 0.001					
b	6.04 ± 0.01	-0.187 ± 0.002					
c	5.10 ± 0.01	-0.503 ± 0.002					
d	—	—					
e	2.56 ± 0.04	-1.032 ± 0.008					
f	(3.58) ^e	(1) ^f					

^a Mean accuracy: ± 0.01 ppm.^b Relative concentration (molar) of LSR versus substrate; substrate concentrations are fixed at 0.20 M.^c Shifts of this proton obscured throughout the run.^d Resonances of other protons are plotted versus the incremental shift of f.^e Measured directly.^f By definition.**Table 3. Results of Eu(fod)₃ Experiments^a**

Raw Shifts (ppm):							
ρ	δ_a	δ_b	δ_c	δ_d	δ_e	δ_f	$ \Delta\delta_f $
0.0	6.50	6.03	5.10	2.23	2.53	3.58	0.0
0.051	6.57	6.10	5.34	2.59	3.11	4.12	0.54
0.085	6.62	6.19	5.58	2.95	3.68	4.66	1.08
0.135	6.71	6.31	5.93	3.60	4.48	5.38	1.80
0.173	6.79	6.41	6.21	4.10	5.16	6.01	2.43
0.221	6.87	6.53	6.54	4.74	6.02	6.79	3.21
0.244	6.91	—	—	5.07	6.46	7.18	3.60

Linear regression results:							
Proton	δ_0	Relative shift slopes					
a	6.50 ± 0.004	0.114 ± 0.002					
b	6.02 ± 0.004	0.158 ± 0.002					
c	5.10 ± 0.01	0.453 ± 0.005					
d	2.16 ± 0.03	0.800 ± 0.014					
e	2.52 ± 0.01	1.092 ± 0.004					
f	(3.58)	(1)					

^a See the footnotes of Table 2 for an explanation of the various quantities given here.

it is deemed inappropriate to use both LSRs, Eu(fod)₃ is the preferred one to use. Generally, the down field direction of its LIS gives spectra which are easier to obtain. Also, it has less tendency to broaden spectral lines than does Pr(fod)₃ (5).

Summary

The synthesis and NMR studies of methyl 7-cycloheptatrienylacetate afford an excellent project for advanced undergraduate students. Several different synthetic, purification, and spectroscopic techniques are used. Students are allowed an opportunity to carry out three types of NMR experiments: obtaining a basic spectrum, spin decoupling to confirm assignments, and the use of lanthanide shift reagents as an alternative method of making assignments and in confirming the compounds structure.

Experimental

Materials

The chemicals required are listed below. Most of these were reagent grade and readily obtainable from the usual commercial sources. In

most cases no further purification was required. Where a particular commercial source is more convenient or where special treatment is needed for a particular chemical it will be given when required.

Chemicals used: triphenylcarbinol (Arapahoe), fluoroboric acid (J.T. Baker, purified, 48–50% aqueous solution), acetic anhydride, malonic acid, pyridine, pentane, petroleum ether (30–60°C), methanol, cycloheptatriene, oxaly chloride, and thionyl chloride. The SOCl₂ was distilled from boiled linseed oil, using 10 g of SOCl₂ per milliliter of oil. The fraction removed for use boiled at 76°C. The distillation was performed in a hood.

The lanthanide shift reagents (LSR) employed were Eu(fod)₃ and Pr(fod)₃. Both were Aldrich "Gold Label" and were sublimed and stored for at least 24 hr over P₄O₁₀ *in vacuo*. No impurities were observed in LSR NMR spectra; the only resonances observed for each were the *tert*-butyl peaks of the fod ligand. The Aldrich "Gold Label" LSRs can be used without further purification. The only precaution which need be taken is to store them in a vacuum desiccator over P₄O₁₀.

To prepare samples for shift reagent studies, first make about 2 ml of ~0.2 M solution of the substrate. Then place about 0.5 ml of this solution in a tared NMR tube. Take the spectrum, weigh the sample, add a small amount (~20 mg) of LSR to the tube, and then reweigh. Next take the shifted spectrum and repeat the above procedure until finished (generally 5 or 6 samples with relative concentrations of LSR to substrate ranging from 0 to ~0.25 are sufficient).

Instruments

The NMR spectra were taken on Varian A-60 and EM-360 spectrometers; the latter was equipped with a Model EM-3630 spin decoupler. Sweep widths corresponding to 1 Hz/mm and 2 Hz/mm were used.

A Perkin-Elmer Model 710 spectrometer was used for the infrared spectra; a Cary Model 14 spectrometer was used to obtain ultraviolet spectra, and a Varian EM-600 was used to obtain mass spectra.

Tropenium fluoroborate (7).

In a one liter Erlenmeyer flask protected with a drying tube, 33.3 g (0.128 mole) of triphenylcarbinol was dissolved in 300 ml of acetic anhydride. In order to dissolve the alcohol the mixture was warmed on a steam bath until all the solid disappeared. After solution was completed, the mixture was cooled to room temperature with tap water, carefully avoiding reprecipitation of the alcohol. Fluoroboric acid (27.4 g, 0.140 mole) was added to the solution in small portions (0.5 ml) while the mixture was constantly swirled and cooled in an ice bath so as to maintain the temperature between 0–10°C. Excessive heating must be avoided to obtain a satisfactory yield of pure product. During the addition the color changed from colorless to a deep reddish-brown color. After the addition of the acid was complete the solution was allowed to stand at room temperature for at least 5 min. To the resulting solution of carbonium ion 13.8 g (0.150 mole) of cycloheptatriene was added at a rate of one drop per second over a period of about 30 min. The reaction mixture was kept in an ice bath at 0°C with constant swirling. After one half of the alkene was added, a white precipitate became visible. After the addition was complete, enough dry ether was added to the reaction mixture to precipitate the remainder of the organic salt; the addition of ether is carried out until no more precipitate forms. After all the salt had precipitated, it was collected in a Büchner funnel and washed repeatedly with ether until the smell of anhydride was gone. After drying one obtains 21.7 g (0.122 mole) of the white tropenium fluoroborate (95.3% yield) with a melting point of 209° (dec) NMR (CH₃CN), δ 9.38 (s); IR (KBr disc); 3000 (C—H), 1475 (C . . . C), 1300, 1025–1070 (BF₄) cm⁻¹, uv (max) (CH₃CN) 274 nm.

Cycloheptatrienylacetic acid (8).

To a stirred solution of 22.0 g (0.211 mole) of malonic acid in 105 ml of pyridine was added 21.7 g (0.122 mole) of tropenium fluoroborate. The mixture was placed in a 500 ml round bottomed flask fitted with a reflux condenser and a drying tube and placed on the steam bath to reflux for 12 hr. After cooling, the reddish-brown reaction mixture was poured into 400 ml of 4.0 N hydrochloric acid and extracted with several 50 ml portions of pet. ether. The organic extracts were decolorized with charcoal and dried over MgSO₄. The pet. ether was evaporated and a red-brown oil remained. The acid was purified by recrystallizing from pentane at dry ice-acetone temperatures and in all cases the yields of the recrystallized acid exceeded 90%. The purified white crystalline acid (16.7 g, 0.111 mole) melted at 30–31°; NMR (CCl₄) δ_d 2.27 (m, 1), δ_e 2.62 (d, 2) δ_c 5.18 (q, 2), δ_b 6.18 (m, 2), δ_a 6.60 (m, 2), δ 11.63 (s, 1); IR (CCl₄) 3400–2500 (acid O—H); 3000

(unsat. C—H), 1720 (C=O), 1420, 1305, 940, 705 cm⁻¹; uv max (CH₃CN) 257 nm.

Cycloheptatrienylacetyl chloride

An attempt to make the acid chloride using unpurified thionyl chloride proved unsuccessful. However, the synthesis was successful with purified thionyl chloride and with unpurified oxalyl chloride using the method of Adams and Ulich (9). If oxalyl chloride is used care should be taken, since CO is evolved in the reaction.

Purified thionyl chloride (12.0 g, 0.101 mole) was added to a flask containing 7.20 g (0.0479 mole) of cycloheptatrienylacetic acid and 20 ml of 30–60°C petroleum ether protected by a reflux condenser fitted with a drying tube. After 30 min of gas evolution, the mixture was refluxed for 6 hr using either a steam bath or heating mantle. After the excess thionyl chloride was removed by aspiration, the reddish mixture was extracted several times with pentane, leaving behind a small amount of dark solid. The pentane layer was evaporated leaving (8.00 g, 0.0474 mole of an orange-red liquid (99%), IR (neat) 3045 (aromatic C—H), 2980 and 2790 (aliphatic C—H), 1795 (C=O) 1405, 1350, 975, 750, 710, and 680 cm⁻¹; NMR (CCl₄), δ_d 2.40 (m, 1), δ_e 3.07 (d, 2, J = 8 Hz), δ_c 5.17 (q, 2), δ_b 6.13 (m, 2), δ_a 6.53 (m, 2); uv max (CH₃CN) 255 nm.

Methyl 7-cycloheptatrienylacetate

The ester was made by the general method of making esters, cooling the mixture as a precaution. Dry methanol (3.10 g, 0.0938 mole) was added dropwise to a flask containing 8.00 g (0.0474 mole) of cycloheptatrienylacetyl chloride while the flask was cooled (in an ice bath) and swirled constantly. The reaction mixture was allowed to stand at room temperature for 10 min and then the excess methanol was removed by aspiration.

A light yellow oil (7.64 g, 0.0465 mole) remained and it was vacuum distilled at 0.2 mm Hg and a colorless liquid boiling at 58–60°C was retained (5.20 g, 0.0317 mole); the final step yield was 66.9%. IR (neat) 3020 (aromatic C—H), 2955 and 2850 (aliphatic C—H), 1730 (C=O), 1440, 1405, 1365, 1300, 1260, 1220, 1200, 1165 (C—O—C), 1005, 755, 715 cm⁻¹, NMR (neat) δ_d 2.20 (m, 1.00), δ_e 2.64 (d, 1.80), δ_f 3.60 (s, 3.00), δ_c 5.25 (q, 1.95), δ_b 6.15 (m, 2.00), δ_a 6.68 (m, 2.00); mass spectrum (70 eV) m/e (rel intensity) ion, 164 (19) Parent ion, 149 (5.0) C₇H₇—CH₂—C(O)—O, 133 (11.6) C₇H₇—CH₂—C(O), 105 (100) C₇H₇—CH₂, 104 (83) C₇H₆=CH₂, 91 (45) C₇H₇, 78 (19) C₆H₆, 77 (16) C₆H₅, 76 (19) C₆H₄, 65 (5.4) C₅H₅, 51 (9.1) C₄H₃.

Analysis

Calculated for C₁₀H₁₂O₂: C, 73.15; H, 7.36

Found: C, 72.98; H, 7.30

Acknowledgment

We wish to thank the many students in CHM 447, who did this project, for their suggestions.

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