J. Org. Chem. **1983**, *48*, 879–881

total yield of **2** and **3** between this thiolate-containing complex base and $NaNH_2$–NaO-*t*-Bu (system 7) indicates that one-electron-transfer processes are unimportant.

Constancy in the relative proportions of **2** and **3** in reactions of **1** with complex bases that contain $NaNH_2$ and a wide variety of sodium oxyanion (and other anionic) components strongly indicates that the latter function only to activate the surface of the elimination-inducing $NaNH_2$. Although the precise nature of this surface activation remains unclear, it is evident that for alkoxides a certain level of bulk is necessary. Thus, alkoxides derived from tertiary, secondary, and branched primary alcohols, but not those from *n*-alcohols, are effective complex-base components.

All the evidence that we have accumulated to date regarding the nature of complex-base-promoted syn eliminations is consistent with the transition-state structure represented in **4** in which B is the amide ion and M is the sodium cation.

Registry No. *trans*-1-Bromo-2-chlorocyclohexane, 13898-96-9; sodium amide, 7782-92-5; 15-crown-5, 33100-27-5.

Supplementary Material Available: Table II listing data for the elimination reactions of *trans*-1-bromo-2-chlorocyclohexane induced by $NaNH_2$–Na(anion) in THF at room temperature (1 page). Ordering information is given on any current masthead page.

Notes

Magnesium Anthracene Dianion

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In contrast to the black precipitate of magnesium which forms when magnesium bromide reacts with sodium naphthalene,[1] we have found that the corresponding reaction with sodium anthracene (deep blue) gives a white precipitate and a green-yellow solution. With lithium anthracene there is no visible reaction. It was also discovered that metallic magnesium reacts with anthracene in the presence of excess magnesium bromide to give rise to a green-yellow solution identical in color with that obtained from sodium anthracene. This solution has the curious property of reversibly changing color as the temperature is varied. At approximately 40 °C the solution is bright yellow, at 20 °C it is green-yellow, and as the temperature is lowered to –40 °C, the color smoothly changes to deep blue. Upon continued stirring of the reaction mixture at room temperature, an orange-yellow flocculent precipitate slowly formed. As no reports have yet appeared in the literature concerning the structure or physical properties of benzenoid aromatic radical anions or dianions which contain other than group 1A metals in ether solvents[2] and since the magnesium–anthracene complex was a solid, it was hoped that it could be crystallized for chemical and perhaps X-ray structure analysis. It quickly became obvious that the complex is only sparingly soluble in THF, and attempts to prepare the complex in DME or diethyl ether were unsuccessful. Conventional techniques of crystalization could not be used due to the low solubility and extreme air sensitivity of the complex. Extraction of the orange-yellow precipitate over a period of 2 months in the DeKock–Streitwieser Soxhlet extractor[3] with THF gave large clear orange needles in a yellow solution. The material left on the frit of the extractor was a yellow-green solid, apparently insoluble in THF. This material was not examined further. The composition of the orange pyrophoric crystals was determined to be MgA·3THF, where A stands for anthracene. The analysis was achieved by EDTA titration for magnesium and gas chromatographic analysis for anthracene, with THF determined by weight difference. Since the value of three for the number of THFs of solvation is rather odd, the ratio of THF to anthracene was also determined by the relative integrations of THF to anthracene in the NMR spectrum of a carbon tetrachloride solution of a sample of the solid which had been treated with oxygen gas. As expected for an anthracene dianion, hydrolysis with water gave 9,10-dihydroanthracene with only 2% anthracene.[4] The small amount of anthracene was probably formed from adventitious oxygen.

X-ray single-crystal work on the MgA·3THF crystals proved to be quite difficult both from the standpoint of obtaining a suitable crystal free of twinning and analyzing the data. The method by which an untwinned crystal was finally obtained is described in the Experimental Section. It was determined that the unit cell was triclinic with a volume of 4668 Å^3. The calculated density, assuming eight MgA·3THF units per unit cell, of 1.19 g/cm^3 is in excellent agreement with the experimental density of 1.18 g/cm^3. Because of the very large size and lack of symmetry of the unit cell, plans for a structure determination were abandoned.

Returning to the interesting color changes described earlier, it would seem that a ready explanation is now available. This is illustrated in eq 1 and 2, where the first

$$MgBr_2 + A + Mg^{2+},A^{2-}{}_{yellow} \rightleftharpoons 2MgBr^+,A^{-\cdot}{}_{blue} \quad (1)$$

$$A + Mg^{2+},A^{2-} + 2LiBr \rightleftharpoons MgBr_2 + 2Li^+,A^{-\cdot} \quad (2)$$

equilibrium lies on the right at low temperatures and on

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(1) Hutchinson, L. L. Ph.D. Thesis, Oregon State University, 1976. Rieke, R. D.; Li, P. T.-J.; Burns, T. P.; Uhm, S. T. *J. Org. Chem.* **1981**, *46*, 4323.

(2) Organomagnesium radical anion complexes of the type $RMg^+, A^{-\cdot}$, where A is an N heterocycle, as well as analogous species with group 2A, 2B, and 3A metals, have been prepared: Kaim, W. *J. Am. Chem. Soc.* **1982**, *104*, 3833. Kaim, W. *Chem. Ber.* **1981**, *114*, 3789. Kaim, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 140, 141. Kaim, W. *J. Organomet. Chem.* **1981**, *222*, C17. Kaim, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 1110.

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(4) Stevenson, G. R.; Valentin, J.; Williams, E., Jr.; Caldwell, G.; Alegria, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 515.

0022-3263/83/1948-0879$01.50/0

the left at higher temperatures. Starting from purified MgA·3THF crystals, it was found that both excess anthracene and magnesium bromide must be present for the blue or green color to form. Addition of lithium bromide to a solution of magnesium anthracene dianion containing excess anthracene gave a deep blue color, indicating that the equilibrium 2 lies to the right. Thus the basis for an explanation as to why sodium anthracene reacts with magnesium bromide while lithium anthracene does not is the fact that sodium bromide is insoluble in THF, while lithium bromide is quite soluble.

The fact that magnesium anthracene dianion is yellow in solution seems significant. The alkali metal anthracene dianion solutions are reported to be purple.[5] Thus the structural difference between the alkali metal dianion and the magnesium dianion must be quite great to cause such an extreme shift in spectra.

Attempts to obtain an NMR spectrum of the magnesium anthracene dianion were fruitless except for one low-intensity sharp singlet at approximately δ 6. The solubility in THF may be too low but more likely the absorptions are shifted upfield into the THF peaks. The chemical shifts of the 1-, 2-, and 9-positions of the alkali metal anthracene dianion are reported to be at δ 3.36, 4.25, and 1.89, respectively.[6] None of these regions could be observed due to THF absorptions.

Experimental Section

Preparation of Crystalline Magnesium Anthracene Dianion in THF. To 1 g of magnesium turnings (Grignard grade) contained in a 100-mL flask equipped with a glass-covered magnetic stirring bar and attached to a high-vacuum line was transferred 3–4 mL of THF from sodium benzophenone dianion. The flask was repressurized, 40 μL of ethylene dibromide was added, and the solution was heated to 40 °C for 1 h to activate the Mg surface. A side arm containing 2 g of anthracene (recrystallized five times from ethanol) was attached, and the assembly was immediately evacuated. High vacuum was maintained for 15 min to dry the side arm and to remove any excess ethylene dibromide. THF (40 mL) was then transferred in and the side arm rotated to allow the anthracene to drop into the THF solution. After being stirred for 1 h at room temperature, the solution was a clear green color. Heating the solution to ca. 40 °C caused the color to shift to a bright yellow, while cooling to the vicinity of −40 °C or so gave rise to a deep blue color. The color changes are continuous and reversible. After 24 h at room temperature, the mixture consisted of an orange-yellow flocculent solid in a green-yellow solution. The mixture was then heated to 30–40 °C with stirring for 1 week. At this time the orange precipitate was quite thick.

Purification and Growth of Magnesium Anthracene Dianion Crystals. The above suspension of magnesium anthracene was syringed into the extraction chamber of a DeKock–Streitwieser Soxhlet extractor[3] which had been dried on the high-vacuum line for 3 h and then filled with nitrogen. The extractor was then carefully evacuated and held at a high vacuum for 1 h. THF (50 mL) was then transferred in and the apparatus removed from the line. The orange solid was washed four times by distilling THF from the bulbs up to the extraction chamber, with the washings being poured into the side-arm bulb. The THF was then distilled into the left-hand bulb, and the apparatus was placed in a constant-temperature box. Both the bulbs were immersed in an oil bath such that the THF level was 1–2 cm above the oil level. The constant-temperature box was heated to 40 °C, and the oil bath was heated by means of a nichrome coil to such a power level that the extraction proceeded at a slow rate. The proper power level was determined by trial and error over a period of 1 week, while the extraction took place over a period of 2 months.

The magnesium anthracene dianion grew as clear orange needles up to 4 cm in length and 3–4 mm in width. A yellow-green solid of undetermined composition was left on the frit of the extractor. After the completion of the crystallization, the THF was poured into the side-arm bulb and then removed on the high-vacuum line. The crystals were then transferred to storage tubes in a drybox.

Analysis of the Magnesium Anthracene Dianion Crystals. A portion of the purified material was transferred to a tared flask in the drybox and the weight determined to be 0.6565 g. The flask was then connected to the high-vacuum line and evacuated, and 1–2 mL of degassed water was transferred in. The mixture was allowed to stand for 1 h. Standardized nitric acid (10.00 mL, 3.94 mmol) and benzene (20 mL) were then added, and the mixture was stirred for 1 h. The aqueous phase was separated and back-titrated with 0.200 M NaOH, requiiring 4.09 mL. Thus, 3.12 mequiv of base was formed in the treatment of the orange solid with water, equivalent to 1.56 mmol of Mg. The neutralized solution was then diluted to 100.0 mL. Titration of a portion with $AgNO_3$ showed the absence of bromide ion. Titration of the remainder in 25.00-mL lots with 1.022×10^{-2} M disodium EDTA using erichrome black-T indicator and pH 10 buffer required an average of 39.0 mL, equivalent to 1.60 mmol of Mg.

GC analysis of the organic phase showed the ratio of anthracene to 9,10-dihydroanthracene to be 0.0246 ± 0.0009 (ten injections). To the benzene solution was then added 0.3270 g of anthracene as an internal standard, and the ratio of dihydroanthracene to anthracene was determined to be 0.872 ± 0.014. The response factor for dihydroanthracene vs. anthracene was determined to be 1.015 ± 0.014. Thus, present in the benzene layer was 0.2957 g of dihydroanthracene and 0.0073 g of anthracene, or 1.68 mmol of anthracene, in the original sample. If the quantities of both anthracene and magnesium in the original sample are taken to be 1.60 mmol (the EDTA titration is expected to be more accurate than the GC analysis) and the remainder by weight taken to be THF, the empirical formula is MgA·2.88THF, or MgA·3THF when rounded off.

Confirmation that the ratio of THF to anthracene is 3 was obtained by NMR. In the drybox, a portion of the crystals was placed in a vacuum-dried NMR tube. Exposure of the crystals to O_2 gas was followed by the addition of CCl_4. NMR integration of the anthracene protons relative to the THF protons indicates a 3.1 ± 0.4 mol ratio of THF to anthracene.

Preliminary X-ray Single Crystal Analysis of Magnesium Anthracene Dianion. A single crystal suitable for structure analysis was obtained in the following manner. In the inert-atmosphere box, a small pile of crystals was placed on a smear of Apiezon N grease on a microscope slide and quickly mixed. The slide was placed in a miniature inert-atmosphere container composed of a piece of Pyrex tubing with large rubber balloons capping the ends. The crystals were manipulated by means of short pieces of tungsten or stainless steel wire epoxied to the ends of a glass rod. The crystals were observed through a dissecting microscope during the manipulations. The crystals were cleaved in a small pool of mineral oil in hopes of cleaving single crystals from twined ones. Selected crystals were set off to one side and later loaded into 0.3- and 0.5-mm X-ray capillaries in the inert-atmosphere box.

The chosen crystal was mounted on a Syntex P$\bar{1}$ computer-controlled four-circle diffractometer equipped with a graphite-monochromatized Mo Kα X-ray source. Examination of the output from the Syntex autoindexing routine indicated that the crystal was triclinic and with a rather large unit cell. Execution of the Syntex least-squares refinement program with three selected axes from the autoindexing routine resulted in the following unit cell parameters (standard deviations): a = 19.193 (0.029) Å, b = 8.127 (0.009) Å, c = 30.503 (0.409) Å, α = 97.14 (0.11)°, β = 98.54 (0.13)°, γ = 89.92 (0.11)°. The unit cell volume is 4668 (12) Å^3, and assumption of eight MgA·3THF units per unit cell gives a calculated density of 1.19 g/cm^3, in good agreement with the experimental density of 1.18 g/cm^3 obtained by flotation in a benzene–bromobenzene mixture.

That the crystal is single is shown from examination of partial rotation photographs taken about each of the three chosen axes.

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No reflections off the layer lines were observed. In addition, ω scans of several reflections gave sharp symmetrical peaks with no evidence of twinning.

Acknowledgment. We thank Professor Carroll W. DeKock for helpful discussions and for his assistance with the X-ray diffraction work.

Registry No. Magnesium anthracene dianion, 84559-48-8.

Cycloaddition Reactions of Benzothiet

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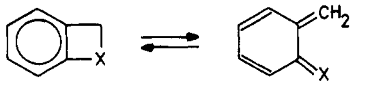
Benzo-condensed four-membered heterocyclic ring systems are of special theoretical and synthetic interest because of their valence isomerization between the strained benzenoid form (**1–3**) and the *o*-quinoidal form (**4–6**).

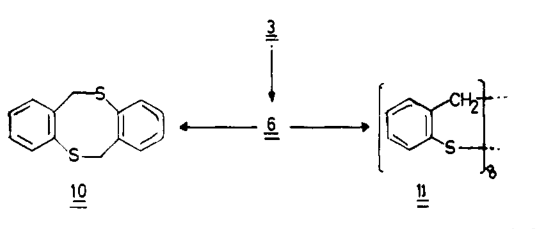


1 (X = NR) 4 (X=NR)
2 (X=O) 5 (X=O)
3 (X=S) 6 (X=S)

Although benzazetines **1** are well documented since the work of Burgess and McCullagh, all the published benzoxetes **2** in reality have been found to have different structures.[4-6] A few years ago we succeeded in the synthesis of the first benzothiet **3a**.[7,8] The parent compound **3** has been prepared by degradation of the ester **3a**[9] or more conveniently by flash pyrolytic methods, namely by decarboxylation of the benzothiophene dioxide **8**[10,11] or by decarbonylation of the thiolactone **9**[12] (Scheme I).

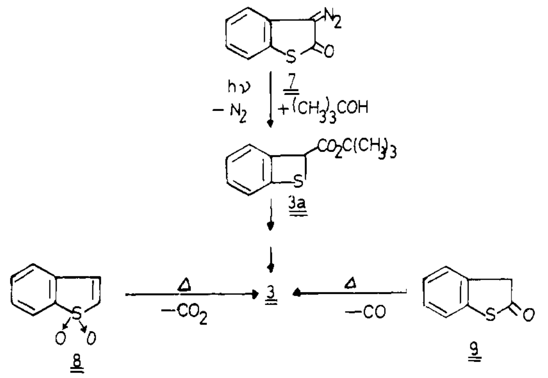
This easy access renewed the interest to continue our studies of the chemistry of **3**. Here we report the cycloaddition products from the thermal or photochemical activation of **3** in the presence of dienophiles. The aim was to find a convenient synthesis of 4*H*-1-benzothiopyrans and their 2,3-dihydroderivatives.

In boiling toluene, benzothiet (**3**) dimerizes to give 1,5-dibenzo[*b*,*f*]dithiocin (**10**),[10] whereas on being allowed to stand at room temperature in pure state for several days, **3** oligomerizes. ^{13}C and ^{1}H NMR spectra and the mass spectrum gained with the field-desorption technique reveal that the main component is the octamer **11**. Both reactions are regiospecific and presumably proceed via the intermediate formation of **6** by the opening of the four-membered ring.



In the presence of dienophiles these processes can be largely suppressed in favor of $[{}_\pi 4_s + {}_\pi 2_s]$ or $[{}_\pi 8_s + {}_\pi 2_s]$ cycloaddition reactions; however, depending on the reactivity of the dienophile a small portion of benzothiet is converted to the dimer **10** (see Table I). In the case of unsymmetrical dienophiles a regioselectivity can be observed which corresponds to the polarity of both components; i.e., the negative sulfur adds preferentially to the

Scheme I



Scheme II

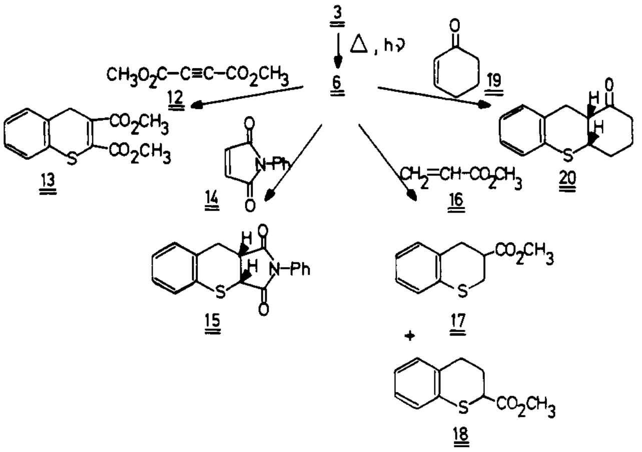


Table I. Yields of Cycloadducts 13, 15, 17, 18, and 20 and the Dimer 10

dienophile	method	cycloadduct (yield, %)	yield of dimer 10, %
12	Δ	13 (65)	20
12	hν	13 (57)	
14	Δ	15 (76)	10
14	hν	15 (66)	
16	Δ	17 (52), 18 (13)	20
19	Δ	20 (25)	55

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† Alexander von Humboldt Fellow.

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