and 1.2×10^9 M^{-1} s^{-1}, respectively. Thus, for these two carbon-centered radicals, oxygen is about twice as reactive as ABNO, a result which might be rationalized by noting that oxygen has two sites for reaction compared with one site for ABNO, or by noting the spin-statistical factors for the two reactions, viz., $^1/_2$ for oxygen and $^1/_4$ for ABNO.

Finally, the undoubted kinetic and presumed[41] thermodynamic superiority of ABNO as a carbon radical trap makes it a valuable alternative or adjunct to the usual di-*tert*-alkyl nitroxides for purposes such as "calibrating" radical clocks that are *ultrafast* or which involve resonance stabilized radicals.[30] However, ABNO's advantages will be offset to some extent by its thermal instability in solution[18] and, under the conditions we have frequently employed, by an apparent higher reactivity than Tempo toward *tert*-butoxyl radicals. In addition, the decrease in the magnitude of k_T which is seen with high concentrations of nitroxides is much more pronounced with ABNO than with Tempo (see eqs 13 and 14). We have previously attributed the reduction in k_T at high Tempo concentrations to an overall increase in the polarity of the solvent.[9] The same effect is expected to depress k_T at high concentrations of ABNO. However, in this case an additional factor comes into play since ABNO and other nonhindered nitroxides are known to dimerize reversibly in nonpolar solvents.[42-44] Thus, at high concentrations of ABNO the effective concentration of the trap, i.e., of the monomeric nitroxide, will be reduced because of dimerization with a consequent (apparent) reduction in k_T.

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Registry No. 1 diacyl peroxide, 762-12-9; **1**•, 32757-65-6; **2** diacyl peroxide, 1808-38-4; **2**•, 3744-21-6; **3**, 50876-33-0; **3**•, 139583-98-5; **4** diacyl peroxide, 54808-54-7; **4**•, 2417-82-5; **5** diacyl peroxide, 4904-55-6; **5**•, 4548-06-5; **6** diacyl peroxide, 101448-33-3; **6**•, 3889-74-5; **7** diacyl peroxide, 139584-01-3; **7**•, 3170-58-9; **8** ketone, 815-24-7; **8**•, 1605-73-8; **9**•, 50517-76-5; **10** ketone, 102-04-5; **10**•, 2154-56-5; **11**, 90-12-0; **11**•, 7419-60-5; **12**, 91-57-6; **12**•, 7419-61-6; **13**, 100-41-4; **13**•, 2348-51-8; **14**, 4489-84-3; **14**•, 139583-99-6; **15**, 4410-78-0; **15**•, 139584-00-2; **16**, 98-82-8; **16**•, 4794-07-4; **17**, 101-81-5; **17**•, 4471-17-4; **18**, 612-00-0; **18**•, 51314-23-9; **19**•, 139606-48-7; **20**, 519-73-3; **20**•, 2216-49-1; TMIO, 80037-90-7; DBNO, 6146-35-6; ABNO, 31785-68-9; $Ph_2C{=}CH_2$, 530-48-3; $(CH_3)_3C(O)_2C(CH_3)$, 110-05-4; Tempo, 2564-83-2; di-*tert*-butyl hyponitrite, 14976-54-6.

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The Surface Nature of Grignard Reagent Formation:[1] Cyclopropylmagnesium Bromide

H. M. Walborsky* and Christoph Zimmermann[2]

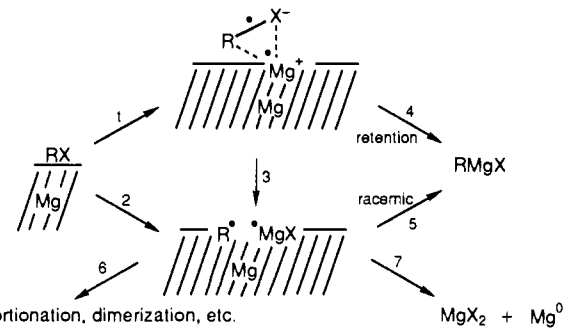
Contribution from the Dittmer Laboratories of Chemistry, Florida State University, Tallahassee, Florida 32306. *Received December 12, 1991*

Abstract: The reaction of cyclopropyl bromide with magnesium in diethyl ether yielded directly, during formation of the Grignard reagent, ~25-30% cyclopropane. Also formed in the reaction was ~25% cyclopropylmagnesium bromide. The reaction, when conducted in perdeuterated diethyl ether and in diethyl ether in the presence of the radical trap deuterated dicyclohexylphosphine, showed that the cyclopropane is formed mainly by disproportionation of the cyclopropyl radicals on the magnesium surface (~85%) and only a small amount (~15%) by reaction of a "freely diffusing radical" with the solvent. The reaction in methanol-*O*-*d* yielded almost exclusively 1-deuteriocyclopropane. These results provide further experimental evidence that the basic assumption of the D-model "that all radicals leave the surface and diffuse freely in solution" is not valid.

Introduction

Although Grignard reagents are one of the most often used organometallic intermediates,[3] there is still disagreement on the mechanism of their formation. Currently two views are under consideration. One is represented by a mathematical model based on a kinetic analysis of the product distribution. In this model,[4] called the D-model, the alkyl halide accepts an electron from the magnesium surface to form a radical R•. In order for the existing kinetic data in the literature obtained under homogeneous solution conditions to be applicable, all the radicals must "leave the surface and diffuse freely in solution at all times". The radical can, while in solution, rearrange, disproportionate, dimerize, react with solvent, or, by diffusing back to the surface, react to form the

Scheme I. Proposed Mechanism for Grignard Reagent Formation



(1) This work was supported by a grant from the National Science Foundation, to whom we are grateful.
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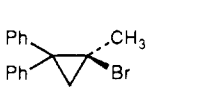
Grignard reagent. This model as well as our mechanism, vide infra, has been reviewed recently.[5]

The other view is based on experimentally established product distributions and stereochemistry observed in the formation of the Grignard reagent. It is on this type of data that the mechanism depicted in Scheme I has been based.[6] In this mechanism, two species can be formed after the initial electron transfer. Pathway 1 involves an electron transfer into the σ^* antibonding orbital of the carbon–halogen bond to produce a tight radical anion–radical cation pair which can either collapse to form Grignard reagent with conserved stereochemistry (pathway 4) or give a loose R$^\bullet$ $^\bullet$MgX radical pair by pathway 3. Alternatively, the loose radical pair can be formed directly by an electron transfer (pathway 2). In the loose radical pair the rotation of R$^\bullet$ can result in a loss of stereochemistry when the loose radical pair combines (pathway 5) to form product. The R$^\bullet$, adsorbed on the surface, can also dimerize or disproportionate, and some small fraction of the radicals may escape the surface and react in solution.

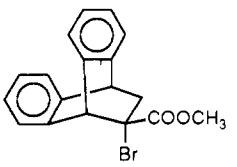
The experimental evidence to support this mechanism has been reviewed recently.[6l,m] The mechanism is in agreement with kinetic analyses for Grignard reagent formation[7-10] which show that one or both of pathways 1 and 2 are involved in the rate-determining step. It also accounts for the retention of configuration observed when a variety of chiral substrates (**1–4**) are used[6] and also for the hydrocarbon products that are not due to hydrolysis of the Grignard reagent but have been formed during Grignard formation.[6,11,12] The mixture of hydrocarbons found under these conditions differs from that found under homogeneous conditions.[6l,m] The mechanism is consistent with the intermediacy of free radicals[3,6,13-16] in the reaction and with the concomitant CIDNP effect.[16a] Using perdeuterated ether solvents, it was shown that only a small percentage of the radicals leave the surface of the magnesium.[6e] This mechanism has found general acceptance.[7,8,10,16-18]

The two views of Grignard reagent formation differ on the following important questions: Does Grignard reagent formation proceed entirely via free radicals, or are other intermediates such as radical anions involved? Do these intermediates remain largely on the surface, or do they "diffuse freely in solution at all times"? We now address these questions and present our findings on the reaction of cyclopropyl bromide with magnesium.



(*S*)-(+)-**1**

(*S*)-(+)-**2**



(*S*)-(+)-**3**

(*S*)-(+)-**4**

Results and Discussion

The most compelling evidence against the D-model with its basic premise that "all radicals leave the surface and diffuse freely in solution at all times" is the observation that the chiral substrates **1–4** all form Grignard reagents with partial retention of configuration in spite of the facts that σ cyclopropyl radicals invert their configuration[19] at a rate of 10^{11} s^{-1} at 71 °C, σ vinyl radicals[20] invert theirs at 10^8–10^{10} s^{-1} at −173 °C, and partial inversion of configuration is still obtained from **3**, which should give rise to an achiral delocalized planar π radical.[6l] In a recent publication, Garst,[21] in an attempt to "falsify" the mechanism proposed in Scheme I, claims that **1** is an "atypical" alkyl halide since it is strained and "pseudoconjugated" to the attached phenyl rings and could therefore react, in solution, via a radical anion and not a free radical. Moreover, he adduces the argument that Boche[6k,22] has shown that **1** can form radical anions in solution with partial retention of configuration. However, he neglects to point out that the amount of retention found by Boche is halogen dependent with I > Br > Cl whereas the *reverse* order Cl > Br > I is found for **1** in Grignard formation. Radical anions are indeed formed (pathway 1, Scheme I), but on the surface of the magnesium, leading to the observed reverse order.

EPR studies by Sergeev and co-workers[18] on the condensation of aryl and alkyl halides on magnesium surfaces at low temperature are in excellent agreement with our mechanism. These experiments support the existence and participation of radical anions and radicals on the surface of the magnesium. This work also showed that the decreasing stability of radical anions toward dissociation to radicals was in the order F > Cl > Br > I, which is correlated with the decreasing bond strength of the carbon–halogen bond and would be in keeping with our observation that the optical purity decreased in the order Cl > Br > I. The greater the stability of the alkyl halide radical anions on the surface toward dissociation to radicals, the greater the retention of configuration. Conversely, the less stable the radical anion, leading to the formation of more radicals, the less retention of optical activity and configuration will be observed. Their work also showed that radical anions are stabilized by charge delocalization into the magnesium metal, and hence that they are bound to the surface. The effect of a polyatomic metal surface on the stabilization of radical anions was shown in their experiments in which they simultaneously condensed atomic magnesium and an alkyl halide. They observed that the amount of free radicals formed was higher with atomic magnesium and that the formation of radical anions

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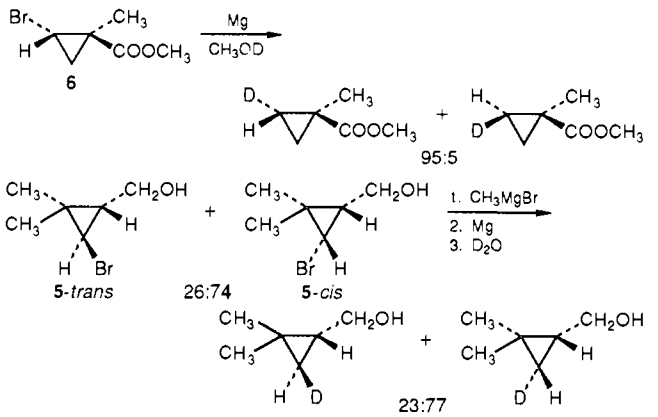
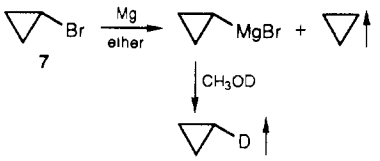
was increased by using polyatomic magnesium clusters or magnesium films.

Also overlooked by Garst are the important results of Richey[23] and Kirmse,[24] who demonstrated that almost complete retention of configuration is obtained in Grignard reagent formation from **5** (cis and trans) and **6**, respectively. In these substrates the cyclopropane derivatives do not have any phenyl groups attached. In **2** and **4**, one should note that not only are there no phenyl groups, but there is a lack of strain as well.



According to Garst,[21] cyclopropyl bromide (**7**), which is not "pseudoconjugated", behaves more like a "typical" alkyl halide and his data "are consistent with a mechanism of Grignard reagent formation in which R• diffuses freely in solution". In the reaction of **7** with magnesium he found 51% Grignard reagent (**8**), 41% cyclopropane, and 13.4% other products resulting from coupling reactions of the cyclopropyl radical with itself as well as with solvent radicals. He claimed that he was able to account for 100% of the cyclopropyl groups in these products and thus he could eliminate the formation of cyclopropene. From his results he concludes that his data are consistent with calculations based on the D-model, in which cyclopropyl bromide (**7**) is exclusively converted to the cyclopropyl radical, which diffuses into the solvent, reacting there mainly by hydrogen abstraction from the solvent and by coupling. The radical also diffuses back to the surface of the magnesium to form Grignard reagent.



In our experiments we determined the yield of cyclopropane and 1-deuteriocyclopropane by trapping the gas (bp −33 °C) in a glass bead filled test tube which was sealed with a septum and cooled to −78 °C. The trapping was shown to be efficient since in a second identical cooling trap attached to the first no cyclopropane could be detected. The amount of Grignard reagent formed was determined by careful quenching of the reagent with an excess of methanol-*O*-*d* at 0 °C and trapping of the 1-deuteriocyclopropane in a second set of cooling traps. The liquids in the cooling traps were diluted with deuterated chloroform, and a known concentration of methylene chloride (0.2 mL, 3.12 mmol for 10 mmol of cyclopropyl bromide (**7**)) was added as an internal standard. After the cooling traps were shaken vigorously to ensure complete homogenization, a sample was withdrawn by means of a gas-tight syringe and analyzed by ^{1}H NMR (300 MHz).[25] Cyclopropane and 1-deuteriocyclopropane can be easily distinguished by ^{1}H NMR since the former gives rise to a singlet at ca. 0.22 ppm (relative to $CHCl_3$ at 7.24) while the latter produces a multiplet at 0.21 ppm. In this manner we could show that the cyclopropane formed during the reaction was trapped completely because the 1-deuteriocyclopropane trapped after quenching was not contaminated by any cyclopropane which might have remained in the apparatus.

Table I. Yields of Cyclopropane Formed Directly during Formation of Cyclopropylmagnesium Bromide in the Reaction of **7** with Magnesium in Ether

expt	1	2	3	4	5	av
Cp, % yield[a]	30	23	24	31	24	26
CpMgBr, % yield[b]	21	27	23	18	31	24

[a] Cp = cyclopropane. [b] Determined by quenching with methanol-*O*-*d*.

To make the integration by NMR as accurate as possible, the spectrum was recorded with 32768 points/15 ppm (7 points/Hz) and with a delay between each pulse of 5 s to ensure complete relaxation of the nuclei. Nevertheless, there may still be a deviation of ±5% for each reported yield.

Our own experiments on the Grignard reaction of cyclopropyl bromide (**7**) were performed to find the source of the hydrogen atoms donated to the cyclopropyl radical. In the D-model the main source would be the solvent, while on the basis of our mechanism, one would expect that disproportionation on the surface would be the most probable source for direct cyclopropane formation. We also found yields of Grignard reagent and of cyclopropane substantially different from those reported by Garst.[21] As one can see from Table I, the average of five runs showed that only 26% cyclopropane and 24% cyclopropylmagnesium bromide were formed, a result which contrasts with 41% cyclopropane and 51% Grignard reagent reported by Garst. Also we could only find a maximum of 8% nonvolatile products. The starting material, cyclopropyl bromide (**7**), could not be detected after the reaction, so incomplete reaction cannot be the reason for the difference in yields. About 40–45% of cyclopropyl groups were missing; a portion of the loss, ~20%, we ascribe to the formation of cyclopropene by disproportionation of the cyclopropyl radicals on the surface of the magnesium. As we shall see later, most of the cyclopropane formed is also a result of disproportionation. This assumption is consistent with our earlier findings[6e] on the Grignard reaction of 1-bromo-1-methyl-2,2-diphenylcyclopropane (**1**), where 23% of 1-methyl-2,2-diphenylcyclopropane (**8**) was obtained along with 16% other hydrocarbons of which 12% were formed by disproportionation (**9** and **10**) and 4% by coupling (**11**). Although we recognized that substituted cyclopropenes such as **10** are stable under the conditions of Grignard formation while cyclopropene itself would not be expected to survive,[27] we nevertheless attempted to trap the cyclopropene as a Diels–Alder adduct with furan and 1,3-diphenylisobenzofuran.[28] As anticipated, none of the Diels–Alder products could be isolated.

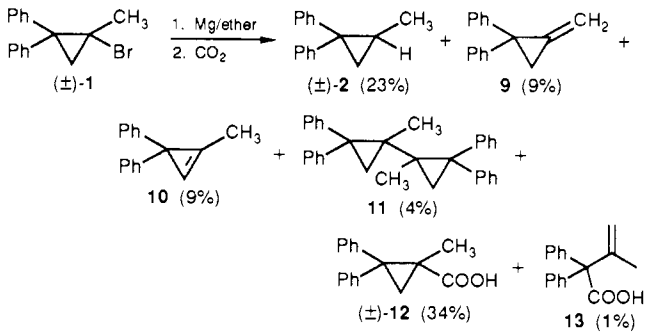


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Table II. Yields of Cyclopropane Formed Directly during Formation of Cyclopropylmagnesium Bromide in the Reaction of **7** with Magnesium in THF

expt	1	2	3	4	av
Cp, % yield[a]	6	10	11	12	10
CpMgBr, % yield[b]	33	43	23	39	35

[a] Cp = cyclopropane. [b] Determined by quenching with methanol-*O*-*d*.

Reaction of cyclopropyl bromide with magnesium in diethyl ether-d_{10} yielded about 23% cyclopropane of which 87% was protonated and only 13% was deuterated. This result shows again that only about 3% of the cyclopropyl bromide consumed formed radicals which reacted with the solvent, clearly different from the 41% claimed by Garst for the same reaction. A result comparable to the reaction of cyclopropyl bromide was previously[6e] obtained in the reaction of 1-bromo-1-methyl-2,2-diphenylcyclopropane (**1**) with magnesium in diethyl ether-d_{10}, which gave a 20% yield of 1-methyl-2,2-diphenylcyclopropane that was only 7% deuterated in the 1-position.

In another test to ascertain the extent of radical departure from the surface of the magnesium, the Grignard reaction was carried out in the presence of 3 equiv of deuterated dicyclohexylphosphine (DCPD). This gave a 26% yield of cyclopropane of which only 15% was deuterated (4% based on cyclopropyl bromide). Ashby[29] has previously used dicyclohexylphosphine (DCPH), which has been shown to be an effective radical trap by Kuivila,[30] to trap radicals produced during Grignard reagent formation. The small amount of 1-deuteriocyclopropane formed (4% based on cyclopropyl bromide) using DCPD or diethyl ether-d_{10} (3% based on cyclopropyl bromide) provides strong experimental evidence that not very many radicals leave the surface of the magnesium.

Table II reveals that the ratio of Grignard reagent to cyclopropane is much higher in THF (~3.5:1) than in diethyl ether (~1:1). This result is inconsistent with the D-model, since both the higher viscosity and the greater reactivity exhibited by THF in hydrogen abstraction reactions[26] should give more and not less cyclopropane. The product ratios in diethyl ether and in THF are in excellent agreement with the findings in the Grignard reaction of 1-bromo-1-methyl-2,2-diphenylcyclopropane (**1**). Not only did the reaction of **1** in THF-d_8 give less hydrocarbon than in ether-d_{10} but the hydrocarbon also had a higher deuterium content,[6e] which is consistent with the observed greater reactivity of THF toward hydrogen atom abstraction reactions.

Reaction of cyclopropyl bromide with magnesium in methanol-*O*-*d* at ~40 °C gave 33% cyclopropane which was nearly completely deuterated; only about 2% was found to be protonated as shown by NMR analysis. A freely diffusing radical would have been expected to react with the methyl group of the methanol by abstraction of a hydrogen atom.[6i] The small amount of protonated product formed speaks for the surface nature of the reaction.[31]

Conclusion

Our experimental results are in complete accord with the mechanism for Grignard reagent formation depicted in Scheme I, which involves the formation of a tight radical anion–radical cation pair as well as a loose radical pair all adsorbed on the surface of the magnesium with only a small percentage of the radicals leaving the surface. The experimental evidence presented disproves the basic assumption of the D-model for Grignard reagent formation, which is that "all radicals leave the surface and diffuse freely in solution at all times".

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(31) When methanol is employed as a solvent in the Grignard reaction, the products do not contain any appreciable amounts of side products resulting from disproportionation or dimerization.[6i,24] The reason for this is not clear at this time, but one can safely exclude the notion that "the radicals leave the surface and flow freely in solution at all times".

Experimental Section

All rections were carried out in flame-dried glassware under argon. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium–benzophenone. Cyclopropyl bromide (Aldrich, 99%) and diethyl ether-d_{10} (D, >99%, Cambridge Isotope Lab.) were dried over molecular sieves (3 Å) under argon. Methanol-*O*-*d* (Aldrich, 99.5% D) was stored under argon. Magnesium turnings (Fisher Scientific Co., "for Grignard reaction") were used after stirring under argon for several days to activate the surface.[32] Unactivated magnesium turnings gave comparable results. Dicyclohexylphosphine (Strem) was transferred from an ampule to a flask flushed with argon. All reactions were carried out under an argon atmosphere.

Reactions of Cyclopropyl Bromide with Magnesium in THF or Diethyl Ether. The reactions were carried out in a 25- or 50-mL three-necked flask equipped with a stirring bar, a septum, a gas inlet tube, and a condenser. The top of the condenser was closed with a rubber septum, and an 18-gauge double-tipped needle connected the top of the condenser with a collection test tube filled with glass beads. The needle reached close to the bottom of the test tube. The test tube was placed in an acetone–dry ice bath and connected to a bubbler.

Magnesium turnings (usually 1.5–2 g, 62–82 mmol) were placed under positive argon pressure in the flask, and solvent (10–20 mL) was added with a syringe. The flask was warmed on a water bath (~36–40 °C), cyclopropyl bromide (0.8 mL, 10 mmol) was added all at once with a syringe, and the mixture was stirred. After an induction period of ~10–20 min, the reaction started, as evidenced by the solution turning a greenish color and by the evolution of gaseous cyclopropane. After gas evolution ceased, the mixture was warmed for an additional 45–60 min to ensure a complete reaction. During the last 15 min a slight stream of argon was passed through the apparatus to force any residual cyclopropane into the cooling trap.

The collection tube was disconnected and replaced by an identical empty collection tube. The reaction mixture was cooled to 0 °C, and methanol-*O*-*d* (2 mL, 50 mmol) was added at a rate that permitted the slow evolution of cyclopropane. The reaction mixture was again warmed to reflux under a slight stream of argon for about 15 min to drive all the gas into the collection tube. Both tubes were placed in an acetone–dry ice bath, and deuterated chloroform (4 mL) was added, followed by the addition of methylene chloride (200 μL, 3.12 mmol) as an internal standard. The tubes were shaken to mix the contents completely, and then a small amount (ca. 0.1 mL) was removed with a gas-tight syringe and added to a precooled NMR tube containing $CDCl_3$. It was demonstrated that the concentration of cyclopropane in the capped NMR tube did not change after several days at room temperature.

Water (10 mL) and ether (10 mL) were added to the residue and decanted from the excess magnesium, which was washed with additional ether. The aqueous layer was extracted several times with ether, and the combined ether extract was filtered and dried over anhydrous sodium sulfate. The ether was removed by distillation (water bath temperature 40–45 °C), and the residue (average 71 mg from four runs) was shown by NMR spectroscopy to contain ethoxy groups (δ (ppm) 3.3–3.6 (br m), 1.12–1.22 (m)) and cyclopropyl groups (δ(ppm) 0–0.5). On the basis of the smallest molecular weight product expected to be present in the mixture, dicyclopropyl, the maximum yield of residue products would be 8.6%.

Reaction of Cyclopropyl Bromide with Magnesium in Diethyl Ether-d_{10}. Magnesium turnings (1.5 g, 62 mmol) in 5 mL of refluxing diethyl ether-d_{10} were activated by addition of 1,2-dibromoethane (10 μL, 0.12 mmol). The mixture was stirred for 20 min, and cyclopropyl bromide (0.4 mL, 5 mmol) was added all at once. The reaction started within 10 min, and the cyclopropane was trapped as describe above. NMR analysis showed that 23% cyclopropane was trapped and that it consisted of 87 ± 3% cyclopropane-d_0 and 13 ± 3% cyclopropane-d_1. After quenching with methanol-*O*-*d*, 36% cyclopropane-d_1 was trapped (contaminated with traces of cyclopropane-d_0).

Reaction of Cyclopropyl Bromide with Magnesium in Methanol-*O*-*d*. Magnesium turnings (1.77 g, 0.73 mmol) and 15 mL of methanol-*O*-*d* in an apparatus such as described above were warmed to 35–40 °C, a slow stream of carbon dioxide was passed through the reaction mixture[6i] as 0.8 mL (10 mmol) of cyclopropyl bromide was added, and stirring was continued for 2 h. The cyclopropane (33%) which was trapped in the cooling traps was determined by ^1H NMR spectroscopy to be >95% cyclopropane-d_1.

Reaction of Cyclopropyl Bromide with Magnesium in Diethyl Ether in the Presence of DCPD. Magnesium turnings (620 mg, 25.5 mmol) in 10 mL of ether (95.4 mmol) under argon were activated by addition of

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1,2-dibromoethane (50 μL, 0.58 mmol). After addition of 3 g of DCPD (15 mmol) the mixture was warmed on a water bath to slight reflux, and cyclopropyl bromide (0.4 mL, 5 mmol) was added all at once. The reaction started within 5 min, and the cyclopropane was trapped as previously described. The yield was determined by ^{1}H NMR spectroscopy to be 1.34 mmol (26%), of which 15% was cyclopropane-d_1 and 85% cyclopropane-d_0.

The remaining solution was cooled to 0 °C, and 2 mL of methanol was added. The cyclopropane was trapped in a second cooling trap. The yield of cyclopropane was determined to be 0.33 mmol (6%).

Preparation and Solid-State Structural, Electronic, and Magnetic Properties of the 1,3,5-Benzene-Bridged Tris(1,2,3,5-dithiadiazolyl) [1,3,5-$C_6H_3(CN_2S_2)_3$]

A. W. Cordes,*[1a] R. C. Haddon,*[1b] R. G. Hicks,[1c] R. T. Oakley,*[1c] T. T. M. Palstra,[1b] L. F. Schneemeyer,[1b] and J. V. Waszczak[1b]

Contribution from the Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, AT&T Bell Laboratories, Murray Hill, New Jersey 07974, and Guelph Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada.
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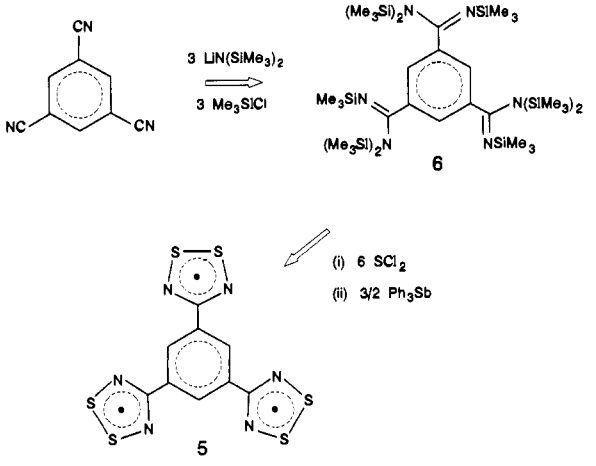
Abstract: The preparation and solid-state characterization of the trifunctional radical 1,3,5-benzenetris(1,2,3,5-dithiadiazolyl) [4,4′,4″-(1,3,5-benzenetriyl)tris[1,2,3,5-dithiadiazolyl], 1,3,5-$C_6H_3(CN_2S_2)_3$] are described. The crystals belong to the monoclinic space group $P2_1/c$, with a = 6.927 (2), b = 19.798 (3), c = 19.393 (3), and β = 99.80 (2) Å^3. The crystal structure consists of stacks of triradicals running parallel to x. Each radical center associates with a neighboring radical, generating alternating long (mean 3.832 Å) and short (mean 3.117 Å) interradical S···S contacts along the stack; only two of the three crystallographically distinct bond alternation waves so generated are in-phase. The packing of triradical stacks produces an extensive network of close interstack S···S contacts. The compound is diamagnetic at room temperature, but paramagnetic defects begin to appear near 450 K. The room-temperature single-crystal conductivity is near 10^{-7} S cm^{-1}. Extended Hückel band structure calculations reveal a band gap of 0.8 eV.

Introduction

Our interest in the design of molecular conductors based on neutral[2] as opposed to charged radicals has focused on the use of heterocyclic 1,2,3,5-dithiadiazolyl and 1,2,3,5-diselenadiazolyl systems **1**.[3] The basic architectural strategy we have pursued involves the design of molecular "building blocks" which, in the solid state, adopt stacked structures, e.g., **2**, with strong intra- and interstack interactions. We have demonstrated that stacking of monofunctional radical dimers can be induced by the use of cyanoaryl[4] or cyanofuryl[5] substituents, but the long-range E···E (E = S, Se) contacts between and within the dimer stacks are generally weak. Tighter structures, with better conductivity characteristics, can be generated from bifunctional radicals, such as the 1,4- and 1,3-phenylene bridged systems **3** and **4**, respectively. Molecular stacks, however, are not always found; indeed the crystal structure of the 1,4-derivatives (E = S and Se) consists of dimers packed in a herringbone-like fashion.[6] Stacks of diradical units, linked vertically through alternate ends, are observed in the α-phase of 1,3-derivatives (E = S and Se),[7] but in the β-phase of

Scheme I



4 (E = Se) the radicals associate as dimers which coil together to generate a chainlike motif.[8]

As an extension of this work, we have prepared and characterized the trifunctional radical 1,3,5-benzenetris(1,2,3,5-dithiadiazolyl) [4,4′,4″-(1,3,5-benzenetriyl)tris[1,2,3,5-dithiadiazolyl],

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