chromatographic separation, and rotary evaporation. Furthermore, we believe the new method to be relatively inexpensive. More work is being carried out to optimize the yield of C_{60} and perhaps to obtain pure C_{70} and the higher fullerenes by use of different solvents.

Experimental Section

The soot was prepared from graphite rods (United Graphite Products Co., Inc., Bay City, MI) as reported previously.[8] *n*-Hexane (American Burdick & Jackson) was supplied by American Scientific Products. Aluminum oxide (activated neutral; 150 mesh, 58 A) was supplied by Aldrich Chemical Co. The Kauffman chromatographic column was obtained from Ace Glass.

In a typical run, 110 g of neutral alumina was loaded in the inner column to which 0.356 g of soot was added. Extraction was begun with 135 mL of *n*-hexane in a previously weighed flask. The extraction was stopped after 6 h when the violet band was eluted from the column. The C_{70} and higher fullerenes remained on the column. The flask was removed, and solvent was stripped from the extract in a rotary evaporator. The flask was weighed, and from the difference, the amount of pure C_{60} obtained was 0.015 g for a yield of 4%. The large-scale apparatus gave similar results using 4.5 g of soot, 200 g of alumina, and 250 mL of hexane to obtain a yield of 0.268 g of pure C_{60} (6%) after 11 h of extraction.

Acknowledgment. We thank Alex Parker who converted our ideas to reality by suggesting the glass apparatus and Joe Gregar of Argonne who built a large-scale apparatus.

Registry No. C_{60}, 99685-96-8; C_{70}, 115383-22-7; C, 7440-44-0; aluminum oxide, 1344-28-1.

A Simple Soxhlet Chromatographic Method for the Isolation of Pure C_{60} and C_{70}

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Large isolable quantities of C_{60} and smaller amounts of C_{70} can be obtained by striking an arc between two graphite rods at 60–150 A in a He (100 Torr) atmosphere in a modified evaporator,[1] followed by extraction of the resulting soot with toluene. Purification of the toluene extract by column chromatography over neutral alumina (5% toluene in hexane as eluent)[2] affords pure C_{60} and C_{70} (contaminated with C_{60}). This chromatographic process is inexpedient because (a) it often requires constant attention and involvement of at least one person for a whole day, (b) it makes use of large amounts of solvents (for a 0.5-g amount of the mixture, for example, one may require as much as 12 L of hexane and 0.6 L of toluene), and (c) the C_{70} obtained this way is generally contaminated with C_{60} and higher fullerenes.

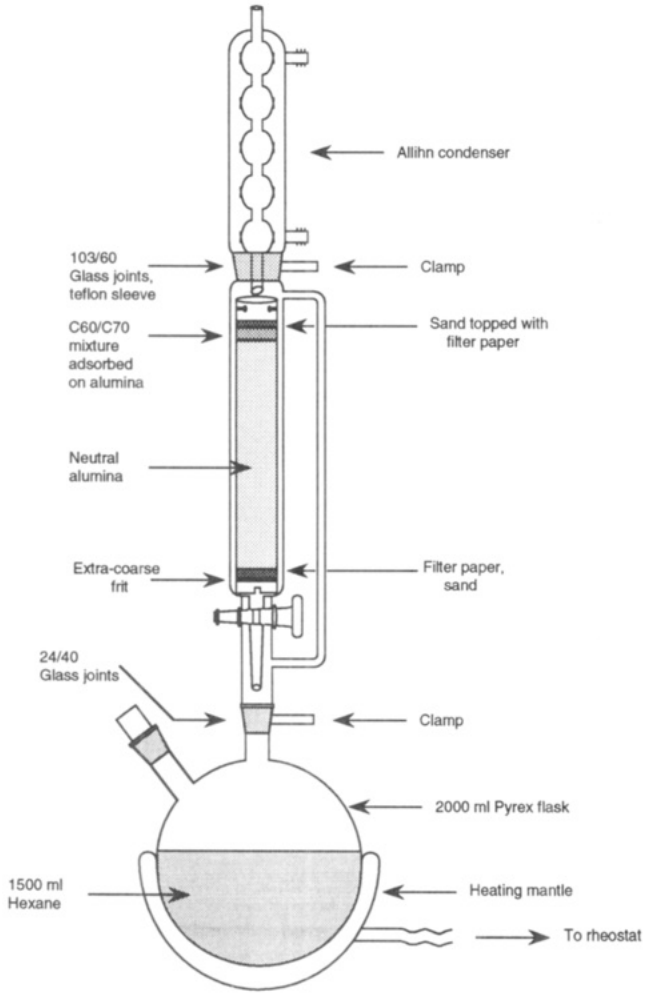

Figure 1. Schematic representation of the modified Soxhlet chromatography apparatus.

In this publication we describe a very simple process for the purification of C_{60} and C_{70} from the soot extracts; this procedure, combined with our fullerene benchtop reactor (FuBR),[3] allows easy preparation of gram quantities of pure C_{60} and tenth gram quantities of *pure* C_{70}. Our setup, once assembled and started, does not require constant monitoring and uses only about 1.5 L of pure hexane[4] per run.[5] The apparatus is shown schematically in Figure 1. In essence, the equipment is nothing but a regular alumina column with continuous solvent recycling using a modified Soxhlet extractor.[6] The glassware is very easily fabricated by simple glass-shop modifications (as per the specifications shown in Figure 2) of the following commercially

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(3) Koch, A. S.; Khemani, K. C.; Wudl, F. *J. Org. Chem.* **1991**, *56*, 4543. We noticed that the quality of the Corning 4-L kettle reactor varied unpredictably from batch to batch, in some cases resulting in unprovoked cracking of the vessel. We therefore suggest use of a stainless steel kettle reactor lined with a Pyrex sleeve. The Cu guide sleeve was replaced with a tantalum guide to prevent melting of the metal.

(4) The solvent used was actually "hexanes" (ACS reagent grade) from Fisher.

(5) If a clean, efficient rotary evaporator is used, then the solvent waste is essentially zero because the recovered solvent can be used for the next batch.

(6) Marciniak et al. (Marciniak, B.; Swierczynsky, T.; Waclawek, W *Chemik* **1980**, *33*, 58) have used a more complex apparatus where the solvent vapors *and* column were cooled and the eluent monitored with a detector device. Meier, R.; Fletschinger, J. *Angew. Chem.* **1956**, *68*, 373. Sangster, R. C.; Irvine, J. W., Jr. *J. Chem. Phys.* **1956**, *24*, 670.

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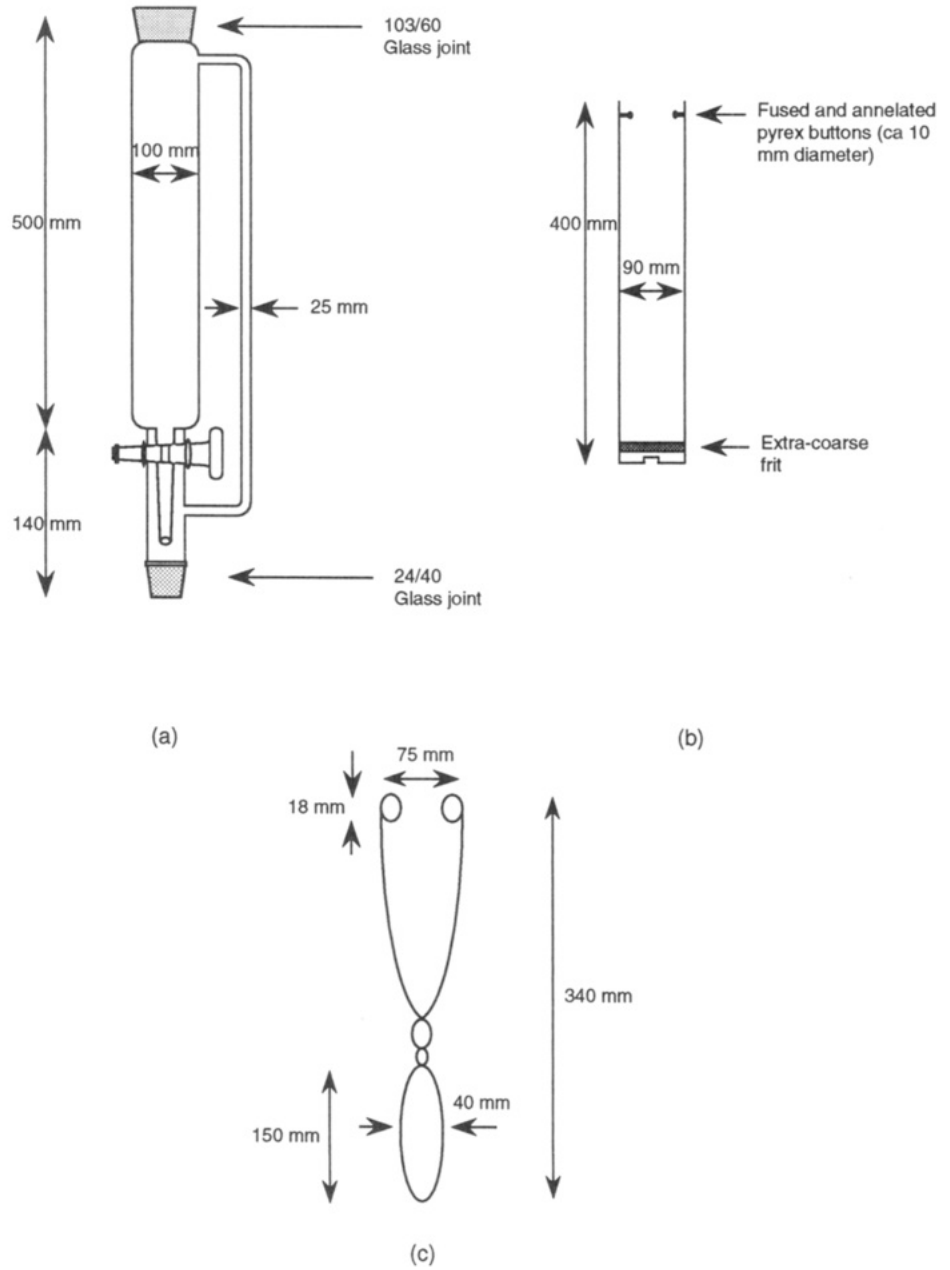

Figure 2. (a) Modified addition funnel, (b) modified glass extraction thimble, and (c) long copper wire "extrication tongs" made of ~2-mm-diameter wire.

available glassware (Fisher Scientific Co.): an addition funnel, 2000 mL, cat. no. 634530-2000, where the top joint was changed to a standard taper 103/60 ground joint (cat. no. 661500-0360) and the pressure-equalizing tube was expanded to 25-mm diameter (cf. Figure 2a); an extra coarse frit glass extraction thimble, cat. no. 586500-0025, expanded from 175-mm height to 400 mm (cf. Figure 2b); an Allihn condenser 103/60, cat. no. 456000-0025. The only homemade tool is a long copper wire "extrication tongs" made of ~2-mm-diameter wire from Belden Electronic Wire and Cable Co. (Richmond, IN 47375) and shown in Figure 2c.

The actual separation process is quite straightforward. An alumina column was prepacked in the usual fashion in the modified extraction thimble (Figure 2b) and lowered gently (with the aid of the copper-wire tongs shown in Figure 2c) into the modified addition funnel (Figure 2a). To prevent fracture of the Pyrex "buttons" (see Figure 2b), the prepacked column should **not** be lowered into the 2000-mL addition funnel vertically[7] but with the funnel held in an inclined position. The same precaution should be observed when removing a spent column.

Typically, we found excellent separation of C_{60} and C_{70} under the following load conditions. Prior to the attachment of the condenser to the apparatus shown in Figure 1, a 400-mg C_{60}/C_{70} (plus trace higher fullerenes)[8] mixture was adsorbed onto 100 g of neutral alumina and loaded on top of the above dry prepacked (to 250-mm height, 1.5 kg alumina[9]) column. The condenser was replaced (using a Teflon sleeve, ACE Glass Inc. cat. no. 7642-31), the still-pot was filled with 1.5 L of hexane (plus a few boiling chips), and the solvent heated to reflux vigorously so as

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[7] On several occasions, the fully packed column was lowered and lifted vertically without breakage of the "buttons" but to prevent possible accidents we stopped this practice.

[8] In this particular case extracted from soot obtained from MER Corp., Tucson, AZ.

[9] It is clear from the slow rate of elution and the complete separation of the bands that in the future the ratio of substrate to alumina could be decreased considerably. This is being examined.

to give a continuous stream emanating from the condenser tip (for heat insulation the pressure-equalizing side arm of the addition funnel was wrapped with several layers of paper towel). The Teflon stopcock on the addition funnel was opened only slightly so as to minimize the entry of the hexane vapors from this inlet and yet fully drain all eluted solvent into the still-pot. Once started, the system was allowed to continue until all of the purple C_{60} had collected in the still-pot (20–30 h). The still-pot was then removed and the solvent evaporated[5] to afford ca. 170 mg of pure (HPLC, UV–vis) C_{60} which was separated from the boiling chips by dissolution in CS_2 followed by suction filtration and precipitation from the filtrate with pentane. A new 2000-mL two-neck round-bottom flask containing 1.5 L of hexane was then installed and the above process repeated to elute pure C_{70} from the column (70 h). The solvent was evaporated, and 30 mg of pure (HPLC, UV–vis) C_{70} was isolated. So far we have performed about 15 of these separations, all with high reproducibility.

We believe the reason for the success of the separation lies not only in the use of lowest polarity solvents but also in the elevated temperature[10] due to the Soxhlet extraction process. It is possible that our results would not have been nearly as good had we tried the related apparatus of ref 6.

Acknowledgment. We thank the National Science Foundation for support through Grants DMR-88-20933, DMR-91-11097, and CHE-89-08323. We also thank Miklos Csuja for the glassware modifications.

Registry No. C_{60}, 99685-96-8; C_{70}, 115383-22-7; C, 7440-44-0; alumina, 1344-28-1.

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[10] Pirkle and Welch (Pirkle, W. H.; Welch, C. J. *J. Org. Chem.* **1991**, *56*, 6973) have found that better separations of C_{60}/C_{70} occur at higher temperature.

Quinone Photochemistry. A General Synthesis of Acylhydroquinones

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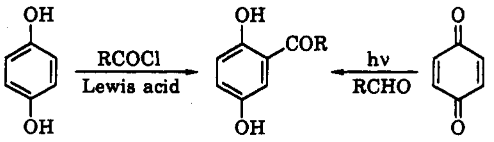
The synthesis of dihydroxy ketones such as 1 is usually accomplished by a sequence involving Friedel–Crafts acylation and hydrolysis.[1] This sequence works well in



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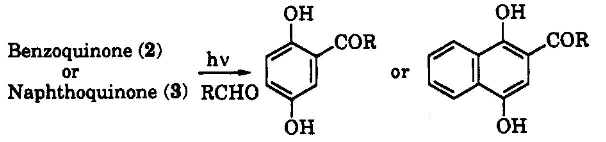
many instances, but imposes certain restrictions on functionality that can be accomodated in both the acyl unit and the aromatic substrate. A direct and potentially general route to these dihydroxy ketones might be the photochemically mediated reaction between a quinone and an aldehyde. Isolated examples of this reaction have been reported.[2,3] In connection with a program designed to explore the biological consequences of modifications on the pyranoquinone skeleton, we have examined this little-used photochemical method for the preparation of our starting materials. Although we had initially used the Friedel–Crafts approach, the poor solubility of some of the intermediates and the modest yields in the acyl-transfer step forced us to examine alternate pathways.

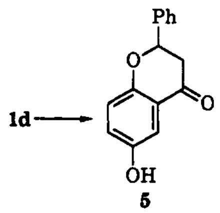
Table I. Synthesis of 2-Acylhydroquinones



entry		R	% yield	
1	2	Pr	82	**1a**
2	2	Ph	60	**1b**
3	2	CH$_3$CH═CH	52	**1c**
4	2	PhCH═CH	65	**1d**
5	2	o-CH$_3$OC$_6$H$_4$	62	**1e**
6	2	2-furyl-CH═CH	32	**1f**
7	3	Pr	77	**4a**
8	3	Ph	88	**4b**
9	3	CH$_3$CH═CH	65	**4c**

Benzoquinone (2) and 1,4-naphthoquinone (3) reacted with a series of aldehydes. The reactions were conducted under an inert atmosphere with a Hanovia lamp with a Pyrex filter. The results are collated in Table I. It is clear from these results that the presence of unsaturation in the aldehyde unit is well tolerated. This reaction has been scaled up to produce multigram quantities of **1a**, **1e** and **4a**.

Interestingly, no intramolecular cyclization occurred in the reactions which produced **1c**, **1d**, **1f**, and **4c**. This observation attests to the mildness of this procedure. Although acylhydroquinone **1d** had been previously prepared,[4] it has always been produced in low yield, the major product being the cyclic ketone **5**. Indeed, hydroquinone **1d** has been shown to rapidly cyclize to **5** in the presence of either dilute acid or base. Although hydroquinone **1c** was prepared in 52% yield by the reaction of crotonaldehyde with benzoquinone, **1c** could not be prepared by the $AlCl_3$-mediated rearrangement of the bis-crotonoyl ester of hydroquinone.[5]



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This methodology offers a convenient and versatile pathway for the synthesis of acyl hydroquinones. Functional groups such as alkenes are compatible with the mild reaction conditions. This method offers an alternative method for the formation of precursors to highly reactive acylquinones.[6]

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[6] For a recent preparation of acyl quinones, see: Buchwald, S. L.; King, S. M. *J. Am. Chem. Soc.* **1991**, *113*, 258 and references cited therein.