

Drying of Grossly Wet Ether Extracts

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Problems arising in the drying of organic extracts are routinely faced in undergraduate laboratories; thus, the dissemination of new information concerning desiccants or improved procedures which can be adopted by teaching laboratories as exemplified by a recent report in THIS JOURNAL (1) are to be welcomed.

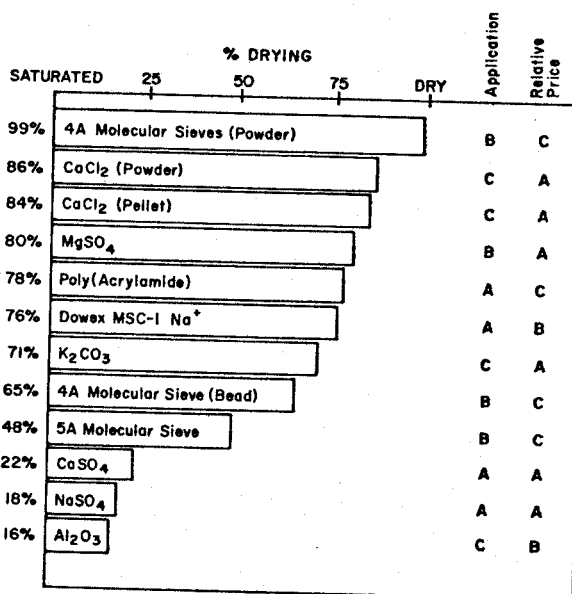
Our previous work (2-6) has been concerned with the ultimate efficiency of desiccants in the drying of reagents and solvents containing relatively small amounts of water and has provided quantitative information for the researcher. However, the drying of grossly wet organic extracts, as routinely encountered in student preparations, presents a new facet of the problem. The results below were obtained using our radiotracer method (2-6) and give information concerning the speed and efficiency of desiccants in the drying of water saturated diethyl ether.

The following points are worth highlighting. First, of the ultimate drying obtainable after 6 hr, for most desiccants at least 80% of this value has already been attained after 15 min. In one case, i.e., powdered molecular sieve, the extent is >99%. This result strongly endorses the customary practice of relatively short drying times. The only exceptions to this are the bead forms of Molecular Sieves, which although characterized by high ultimate efficiency are relatively slow in drying bulk quantities of water. Presumably, penetration of the internal labyrinthine canals is rate determining in these cases.

Sodium and calcium sulfates ("Drierite") are both surprisingly ineffective, more particularly so in the light of the august recommendations (7) and other exhortations (8) which have appeared on their behalf. In the case of calcium sulfate, this may be attributable to the very limited capacity for water absorption, i.e., ~5% w/w, which is exceeded at these desiccant loadings.

Of the more active desiccants, it should be noted that there is little difference in the rate of drying by powdered and granular CaCl₂, presumably indicating the highly porous

nature of the granule form. The applications of this desiccant are, of course, subject to the usual limitations imposed by functional group considerations. Magnesium sulfate and ion exchange resin are fairly efficient, have wide application, and are particularly advantaged in that the dry solutions produced can be decanted easily from the desiccant. On the other hand, although this was not always true for powdered molecular sieve, the siccative *par excellence* in this study, we found that this desiccant was easily voided by gravity filtration through a glass wool plug. It was striking that the potency of sieves in



Application: A No limitation
 B Wide applicability, but may cause dehydration in sensitive compounds
 C Chemically incompatible with some solutes

Relative Price: A Inexpensive
 B Moderate
 C expensive

Extent of drying after 15 min (10% w/v desiccant).

This article is Part 6 of "Desiccant Efficiency in Solvent and Reagent Drying."

Desiccant Efficiency^a in Drying of Water Saturated^b Diethyl Ether

Desiccant ^{c,d}	Residual Water Content (mg/g)			
	15 min	30 min	60 min	360 min
MgSO ₄	2.9(7.4)	2.8(6.8)	2.5(6.3)	1.8(3.6)
CaSO ₄ (Drierite)	11.4	9.2	10.2	10.7
CaCl ₂ (Pellet)	2.4	2.1(2.1)	1.9(2.1)	0.39(0.85)
CaCl ₂ (Powder)	2.1	1.4	0.46	0.24
Ion Exchange Resin (Dowex MSC-1 Na ⁺ form)	3.5(8.4)	2.4(7.4)	2.4(5.3)	1.2(3.4)
Molecular Sieve-5A (Bead)	7.7	4.9	3.2	0.40
Molecular Sieve-4A (Bead)	5.2	3.0	1.0	0.29
Molecular Sieve-4A (Powder)	0.092(0.84)	0.076(0.61)	0.027(0.44)	0.095(0.37)
Na ₂ SO ₄	12.0	12.0	11.8	10.4
K ₂ CO ₃	4.3(4.8)	3.8(4.2)	3.3(4.7)	1.6(3.1)
Poly(acrylamide)	3.3(6.1)	2.8(5.0)	2.6(4.9)	1.9(3.1)
Al ₂ O ₃	12.3	12.8	13.4	13.0

^a Static drying with intermittent shaking. Drying temperature 22°C.

^b Initial water content approximately 14.7 mg/g.

^c Desiccants activated at 350°C overnight except Drierite (220°C); Ion Exchange Resin (140°C) and Poly(acrylamide) (no activation).

^d Desiccant loading. 10% w/v and 5% w/v (values in parenthesis).

this form was such as to cause a noticeable temperature rise in the ether solution. As noted earlier in THIS JOURNAL (1) poly(acrylamide) is a useful desiccant, but the marked tendency of the granules to swell in ethereal suspensions, in our view, constitutes a serious drawback to its use.

While dilute ether extracts of compounds containing weakly or nonpolar functionalities would be expected to show broadly similar drying patterns to those noted here, it must of course be emphasized that deviations will almost certainly occur with the increasingly polar or hydrophilic nature of the solute.

Literature Cited

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An Easy Synthesis of Two Cage Hydrocarbons

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Interest in the synthesis of strained cage molecules has accelerated greatly during the last two decades (1), but most synthetic procedures leading to cage molecules are either lengthy or in poor yield. For example: in the synthesis of prismane, yield in the last step is only 4–6% (2); the first synthesis of cubane consisted of fifteen steps in 2.3% overall yield (3); and dodecahedrane remains an unknown compound despite repeated efforts (4).

We describe here a simple, three-step synthesis of two cage molecules, birdcage hydrocarbon (VIII) (5, 6) and its homologue, the homobirdcage hydrocarbon IX (7), suitable for an advanced undergraduate laboratory course.

The polychlorinated compounds involved in the first two steps have the great advantage of being highly crystalline, high melting solids, so that isolation of intermediates is easy. Additionally, the steric and electronic properties of chlorine are important in directing the course of the reactions (see the questions below), so that every step takes place with very high yield. Having served its function, the chlorine is removed in the final step by highly efficient procedure due to Winstein et al. (8).

Because all products are easily purified and are formed in high yields, and because of the unusual structure of birdcage (VIII) and its homologue (IX), students will enjoy their preparation.

Reaction Sequence (see structures)

The first step is a stereospecific Diels-Alder reaction of hexachloronorbornadiene (I) with cyclopentadiene (II) giving exclusively *endo-endo* adduct (IV) in 73% yield. Similarly, reaction of I with 1,3-cyclohexadiene (III) gave adduct V in 87% yield.

Discussion for Students: What are other possible isomers of IV and V? Why are they not formed in Diels-Alder reaction? (Steric effects of CCl₂ group, secondary orbital effects in concerted cycloaddition reaction.) Why does only one double bond of I react? Why is hydroquinone added in the preparation of V?

The second step involves (2π + 2π) photocyclization (9) of isodrin (IV) and of homoisodrin (V) in acetone to give respectively the chlorinated cage compounds VI and VII in quantitative yield.

Discussion for students: What are the differences between thermally allowed (first step) and photochemically allowed reactions (second step)? The last step introduces to students

an efficient and generalized method of dechlorination by lithium, *t*-butyl alcohol in dry THF (Winstein's method) in good yield.

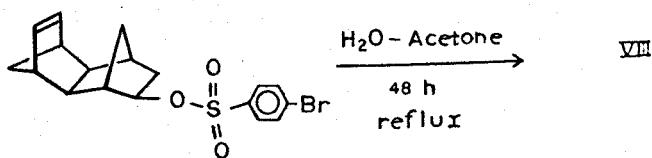
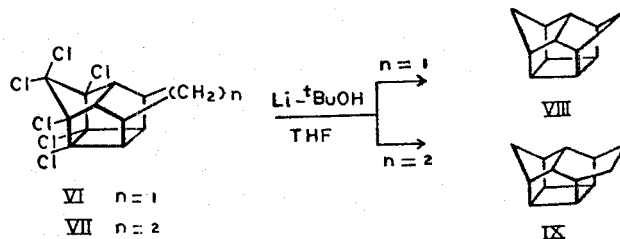
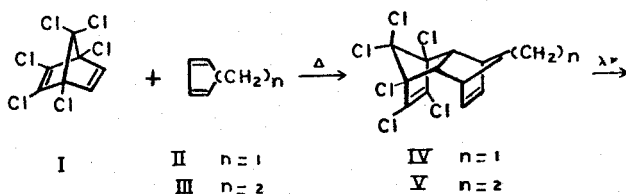
Discussion for Students: Birdcage hydrocarbon VIII has been known since 1954 (5a). While studying the solvolysis of the brosylate X, Winstein discovered that it could rearrange to VIII (eqn. 1). Discuss the rearrangement pathway.

Experimental

Safety precaution: It has been known that many chlorinated compounds (e.g., DDT, chlordane, aldrin, dieldrin, isodrin) are toxic to insects, many others (e.g., dioxin, the PCB's) are also highly toxic to people. It is highly recommended to wear a pair of rubber gloves in handling compounds I, IV–VII, and to carry out all reactions in the fume hood.

Isodrin (IV)

In a round-bottomed flask equipped with a condenser, a mixture of hexachloronorbornadiene² (I) (3.0 g, 10 mmol) and freshly distilled cyclopentadiene (2.0 g, 30 mmol) is heated at 70°C with stirring for 2 hr. A further amount of cyclopentadiene (2.0 g) is added and the solution is heated to 80°C for 2 hr. The operation is repeated. Acetone



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