sources of halide-free phenyllithium (such as the commercial material or that prepared from chlorobenzene and lithium shot) give similarly high yields of the stable lithium derivative.

Experimental Section

Instruments.—Analytical glpc was performed on a Perkin-Elmer Model 800 gas chromatograph (flame ionization detector). Product yields were determined by quantitative glpc using the internal standard method; peak areas were measured with a Disc integrator and the response ratios for all products and standards were determined Preparative glpc was performed on a Varian Aerograph Model 202-1B gas chromatograph (thermal conductivity detector). Nmr spectra were obtained on a Varian Associates A-56/60A spectrometer.

Materials.—β-Methylallyl chloride was obtained from Matheson Coleman and Bell and was distilled at atmospheric pressure before use. Iodobenzene was purchased from either Matheson Coleman and Bell or J. T. Baker Chemical Co.; the former gave by far the better and more consistent results. Phenyllithium in benzene–ether was obtained from Alfa Inorganics, Inc., and *n*-butyllithium in hexane from Foote Mineral Co. Lithium shot was prepared from lithium rod by the method of Worden and Burgstahler.[5] Organolithium reagents were analyzed for carbon-bound lithium by either "double titration"[6a] or the triphenylmethane method[6b] (see below); analysis for inorganic halide was done by Volhard titration. All reactions involving lithium reagents were run under an argon atmosphere.

Preparation of Crystalline Phenyllithium.—The procedure of Scholosser and Ladenberger[4] gave phenyllithium yields of the order of 60%, as judged by titration of an aliquot either by the "double titration" method[6a] using 1,2-dibromoethane or, more conveniently, by the addition of a two- to threefold excess of triphenylmethane in tetrahydrofuran followed by titration of the blood-red solution to a pale yellow end point with ethanol in benzene.[6b] Volhard titration of the aqueous layer from the neutralization of an aliquot of solution showed the absence of halide ion.

Synthesis of 1-Methylcyclopropene.—A solution of 2.75 g (0.030 mol) of β-methylallyl chloride in 50 ml of ether (dried over sodium) was added over *ca.* 30 min at room temperature to a stirred solution of a two- to threefold excess of phenyllithium (crystalline) in ether containing cyclooctane as an internal standard. The mixture was stirred for an additional 30 min. An aliquot was quenched with water and quantitatively analyzed by glpc (20 ft × 1/8 in., Hi-Pak silicone rubber W98 column) for β-methylallylbenzene for which a total yield of 0.051 g (1.4%) was calculated. A second aliquot was treated with cyclopentadiene and water. Analysis on the same column for *endo*-2-methyltricyclo[3.2.1.$0^{2,4}$]oct-6-ene, the Diels–Alder adduct of 1-methylcyclopropene, gave a total yield of 2.92 g (80%); the structure was confirmed by comparison of glpc retention time and nmr spectrum with that of an authentic sample.[2a] Small amounts of β-methylallyl chloride could be detected, indicating that the yield of products may be even higher. In other runs, the yield of coupling product was in the range of 1.8–3.2% and that of Diels–Alder adduct from 54 to 73%.

The remainder of the reaction mixture was placed in the freezer for 3 months. Aliquots were then removed and analyzed as described above giving calculated yields for β-methylallylbenzene and Diels–Alder adduct of 4.5 and 76%, respectively. The remainder of this material was quenched with deuterium oxide and cyclopentadiene. The aqueous layer was extracted several times with ether, and the combined organic phases were washed with saturated NaCl, dried over $MgSO_4$, and concentrated with a rotary evaporator. Preparative glpc (10 ft × 3/8 in., XF-1150 column) gave the completely monodeuterated Diels–Alder adduct (total absence of nmr absorption at δ 1.0); mass spectral analysis confirmed that the sample was better than 95% monodeuterated.

For the purpose of further reaction, 1-methylcyclopropene may either be generated by aqueous neutralization of the lithiocyclopropene and used in the original reaction vessel, or generated and driven into a suitable trap, as illustrated for formation of its Diels–Alder adduct, where the reaction vessel was fitted with a condenser which was connected by a length of Tygon tubing to an ice-cooled gas-washing tower containing cyclopentadiene, pentane, and cyclooctane (internal standard). The reaction vessel was cooled (ice bath) while absolute ethyl alcohol was slowly added; a stream of argon was swept through the flask and into the trap. Upon completion of the neutralization, the reaction flask was slowly warmed until ethanol began to reflux, and gentle reflux was maintained for 2.5 hr. Quantitative glpc analysis for the Diels–Alder adduct indicated that 84% of the methylcyclopropene originally present in the reaction flask had been driven over and converted into the Diels–Alder adduct.

Registry No.—1-Methylcyclopropene, 3100-04-7.

(5) L. R. Worden and A. W. Burgstahler, *J. Chem. Educ.*, **45**, 425 (1968).

(6) (a) H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964); (b) R. M. Magid, S. E. Wilson, T. C. Clarke, and C. D. Duncan, unpublished results.

1,2,3,4-Tetrahydroquinoline 8-Sulfones[1,2]

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Sulfuric acid has been known to cause rearrangement or hydrolysis[3] of arylsulfonanilides. The utilization of the rearrangement technique as a synthetic route to difficultly accessible sulfones has received little attention. Hydrolysis is the predominant reaction for sulfonamides, while either hydrolysis or rearrangement, depending on acid concentration, is possible for the N-substituted sulfonanilides. In their original investigations, Witt and Uermenyi[3] found that high acid concentration with sulfonanilides led primarily to the formation of *o*-amino sulfones rather than the expected hydrolytic products.

Additional work by Witt[4] and later by Halberkamm[5] defined several of the parameters which favored the rearrangement reaction. Where the *N*-alkylaniline was either unsubstituted or possessed *p*-methyl, *p*-methoxy, or *p*-chloro substituents, ortho rearrangement predominated. If, however, the para substituents were amino, nitro, or sulfonic acid, virtually no sulfone was formed and only hydrolytic products were observed. One case of a para rearrangement was reported by Witt[3] in which *N*-ethyl-*p*-toluenesulfono-*o*-toluidide resulted from the rearrangement of *N*-ethyl-4-(*p*-toluenesulfonyl)-*o*-toluidine. Halberkamm, however, observed only ortho rearrangement.

Thus, the rearrangement is generally ortho and appears to be favored by electron-donating groups on the aniline moiety and suppressed by electron-withdrawing groups.

Recently, this reaction has been reinvestigated in this laboratory with a view toward expanding its utility as a synthetic tool. Instead of employing sulfonanilides, the amines were selected such that the amino nitrogen was incorporated in a heterocyclic ring. Thus the heterocyclic sulfonamide **1** would give rise to an aromatic sulfone **2a**. Initially, the rearrangement

(1) Supported by a grant (MH 11489) from the National Institutes for Mental Health.

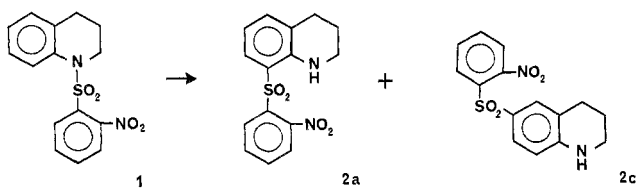
(2) Presented at the 5th Middle Atlantic Regional Meeting of the American Chemical Society, Newark, Del., April 1, 1970.

(3) O. N. Witt and D. Uermenyi, *Ber.*, **46**, 296 (1913).

(4) O. N. Witt and H. Truttwin, *ibid.*, **47**, 2786 (1914).

(5) (a) J. Halberkamm, *ibid.*, **54**, 1665, 1833 (1921); (b) *ibid.*, **55**, 3074 (1922).

of the *o*-nitrobenzenesulfonamide of 1,2,3,4-tetrahydroquinoline (**1**) was studied. In 98% sulfuric acid **1** gave a mixture of isomers (**2a** and **2c**) which was not easily separated. One of the isomers was obtained in a reasonably pure state by continuous extraction of the reaction product with ether, leaving the alternate isomer. The individual isomers were then amenable to purification by crystallization.



1 2a 2c

In order to assign a structure to the two isomers, the 8-sulfone was synthesized unequivocally from 1,2,3,4-tetrahydroquinoline-8-thiol, obtained by the method of Konig[6] and, through interaction with *o*-nitrochlorobenzene in alkali, formed the thioether which was then oxidized to the sulfone **2a**. Comparison of infrared spectra ascertained which of the two isomers was the 8-sulfone, and it was further verified by nmr spectroscopy. The predicted first-order patterns for the protons in the 5, 6, and 7 positions were observed. Splitting patterns for the aromatic protons of the high-melting isomer confirmed the 6-sulfone as the other rearrangement product.

To avoid the formation of a mixture of isomers during rearrangement, further work was done using 6-substituted 1,2,3,4-tetrahydroquinolines. These compounds were converted to the sulfonamides by a modified Hinsberg procedure.

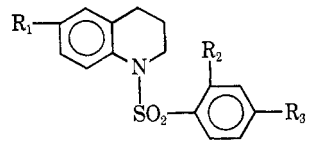
Sulfonamides with a 6-chloro or 6-methyl substituent rearranged smoothly and in good yield. The 6-methoxy compound, however, rearranged with demethylation, contrary to the comparable rearrangement of the sulfonamide of *p*-anisidine in which rearrangement is not accompanied by demethylation.

For the *o*-nitrobenzenesulfonamides, concentrated sulfuric acid at room temperature for from 5 to 60 min was usually sufficient to effect rearrangement, while the unsubstituted benzenesulfonamides required heating at 100° for 1 hr or more. Transient green and blue colors were evident on mixing the reactants, and the sulfuric acid solution of the rearranged material was usually an intense red. Attempted rearrangement of 2,4-dinitrobenzenesulfonamides of tetrahydroquinoline or of indoline gave products which have resisted purification, and thus identification. The synthetic results are summarized in Tables I and II.

Mechanistically, the rearrangement remains to be fully elucidated. The reaction has been compared with the rearrangement of phenylsulfamic acids,[7] and several intramolecular schemes are proposed. One suggested mechanism for the ortho rearrangement postulates the formation of an intermediate (**4**) with subsequent loss of a proton to give the observed product (**2**). A variation of this scheme predicates a preliminary rearrangement to a sulfitoamine (**3**),

(6) W. Konig, W. Kleist, and J. Gotze, *Ber.*, **64B**, 1664 (1931).
(7) C. K. Ingold, "Structure & Mechanism of Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

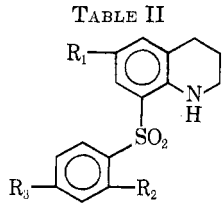
TABLE I



Compd[a,c]	R_1	R_2	R_3	Yield, %	Mp, °C
1[b]	H	H	H	...	67
1a	H	NO_2	H	63	131–132
1b	H	NO_2	NO_2	38	165–166
1c	Cl	H	H	50	91–93
1d	Cl	NO_2	H	56	124–126
1e	Cl	NO_2	NO_2	10	201–202
1f	CH_3O	H	H	80	111–112
1g	CH_3O	NO_2	H	46	121–122
1h	CH_3	NO_2	H	48	112–114
1i	Cl	NO_2	Cl	18	104
1j	CH_3	NO_2	Cl	48	87–88

[a] Synthetic method A was employed for all amides except compound **1**. [b] Mp 67°: C. Schotten and H. Schlomann, *Ber.*, **24**, 3695 (1891). [c] Satisfactory analytical values (±0.3% for C, H, and N) were reported for compounds **1a–j**: Ed.

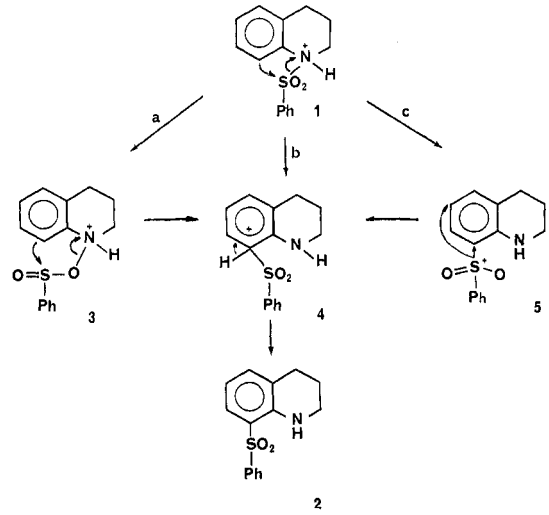
TABLE II



Compd[a]	R_1	R_2	R_3	Yield, %	Mp, °C
2	H	H	H	50	115–116
2a[b]	H	NO_2	H	38	103–106
2b	Cl	H	H	77	147–148
2d[c]	HO	NO_2	H	10	215 dec
2e	CH_3	NO_2	H	50	136–138
2f	H	NO_2	NO_2	...	170–171
2g	Cl	NO_2	H	50	141–142
2h	CH_3	NO_2	Cl	37	109
2i[d]	Cl	NO_2	Cl	10	115

[a] Satisfactory analytical values (±0.3% for C, H, and N) were reported for compounds **2a–h**, inclusive. [b] The 6-sulfone (**2c**) is also formed in this reaction. [c] Formed from **3g** which demethylates upon rearrangement. [d] Confirmed by ir and nmr.

followed by rearrangement to the protonated sulfone (**4**), thence to the product. While these reaction

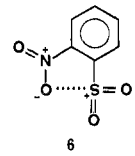


2

courses satisfactorily justify the effect of substituents on the amine portion of the sulfonamide, they fail to explain the activating effect of the *o*-nitro group on the sulfonic acid segment. The formation of the para isomer (6-sulfone, in the case of tetrahydroquinoline) rules out a single overall route to the observed products, especially one which is predicated on an intramolecular rearrangement.

More recent work[8] on amine hydrochloride catalyzed rearrangement and transamidation reactions of arylalkylsulfonamides suggests a bimolecular mechanism. A benzenesulfonylonium species, **5** or **6**, separates and can then attack either position, ortho or para to the nitrogen atom. This mechanism rationalizes the origin of the para sulfone, but fails to fully explain why ortho rearranged products generally predominate.

Recently, Sullivan and White[9] studied the rearrangement of the benzenesulfonamides of para-substituted *N*-methylanilines. In an attempted "cross-over" experiment, using radioactively labeled compounds, no mixed products were observed. These authors concluded that the rearrangment was, therefore, intramolecular. None of their compounds contained a group ortho to the sulfonyl group (such as nitro) which could possibly stabilize the sulfonylonium species **6**.



6

From our work several conclusions are evident. An *o*-nitro group causes both increased rate of rearrangement and the formation of a para isomer. Some intramolecular cyclic-intermediate mechanism (route a or b) operates in the "normal" or ortho rearrangement. However, if a stabilizing group (*e.g.*, nitro) is ortho to the sulfonyl group, lending stability to an intermediate sulfonylonium ion, then step c is the possible route. This stability originates from a dipole–dipole interaction, as in **6**, and is in apparent contradiction to the generally accepted electron-withdrawing tendencies of a nitro group. Kwart[10] has interpreted the anomalous behavior during the chlorination of *o*-nitrobenzenesulfenyl halides as due to this type of influence.

Experimental Section

Formation of 6- and 8-(*o*-Nitrobenzenesulfonyl)-1,2,3,4-tetrahydroquinoline.—A mixture of 20 g of 1-(*o*-nitrobenzenesulfonyl)-1,2,3,4-tetrahydroquinoline (0.13 mol) and concentrated sulfuric acid (40 ml) was heated on a boiling-water bath for 30 min. Complete solution occurred and the reaction mixture turned an intense red. The cooled solution was poured over cracked ice and brownish-yellow solid precipitated, which was collected, thoroughly washed, and air-dried to give 17 g of crude product. The product was mixed thoroughly with an equal volume of diatomaceous earth and continuously extracted with ether for 30 hr. The ether extract, after removal of solvent, yielded several grams of a yellow solid which was recrystallized from ethanol to give the pure 8-sulfone **2a**, mp 103–106°.

The extraction residue was then reextracted with glacial acetic acid to give a solid which, although sparingly soluble in hot glacial acetic acid, was recrystallized from this solvent. This compound was shown to be the 6-sulfone **2c**, mp 256–257°.

Anal. Calcd for $C_{15}H_{14}N_2O_4S$: C, 56.59; H, 4.43; N, 8.80; S, 10.07. Found: C, 56.88; H, 4.30; N, 8.72; S, 10.30.

Synthesis of Arylsulfonanilides. Method A.—A solution of *o*-nitrobenzenesulfonyl chloride (67 g, 0.3 mol) in 400 ml of anhydrous ether was added gradually with stirring to a cooled solution of 1,2,3,4-tetrahydroquinoline (80 g, 0.6 mol) in 120 ml of anhydrous ether. After the addition was complete, the cooling bath was removed and the mixture refluxed for 1 hr. The cooled reaction mixture was filtered and the precipitate washed with hot water to remove the amine hydrochloride. The residue was combined with the ether filtrate and the solvent stripped to give approximately 50 g of crude product. The product was dissolved in ethanol, decolorized, and recrystallized to give 43 g (47%) of **1a**, a pale yellow solid, mp 131–132°.

Method B.—A mixture of 3 g (0.04 mol) of 1,2,3,4-tetrahydroquinoline, benzenesulfonyl chloride (5 g, 0.04 mol), and 20 ml of 10% aqueous sodium hydroxide was stirred until the initial exothermic reaction subsided and then warmed to 50° for a few minutes. The supernatant liquid was decanted; the gummy mass was washed with water and triturated with a small quantity of methanol, whereupon it was converted to a white powdery solid. Crystallization from methanol gave 4 g (36%) of **1**, white crystals, mp 59–61°.

Rearrangement of Arylsulfonanilides. 8-(Phenylsulfonyl)-1,2,3,4-tetrahydroquinoline (2).—A mixture of 2 g of **3** with 6 ml of concentrated sulfuric acid gradually colored, and when complete solution occurred it was heated in a steam bath for 45 min, cooled, and poured over ice. A pale gummy solid precipitated, which was isolated, washed thoroughly with water, and recrystallized from ethanol to give pale yellow needles 1 g (50%) of **2**.

Although rearrangement of the methoxy derivative **1g** was performed at 0° for 10 min, the demethylated sulfone **1d** was formed.

Alternate Synthesis of 2a. 2-Acetylimino-5,6-dihydro-2*H*,4*H*-thiazolo[5,4,3-*ij*]quinoline (7).—The unacetylated imine was prepared by the method of Konig,[6] but, because of a paucity of confirmatory analytical information, some of the imine was converted to the acetyl derivative **7** by warming with acetic anhydride: mp 161–162°, from alcohol and then benzene. *Anal.* Calcd for $C_{12}H_{12}N_2OS$: C, 62.02; H, 5.20; N, 12.08; S, 13.80. Found: C, 62.03; H, 5.09; N, 11.83; S, 13.75.

8-(*o*-Nitrophenylthio)-1,2,3,4-tetrahydroquinoline (8).[6]—Hydrolysis of 1 g (5.25 mmol) of 5,6-dihydro-2*H*,4*H*-thiazolo-[5,4,3-*ij*]quinolin-2-one with alcoholic KOH[11] followed by immediate treatment of the reaction mixture with 0.83 g of *o*-nitrochlorobenzene gave 1.15 g of crude **8**. Repeated crystallization from acetic acid yielded reddish orange crystals, mp 154.5°. The best analytical sample gave the following results. *Anal.* Calcd for $C_{15}H_{14}N_2O_2S$: C, 62.91; H, 4.92. Found: C, 63.35; H, 5.02.

Acetyl Derivative of 8.—Acetylation of 0.8 g (2.8 mmol) of **8** with acetic anhydride yielded 0.50 g (56%) of 1-acetyl-8-(*o*-nitrophenyl)-1,2,3,4-tetrahydroquinoline (**9**), mp 134–5°. *Anal.* Calcd for $C_{17}H_{16}N_2O_3S$: C, 62.10; H, 4.87. Found: C, 62.21; H, 4.86.

Oxidation of 9.—A mixture of 0.48 g of **9** (1.55 mmol), 3 ml of acetic acid, 2 ml of 30% hydrogen peroxide, and a trace of ammonium molybdate was refluxed 2 hr and poured into water to give pale yellow needles of the acetylated sulfone **10**, mp 179.5° (ethanol). *Anal.* Calcd for $C_{17}H_{16}N_2O_5S$: C, 59.31; H, 4.65. Found: C, 59.39; H, 4.72. Hydrolysis of **10**, with 1:1 ethanolic HCl gave **2a**, as determined by mixture melting point and infrared spectra.

Registry No.—**1a**, 24223-38-9; **1b**, 28228-88-8; **1c**, 28228-89-9; **1d**, 28228-90-2; **1e**, 28228-91-3; **1f**, 794-15-0; **1g**, 28228-93-5; **1h**, 28228-94-6; **1i**, 28228-95-7; **1j**, 28228-96-8; **2**, 28228-97-9; **2a**, 28228-98-0; **2b**, 28228-99-1; **2c**, 28229-00-7; **2d**, 28229-01-8; **2e**, 28229-02-9; **2f**, 28229-03-0; **2g**, 28229-04-1; **2h**, 28312-65-4; **2i**, 28229-05-2; **7**, 28229-06-3; **8**, 28312-66-5; **9**, 28229-07-4; **10**, 28229-08-5.

(8) D. Klamann and G. Hofbauer, *Justus Liebigs Ann. Chem.*, **581**, 182 (1953).

(9) J. Sullivan and W. N. White, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, No. S83.

(10) E. N. Givens and H. Kwart, *J. Amer. Chem. Soc.*, **90**, 386 (1968).

(11) I. K. Ushenko, *Ukr. Khim. Zh.*, **21**, 744 (1955); *Chem. Abstr.*, **50**, 16753*f* (1956).

Acknowledgment.—The authors wish to acknowledge the assistance of Pamela Strong and Robert Balchunis in conducting a portion of the experimental procedure.

A Precautionary Note on the Synthesis of Thiete Sulfone[1]

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In the original description[2] of the synthesis of thiete sulfone (thiete 1,1-dioxide), the procedure for the preparation of 3-thietanol 1,1-dioxide called for evaporation to dryness of the solution remaining after oxidation of the sulfide to the sulfone.[3] Since several researchers have reported to us that explosions had occurred during this step, we wish to emphasize that the evaporation must be done in an evaporating dish open to the atmosphere and that under no circumstances must the peroxide-containing solution be concentrated in a closed system. Therefore, the following procedure should be followed for the synthesis of 3-hydroxythietane 1,1-dioxide.

(1) The work on small ring sulfur chemistry has been supported by the National Science Foundation, and the synthesis reported in this note was developed with aid from Grant GP-726.

(2) D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961).

(3) A synthesis of thiete sulfone which does not involve an oxidation step has been reported recently: P. Chang and D. C. Dittmer, *ibid.*, **34**, 2791 (1969).

Experimental Section

3-Hydroxythietane 1,1-Dioxide.—3-Hydroxythietane (45 g, 0.50 mol) is mixed with 105 ml of glacial acetic acid in a 500-ml three-necked flask fitted with an addition funnel, thermometer, condenser, and a magnetic stirring bar. The flask is cooled in an ice bath, and, with stirring, hydrogen peroxide (116 g, 30%) is added dropwise, the reaction temperature not being allowed to rise above 20°.[4] After the addition of hydrogen peroxide the reaction mixture is kept in the ice bath for 1 hr, the stirring is stopped, and the mixture is allowed to stand at room temperature overnight.[5] It is diluted with 800 ml of distilled water in a 9- to 10-in. evaporating dish, and water and acetic acid are evaporated on a steam bath.[6] The colorless oil is cooled to a white, crystalline mass which is crushed in the evaporating dish and air-dried. The nearly dry solid is recrystallized from 100 ml of ethyl acetate.[7] After two recrystallizations from ethyl acetate, 38–40 g (62.3–65.6%) of 3-hydroxythietane 1,1-dioxide, mp 100°, is obtained.

Registry No.—3-Hydroxythietane 1,1-dioxide, 22524-35-2.

(4) Considerable heat is evolved during the first half of the addition of hydrogen peroxide and the addition must be slow. The reaction becomes more moderate and the last half of the peroxide may be added more rapidly.

(5) The flask is kept in a bath of tap water. A precipitate may appear at this point.

(6) This evaporation is crucial. Evaporation must be stopped at the first indication of a yellow color seen around the edge of the liquid in the dish. Yields are much lower if the heating is prolonged beyond this stage. *Do not evaporate in a closed system. Explosions have occurred when this was done.* The final volume of oily product and the slight amount of trapped solvent is usually about 100 ml.

(7) A fluffy, insoluble material is removed by filtration.