

yield 582 g. (69%), m.p. 189–191°. The toluene-ether filtrate was dried over calcium sulfate and then concentrated to dryness *in vacuo*. The residue was taken up in a minimum amount of ether. An ether-insoluble red crystalline material was filtered off. It did not melt at 360°. This is postulated to be a compound of the periflanthene type. The ether solution was evaporated to dryness and the residue recrystallized from ethyl alcohol. This unreacted, starting material weighed 62 g., m.p. 73–75°. There was no melting point depression with 1,2,3,10b-tetrahydrofluoranthene. The recovered material was reused in subsequent preparations.

**Via Lithium.**—Lithium ribbon (Metalloy Corp.), 3.0 g. (0.45 mole), was degreased and weighed under ether, cut into one cm. lengths and added in a stream of nitrogen to 150 ml. of absolute ether (dried over sodium) in a 500-ml. flask. The contents of the bath were chilled to  $-10^{\circ}$  and a solution of 15.3 g. (0.17 mole) of butyl chloride in 50 ml. of ether was added dropwise. The butyl chloride was added over a 30-minute period at  $-10^{\circ}$ . After the addition was complete 29.2 g. (0.14 mole) of 1,2,3,10b-tetrahydrofluoranthene was added in small portions. The reaction was mildly exothermic and there was an immediate evolution of butane. After refluxing for one hour, the reaction mixture was poured over powdered Dry Ice. The solution was then diluted with 200 ml. of water and extracted twice with ether to remove unreacted starting materials. The aqueous layer was acidified with 30% hydrochloric acid to precipitate the acid. The acid was filtered off and recrystallized with ethyl alcohol, 25.5 g. (72% yield).

**$\beta$ -Diethylaminoethyl 1,2,3,10b-Tetrahydrofluoranthene-10b-carboxylate.**—A solution of 12 g. (0.05 mole) of 1,2,3,10b-tetrahydrofluoranthene-10b-carboxylic acid in 90 ml. of anhydrous isopropyl alcohol was set to reflux. To this was added cautiously 6.5 g. (0.05 mole) of  $\beta$ -diethylaminoethyl chloride and the reaction mixture was refluxed for three hours. The ester hydrochloride which crystallized out on cooling the reaction mixture was filtered off and washed

with isopropyl alcohol. It was obtained in 81% yield, m.p. 209.5–211°. A sample recrystallized from ethyl alcohol melted at 227–227.5°.

The other ester hydrochlorides excepting compound no. 11 were prepared in a like manner.

**$\gamma$ -Diethylaminopropyl 1,2,3,10b-Tetrahydrofluoranthene-10b-carboxylate.**—A mixture of 26.3 g. (0.2 mole) of  $\gamma$ -diethylaminopropanol and 0.13 g. (0.005 mole) of sodium was heated in a dry flask for one hour. To the resulting solution 27.8 g. (0.1 mole) of ethyl 1,2,4,10b-tetrahydrofluoranthene-10b-carboxylate was added and the solution then refluxed for two hours at 160–170°. During this time the ethyl alcohol which was formed was collected through a short fractionating column. The residual solution was then distilled under 1 mm. pressure to remove excess  $\gamma$ -diethylaminopropanol. The residue was taken up in dry ether and acidified with 20% alcoholic hydrochloric acid using congo red as an indicator. The ester hydrochloride precipitated immediately. It was recrystallized from absolute ethanol; yield 6.6 g., m.p. 209–211°.

**Methobromide of  $\beta$ -Diethylaminoethyl 1,2,3,10b-Tetrahydrofluoranthene-10b-carboxylate.**—The ester hydrochloride was used without recrystallization. A mixture of 7.0 g. of the ester hydrochloride and 100 ml. of 5% sodium hydroxide was extracted with several portions of ether. The ether extract was dried over sodium sulfate and then the ether was removed *in vacuo*. The residual oil was taken up in 100 ml. of absolute ethyl alcohol and set to reflux under a Dry Ice condenser. Methyl bromide was led into the refluxing solution for 1.5 hours. The reaction mixture was then concentrated *in vacuo* and dry ether added. The precipitated, hygroscopic methobromide was removed by filtration, recrystallized from an alcohol-ether mixture and dried in an Abderhalden pistol at 100°. The dried material weighed 4 g. (50% yield), m.p. 157–159°.

The other methobromides were synthesized in a similar manner.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

## Action of Grignard Reagents. VI. (a) Cleavage by Organomagnesium and Lithium Compounds and by Lithium Aluminum Hydride; (b) Action of Phenyllithium on Phenanthraquinone and Benzil Monoximes

BY AHMED MUSTAFA, WAFIA ASKER, ORKEDE H. HISHMAT, AHMED F. A. SHALABY AND MOHAMED KAMEL

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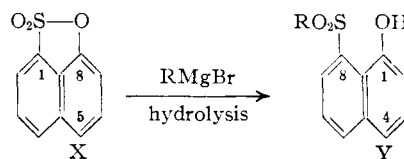
Treatment with Grignard reagents, followed by hydrolysis, caused opening of the hetero ring in substituted 1,8-naphthosultones to give the corresponding derivatives of 8-arylsulfonyl-1-naphthol. Phenylmagnesium bromide also brought about cleavage of the N-S bond in N-arylsulfonyl derivatives, *e.g.*, N-diphenylsulfonylaniline, and cleavage of the N-C bond in N-aroil derivatives, *e.g.*, N-dibenzoylaniline to give benzanilide and triphenylcarbinol. Similar results were obtained with phenyllithium. Hydrogenolysis with lithium aluminum hydride caused opening of the hetero ring of 1,8-naphthosultone and its substituted derivatives and of N-phenylsulfonylnaphthosultam to give the corresponding disulfides.

**Organomagnesium Compounds.**—Mustafa<sup>1</sup> has shown that Grignard reagents act upon 1,8-naphthosultone (I) and its substitution products to open the sultone ring, *i.e.*, to break the S-O linkage, with the formation of the corresponding 8-arylsulfonyl-1-naphthols (II); further investigation of this reaction has led to the synthesis of a number of new compounds as (I and II).

The constitution of the products was deduced from the fact that they are colorless, dissolve in aqueous alkali, contain active hydrogen and give a color reaction with ferric chloride; IIb and b' form the corresponding methyl ethers with ethereal diazomethane.<sup>2</sup>

(1) (a) A. Mustafa, *J. Chem. Soc.*, 2151 (1949); (b) A. Mustafa and M. K. Hilmy, *ibid.*, 1339 (1952); (c) A. Mustafa, *Chem. Revs.*, **54**, 195 (1954).

(2) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 605 (1948).

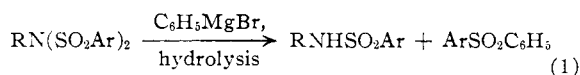


- |                             |  |
|-----------------------------|--|
| I, X = H                    | II, Y = H, R = C <sub>6</sub> H <sub>5</sub>   |
| Ia, X = Br                  | IIa, Y = Br, R = C <sub>6</sub> H <sub>5</sub>   |
| Ib, X = -CH <sub>2</sub> Br | IIa', Y = Br, R = $\alpha$ -C <sub>10</sub> H <sub>7</sub>   |
| Ic, X = -CH <sub>2</sub> Cl | IIb, Y = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> , R = C <sub>6</sub> H <sub>5</sub>                         |
| Id, X = CH <sub>3</sub>     | IIb', Y = CH <sub>2</sub> C <sub>10</sub> H <sub>7</sub> - $\alpha$ , R = $\alpha$ -C <sub>10</sub> H <sub>7</sub> |

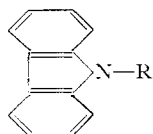
We have likewise found cleavage of the N-S linkage in N-diarylsulfonyl derivatives (IIIa-b) by Grignard reagents. N-Diphenylsulfonylaniline (IIIa) and N-di-(*p*-toluenesulfonyl)- $\alpha$ -naphthalamine (IIIb), treated with excess phenylmagnesium bromide, yield benzenesulfonamide and diphenyl sulfone in the case of IIIa, and *p*-toluenesulfonamide

naphthalide and *p*-tolylphenyl sulfone in the case of IIIb; *cf.* eq. 1.

Similarly, carbazole and *p*-tolylphenyl sulfone are obtained when *N*-*p*-toluenesulfonylcarbazole (IVa)<sup>3</sup> is treated with phenylmagnesium bromide.



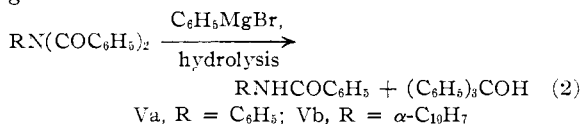
IIIa, R = Ar = C<sub>6</sub>H<sub>5</sub>; IIIb, R =  $\alpha$ -C<sub>10</sub>H<sub>7</sub>, Ar = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*p*



IVa, R = SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*p*  
IVb, R = COC<sub>6</sub>H<sub>5</sub>

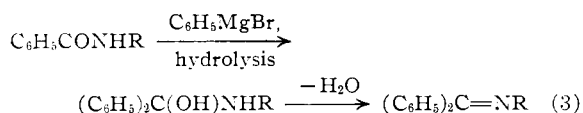
That this cleavage is due to the organomagnesium halide and not to the magnesium halide,<sup>4</sup> present in the equilibrium  $2\text{RMgX} \rightleftharpoons \text{MgR}_2 + \text{MgX}_2$ , is demonstrated by the almost complete recovery of IIIa, IVa and VIa (R = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*p*)<sup>5</sup> which have been treated with magnesium iodide under the same experimental conditions.

When *N*-dibenzoylaniline (Va) and *N*-dibenzoyl- $\alpha$ -naphthylamine (Vb) are treated with excess phenylmagnesium bromide in benzene, they undergo *N*-C bond cleavage, yielding benzanilide and benz- $\alpha$ -naphthalide together with triphenylcarbinol (eq. 2), respectively. Our failure to isolate the corresponding ketone anil as in eq. 3 may be attributed to the insolubility of (RNMgBrCOC<sub>6</sub>H<sub>5</sub>) which prevents further reaction with the Grignard reagent.



*N*-Benzoylcarbazole (IVb) behaves similarly toward phenylmagnesium bromide, forming carbazole and triphenylcarbinol.

Although benzenesulfonanilide is stable toward phenylmagnesium bromide, benzanilide reacts with this reagent to give benzophenone anil<sup>6</sup> (eq. 3) and benz- $\alpha$ -naphthalide reacts to give benzophenone- $\alpha$ -naphthylimide; the reaction was not successful with acetanilide.<sup>6</sup>



**Organolithium Compounds.**—Little seems to be known about the cleavage action of organolithium compounds.<sup>7</sup> We have found in the following examples that phenyllithium, like the organomag-

(3) *Cf.* the stability of *p*-toluenesulfonyldiphenylamine toward phenylmagnesium bromide (H. Gilman and C. C. Vernon, *Rec. trav. chim.*, **48**, 745 (1929)).

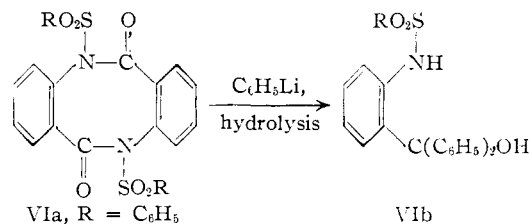
(4) A. Schönberg and R. Moubasher, *J. Chem. Soc.*, 462 (1944).

(5) For the cleavage action of organomagnesium halide on VIa (R = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*p*), see A. Mustafa and A. M. Gad, *ibid.*, 384 (1949).

(6) For the formation of ketone anils by the action of certain Grignard reagents, *e.g.*, ethylmagnesium bromide on butyranilide to give ethylpropyl ketone anil, see M. Montagne and G. Rousseau, *Compt. rend.*, **196**, 1165 (1933).

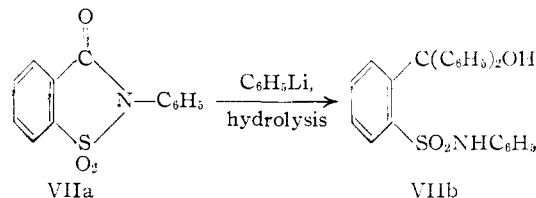
(7) *Cf.* ring cleavage in tetramethyl-1,3-cyclobutanedione (J. L. E. Erickson and G. C. Kitchens, *THIS JOURNAL*, **68**, 492 (1946)) and 4,4',5,5'-tetraphenyltrimethylene-1,3-disulfide by phenyllithium (A. Schönberg, H. Kaltschmitt and H. Schulten, *Ber.*, **66**, 245 (1933)).

nesium compounds, could effect the opening of hetero rings



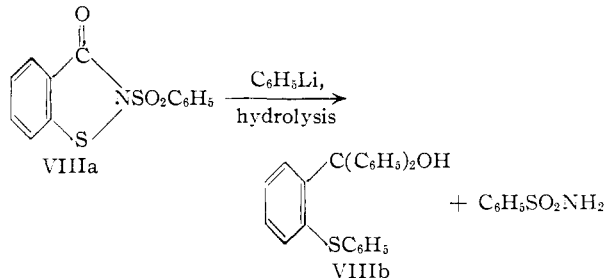
VIa, R = C<sub>6</sub>H<sub>5</sub>

VIb



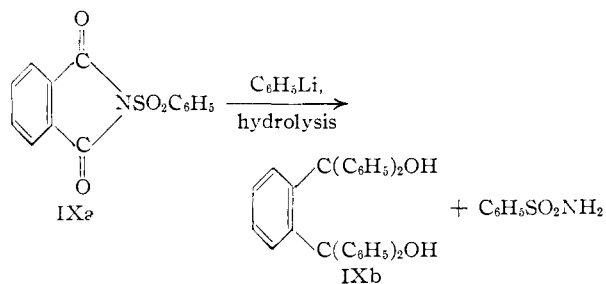
VIIa

VIIb



VIIIa

VIIIb

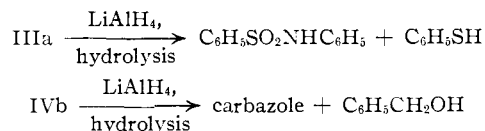


IXa

IXb

1,8-Naphthosultone (I) reacted with phenyllithium to give 8-phenylsulfonyl-1-naphthol. Likewise, treatment of *N*-arylsulfonyl derivatives (IIIa,b and IVa) and of *N*-aroyl derivatives (Va,b and IVb) gave results which are similar to those obtained with phenylmagnesium bromide.

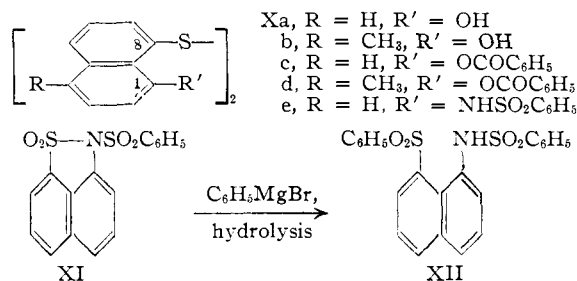
**Lithium Aluminum Hydride.**—The action of lithium aluminum hydride on organic compounds<sup>8</sup> has been shown to be analogous to that of Grignard reagents. We have found that hydrogenolysis with the hydride, like treatment with phenylmagnesium bromide followed by hydrolysis, brings about cleavage of the *N*-S bond of IIIa and of the *N*-C bond of IVb and Va; compare equations 1 and 2. The hydrogenolysis, under the influence of the hydride, of



(8) For a comparison of the action of lithium aluminum hydride and of Grignard reagents on VIa (R = C<sub>6</sub>H<sub>5</sub>) and on the photo-oxides of 9,10-diarylanthracene, see A. Mustafa, *J. Chem. Soc.*, 2435 (1952), and for the action on oxazolidines see E. D. Bergmann, D. Lavie and S. Pinchas, *THIS JOURNAL*, **73**, 5662 (1951).

the acyl or aroyl group attached to a nitrogen compound has been reported in the reduction of N-acetylcarbazole,<sup>9</sup> acylated 2-benzylaminothiazole,<sup>10</sup> 1-benzoylbenzotriazole<sup>11</sup> and dibenzoyl-L-histidine.<sup>12</sup> Lithium aluminum hydride, in the same manner as the Grignard reagents, caused opening of the sultone ring<sup>13</sup> of I and its derivatives; this is a new method of preparing the disulfides of *peri*-hydroxythionaphthol. Thus, treatment of I with the hydride, followed by hydrolysis, yielded 1,1'-dihydroxy-8,8'-dinaphthyl disulfide (Xa). The 5-bromomethyl (Ib), 5-chloromethyl (Ic) and 5-methyl (Id) derivatives yielded 4,4'-dimethyl-1,1'-dihydroxy-8,8'-dinaphthyl disulfide (Xb) in each case; the CH<sub>2</sub>X group of Ib and Ic also reacted with the hydride.<sup>14</sup>

The hydrogenolysis of N-phenylsulfonylnaphthosultam (XI) with the hydride effects the opening of the sultam ring, yielding 1,1'-di-(phenylsulfonylamino)-8,8'-dinaphthyl disulfide (Xe). The opening of the sultam ring of XI was brought about by phenylmagnesium bromide,<sup>15</sup> yielding 8-phenylsulfonyl-1-phenylsulfonylnaphthylamine (XII).



The isolation of disulfides Xa, Xb and Xe and not of the corresponding mercaptans may be attributed to the ready oxidation of the latter during the working up of the reaction products. In the case of I, extraction of the reaction product with petroleum ether, after decomposition with aqueous ammonium chloride solution, gives a pale yellow crystalline substance which analyzes for 1-hydroxy-8-thionaphthol; on standing for a few hours it is oxidized to Xa.<sup>16</sup>

The structure of Xa and Xb was deduced from the following: (a) they dissolve in aqueous sodium hydroxide, (b) give a color reaction with ferric

(9) K. Banholzer, T. W. Campbell and H. Schmid, *Helv. Chim. Acta*, **35**, 1577 (1952).

(10) I. A. Kaye and C. L. Parris, *J. Org. Chem.*, **17**, 737 (1952).

(11) N. G. Gaylord, *THIS JOURNAL*, **76**, 285 (1954).

(12) P. Karrer, M. Suter and P. Wasser, *Helv. Chim. Acta*, **32**, 1936 (1949).

(13) Little is known regarding the cleavage of heterocyclic ring systems with the hydride. The tetrahydrofuran ring (L. H. Briggs and R. H. Locker, *J. Chem. Soc.*, 3020 (1950)), the oxazolidine ring (ref. 8) and cyclic lactams (F. Galinovsky and R. Weisser, *Experientia*, **6**, 377 (1950)) are cleaved, but not hydantoin (I. J. Wilk and W. J. Close, *J. Org. Chem.*, **15**, 1020 (1950)), the thiazole ring (H. L. Conover and D. S. Tarbell, *THIS JOURNAL*, **72**, 522 (1950)), the tetrahydroquinoline ring (A. Stoll, T. Petrzilka and J. Rutschmann, *Helv. Chim. Acta*, **33**, 2254 (1950)) or 1,3-thioxolane systems (ref. 8).

(14) Cf. the action of phenylmagnesium bromide on Ic (A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1339 (1952)) and the action of lithium aluminum hydride on benzyl chloride, yielding toluene (J. E. Johnson, R. H. Blizard and H. W. Carhart, *THIS JOURNAL*, **70**, 3664 (1948)).

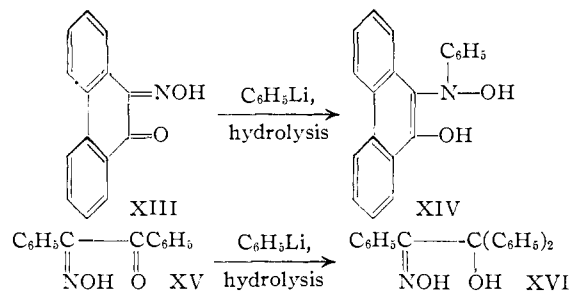
(15) A. Mustafa and O. H. Hishmat, *ibid.*, **75**, 4647 (1953).

(16) Cf. the ready oxidation of 1-carbethoxynaphthol-4-mercaptan to the corresponding disulfide by atmospheric oxygen (T. Zinke and J. Ruppertsberg, *Ber.*, **48**, 120 (1915)).

chloride in alcohol, (c) form dibenzoyl derivatives (Xc-d) when their alkaline solutions are treated with benzoyl chloride and (d) contain active hydrogen.

**Action of Phenyllithium on Phenanthraquinone and Benzil Monoximes.**—Lithium organo compounds react with  $\alpha,\beta$ -unsaturated ketones almost invariably to give high yields of carbinols (1,2-addition), while the corresponding Grignard reagents give high yields of saturated ketones (1,4-addition).<sup>17</sup> However, Tucker and Whalley<sup>18</sup> have found that 9-fluorenyllithium does not react with the highly reactive carbonyl group of mesityl oxide, but gives a good yield of the saturated ketone by 1,4-addition. Gilman and Gainer<sup>19</sup> have found that phenyllithium reacts with benzalquinaldine to give an excellent yield of  $\alpha$ -benzylquinaldine, the product obtained with phenylmagnesium bromide<sup>20</sup>; its formation is probably due to 1,4-addition.

We have found that phenanthraquinone monoxime (XIII) and  $\alpha$ -benzilmonoxime (XV) react with phenyllithium to give the same products as with phenylmagnesium bromide; XIII gives 10-phenylhydroxylamino-9-hydroxyphenanthrene<sup>21</sup> (XIV), and XV gives 1,1,2-triphenyl-1-oximino-2-ethanol (XVI)<sup>22</sup> in an almost quantitative yield.



### Experimental

**Action of Grignard Reagent on Substituted 1,8-Naphthosultones (Eq. 1).**—The following exemplifies the procedure. To a Grignard solution (prepared from 0.9 g. of magnesium and 9 g. of bromobenzene in 50 ml. of dry ether) was added a solution of 1 g. of Ia in dry benzene (50 ml.). After evaporation of the ether, the mixture was heated for three hours on a steam-bath. After standing overnight at 25°, it was poured slowly into 100 ml. of saturated aqueous ammonium chloride solution and the reaction was dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and evaporated. The oily residue was washed several times with hot light petroleum<sup>23</sup> (ca. 50 ml.) and the resulting solid crystallized from benzene and identified as IIa.

The substituted 8-arylsulfonyl-1-naphthols listed in Table I were prepared similarly. They dissolve in aqueous sodium hydroxide solution giving a yellow color; on acidification they are regenerated. In general, they are soluble in hot benzene and chloroform, but are sparingly soluble in light petroleum.

(17) H. Gilman and R. H. Kirby, *THIS JOURNAL*, **63**, 2046 (1941); A. Luttringhaus, *Ber.*, **67**, 1602 (1934); A. Luttringhaus and K. Scholtis, *Ann.*, **557**, 70 (1945).

(18) S. H. Tucker and M. Whalley, *J. Chem. Soc.*, 50 (1949).

(19) H. Gilman and G. C. Gainer, *THIS JOURNAL*, **71**, 2327 (1949).

(20) A. H. Hoffman, M. W. Farlow and R. C. Fuson, *ibid.*, **55**, 2000 (1933).

(21) A. Mustafa and M. Kamel, *ibid.*, **76**, 124 (1954).

(22) See A. Oryekhov and M. Tiffeneau, *Bull. soc. chim.*, **41**, 839 (1927), for the action of phenylmagnesium bromide on  $\beta$ -benzil monoxime.

(23) Light petroleum is the fraction boiling at 40–60° and petroleum ether at 80–100°; the boiling range of other fractions is specified.

TABLE I

## 4-SUBSTITUTED 8-BENZENESULFONYL-1-NAPHTHOLS (II)

Substd. g.	Substd. 8-benzenesulfonyl-1-naphthol, g.	M.p., °C.	Yield g.	Color with H <sub>2</sub> SO <sub>4</sub>	Color with FeCl <sub>3</sub> in alcohol	Formula	Carbon, %		Hydrogen, %		Sulfur, %		Bromine, %		Active H	
							Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Ia <sup>a</sup> 1.0	IIf <sup>a</sup>	162	0.73	Brown	Viol.	C <sub>18</sub> H <sub>11</sub> O <sub>3</sub> SBr <sup>b</sup>	52.9	52.7	3.0	2.9	8.8	8.6	22.0	21.9	0.28	0.26
Ia 1.5	IIf <sup>c</sup>	195	0.9	Green	Red-br.	C <sub>20</sub> H <sub>13</sub> O <sub>3</sub> SBr	58.1	57.8	3.1	3.0	7.7	7.6	19.4	19.2	.24	.23
Ib <sup>b</sup> 2.0	IIf <sup>d</sup>	169	1.1	Purple	Red	C <sub>23</sub> H <sub>13</sub> O <sub>3</sub> S	73.8	73.6	4.8	4.7	8.5	8.5	..	..	.26	.25
Ib 2.0	IIf <sup>e</sup>	232	1.2	Blue-green	Red	C <sub>21</sub> H <sub>22</sub> O <sub>3</sub> S <sup>f</sup>	78.5	78.4	4.6	4.4	6.8	6.5	..	..	..	..

<sup>a</sup> G. Heller, W. Eisenschmidt, G. Reichardt and H. Wild, *Z. angew. Chem.*, **41**, 171 (1928). <sup>b</sup> G. Schetty, *Helv. Chim. Acta*, **31**, 1229 (1948). <sup>c</sup> Crystallized from benzene-light petroleum (b.p. 40–60°). <sup>d</sup> Identified by m.p. and mixed m.p. with authentic specimen; see ref. Ib. <sup>e</sup> Mol. wt.: calcd. 363, found 357. <sup>f</sup> Mol. wt.: calcd. 474, found 460.

Ib and IIf' (1 g.) in 40 ml. of ether were methylated by reaction of ethereal diazomethane solution (prepared from 10 g. of nitrosomethylurea). After standing for 24 hours at 0°, the reaction mixture was washed with cold aqueous sodium hydroxide solution (8%, ca. 40 ml.) to remove unchanged Ib and IIf', and then with water, dried, evaporated and the solid residue crystallized from benzene. Identification was made by melting point and mixed melting point determinations with an authentic specimen.<sup>1b</sup> The methyl ethers are easily soluble in hot benzene, difficultly soluble in light petroleum (b.p. 60–80°) and insoluble in aqueous sodium hydroxide solution; they give no color with ferric chloride in alcohol.

The methyl ether of IIf melts at 199°, yields about 78%. *Anal.* Calcd. for C<sub>21</sub>H<sub>20</sub>O<sub>3</sub>S: C, 74.2; H, 5.1; S, 8.0; OCH<sub>3</sub>, 8.0. Found: C, 74.2; H, 5.1; S, 8.0; OCH<sub>3</sub>, 7.8.

The methyl ether of IIf' melts at 244°, yields about 71%. *Anal.* Calcd. for C<sub>22</sub>H<sub>24</sub>O<sub>3</sub>S: C, 78.7; H, 4.9; S, 6.5. Found: C, 78.5; H, 4.8; S, 6.3.

**Action of Phenylmagnesium Bromide on: (A) Arylsulfonyl Derivatives.** *N*-Diphenylsulfonylaniline (IIIa).—A mixture of IIIa<sup>24,25</sup> and the Grignard reagent was worked up as described above. The oily residue was washed with light petroleum and then extracted with hot petroleum ether. The insoluble material, dissolved in benzene and treated with light petroleum (b.p. 50–60°), yielded colorless crystals (0.19 g., m.p. 124°) which were identified as diphenyl sulfone (m.p. and mixed m.p.). The petroleum ether extract gave, on concentration and cooling, 0.41 g. of benzene-sulfonanilide (m.p. and mixed m.p.).

On slow evaporation, the light petroleum washings gave biphenyl, yield 0.13 g., identified by m.p. and mixed m.p.

*N*-Di-(*p*-toluenesulfonyl)-*α*-naphthylamine (IIIb).—The above procedure applied to IIIb<sup>26</sup> yielded *p*-toluenesulfon-*α*-naphthalide (0.42 g.) and *p*-tolylphenyl sulfone (0.23 g.) which were identified by melting point and mixed melting point determinations. In a blank experiment, IIIb was recovered essentially unchanged from a solution of IIIb in benzene shaken for three hours with saturated aqueous ammonium chloride solution at room temperature.

*N*-*p*-Toluenesulfonylcarbazole (IVa).—Similarly, phenylmagnesium bromide and IVa<sup>27</sup> gave a solid residue, which, on washing several times with hot petroleum ether (b.p. 60–80°) and crystallization from ethyl alcohol, yielded colorless crystals, yield 0.51 g., m.p. 240°; they were identified as carbazole (m.p. and mixed m.p.). The concentrated petroleum ether washings gave colorless crystals (0.1 g.) of *p*-tolylphenyl sulfone.

**(B) Aroyl Derivatives.** *N*-Dibenzoylaniline (Va).—A mixture of phenylmagnesium bromide and Va<sup>24</sup> was refluxed for five hours and kept overnight at room temperature, during which the color changed from red to olive-green and finally to brown. It was decomposed with dilute hydrochloric acid and extracted with ether; the insoluble part was filtered, washed with water and crystallized from alcohol to give colorless crystals (yield 0.6 g., m.p. 162°) which were identified as benzanilide (m.p. and mixed m.p.).

The ether-benzene solution was washed with cold aqueous sodium hydroxide (8%, ca. 45 ml.), dried and evapo-

rated. The solid residue was crystallized from benzene-light petroleum to give colorless crystals (yield 0.27 g., m.p. 163°) which were identified as triphenylcarbinol (m.p. and mixed m.p.).

*N*-Dibenzoyl-*α*-naphthylamine (Vb).—Similarly, phenylmagnesium bromide and Vb<sup>28</sup> gave 0.53 g. of benz-*α*-naphthalide and 0.23 g. of triphenylcarbinol.

*N*-Benzoylcarbazole (IVb).—By the same procedure IVb<sup>29</sup> yielded 0.41 g. of carbazole and 0.27 g. of triphenylcarbinol. They were separated by extraction of the carbinol with hot petroleum ether (b.p. 60–80°), from the solid residue obtained by evaporation of the ether-benzene mixture.

**Benzanilide.**—A mixture of benzanilide (2 g. dissolved in 75 ml. of benzene) and phenylmagnesium bromide was refluxed for eight hours and decomposed with dilute hydrochloric acid; 0.38 g. of benzanilide was recovered from the precipitate. The ether-benzene mixture, on concentration and cooling, gave yellow crystals (0.61 g.) of benzophenone anil (m.p. and mixed m.p.).

*Anal.* Calcd. for C<sub>19</sub>H<sub>15</sub>N: C, 88.7; H, 5.8; N, 5.4. Found: C, 88.7; H, 5.7; N, 5.3.

**Benz-*α*-naphthalide.**—About 0.7 g. of starting material was recovered from a mixture of benz-*α*-naphthalide and phenylmagnesium bromide treated as described above. On slow evaporation the ether-benzene solution gave a solid residue which was crystallized from ethyl alcohol to yield yellow crystals of benzophenone-*α*-naphthylimide<sup>30</sup>; yield 0.33 g., m.p. 136° (m.p. and mixed m.p.).

*Anal.* Calcd. for C<sub>23</sub>H<sub>17</sub>N: C, 89.9; H, 5.5; N, 4.6. Found: C, 89.3; H, 5.6; N, 4.6.

**Action of Magnesium Iodide on: (VIa, R = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*p*), IIIa and IVa.**—To a filtered solution of magnesium iodide (prepared from 1 g. of magnesium powder, 4 g. of iodine in 20 ml. of dry ether and 20 ml. of dry benzene) was added VIa (R = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*p*),<sup>31</sup> IIIa or IVa. The reaction mixture was refluxed for three hours, kept overnight at room temperature and then decomposed with ice in saturated ammonium chloride solution. In each case the starting substance was recovered essentially unchanged from the concentrated ether-benzene solution.

**Action of Phenyllithium on: (a) *N,N'*-Dibenzoyl-*α*-naphthylidene (VIa).**—The following exemplifies the procedure: A cold clear solution of phenyllithium (prepared from 16 g. of bromobenzene, 1.5 g. of lithium and 100 ml. of dry ether) was added to a solution of 2 g. of VIa<sup>32</sup> in 50 ml. of dry benzene. The reaction mixture was kept overnight at room temperature in a nitrogen atmosphere under a positive pressure of 7 mm. The substance dissolved completely and the color of the solution changed from yellow to orange-red and finally to reddish-brown. The reaction mixture was poured slowly into 100 ml. of saturated aqueous ammonium chloride solution, extracted with ether, dried and evaporated. The oily residue was washed several times with cold light petroleum and crystallized from benzene-light petroleum to give colorless crystals of VIb (R = C<sub>6</sub>H<sub>5</sub>)<sup>32</sup>; yield 1.7 g., m.p. 188°, identification by m.p., mixed m.p., and color reaction with sulfuric acid.

*Anal.* Calcd. for C<sub>25</sub>H<sub>21</sub>O<sub>3</sub>NS: C, 72.3; H, 5.1; N, 3.4; S, 7.7; active H, 0.24; mol. wt., 415. Found: C, 72.2; H, 4.9; N, 3.3; S, 7.6; active H, 0.23; mol. wt., 402.

(24) P. Freundler, *Bull. soc. chim.*, [3] **31**, 630 (1903).

(25) One g. of starting material was used unless otherwise noted.

(26) H. H. Hodgson and J. Walker, *J. Chem. Soc.*, 180 (1934) obtained IIfb in 2–3% yield. We prepared it in 78% yield by the interaction of *p*-toluenesulfonyl chloride and *p*-toluenesulfon-*α*-naphthalide in pyridine for two hours on a steam-bath.

(27) T. S. Stevens and S. H. Tucker, *ibid.*, 2147 (1923).

(28) H. H. Hodgson and J. H. Crook, *ibid.*, 1846 (1936).

(29) G. Massara, *Ber.*, **24**, 279 (1891).

(30) G. Reddellien, *ibid.*, **46**, 2721 (1913).

(31) R. Anschütz and L. Hoderius, *Ann.*, **415**, 76 (1918).

(32) G. Heller, *Ber.*, **49**, 547 (1916).

TABLE II

Compound	M.P., °C.	Solubility	Color with H <sub>2</sub> SO <sub>4</sub>	Formula	Carbon, %		Hydrogen, %		Sulfur, %		Active H		Mol. wt.	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1-Hydroxy-8-thionaphthol <sup>a</sup> Xa <sup>a</sup>	58 <sup>b</sup> 168-169 <sup>b</sup>	Sol. org. solvents, NaOH Sol. hot benzene, NaOH; dif. sol. pet. ether	— Brown	C <sub>10</sub> H <sub>8</sub> O <sub>2</sub> S	68.2 68.5	67.1 68.4	4.5 4.0	4.5 3.8	18.2 18.3	18.1 18.1	1.2 <sup>f</sup> 0.57	1.1 0.53	174 152	152
Xb <sup>a</sup>	128 <sup>b</sup>	Sol. hot, benzene, NaOH <sup>e</sup> Sol. hot benzene; dif. sol. al- cohol; insol. NaOH	Olive-gr. Yell.-green changing to brown	C <sub>22</sub> H <sub>18</sub> O <sub>2</sub> S <sub>2</sub>	69.8 73.1	69.7 72.8	4.7 3.9	4.7 3.8	16.9 11.5	16.5 11.2	0.52 ..	0.49 ..	..	..
Xc	189-190	Sol. hot benzene, xylene Sol. hot benzene, chloroform; dif. sol. ether, alcohol	Ill-defined Yell. changing to olive-gr. <sup>d</sup>	C <sub>34</sub> H <sub>22</sub> O <sub>4</sub> S <sub>2</sub>	73.7 61.2	73.5 60.8	4.4 3.8	4.3 3.6	10.9 20.4	10.7 20.3	..	..	586 545	..

<sup>a</sup> Alcoholic solution gives blue-green color with alcoholic ferric chloride. <sup>b</sup> Orange-melt. <sup>c</sup> Compound regenerated on acidification. <sup>d</sup> Red-brown color when a crystal of potassium nitrate is added. <sup>e</sup> Calcd.: N, 4.5. Found: N, 4.3. <sup>f</sup> Two atoms.

(b) 2-Phenyl-1,2-benzisothiazole-3-one-1,1-dioxide<sup>c</sup> (VIIa).—Dry benzene (30 ml.) was added to a mixture of VIIa<sup>33</sup> and phenyllithium (prepared from 1.1 g. of lithium, 12 g. of bromobenzene and 80 ml. of ether). The reaction mixture was decomposed with dilute hydrochloric acid. The oily residue, obtained by evaporation of the ether-benzene mixture, was washed several times with light petroleum and crystallized from benzene as colorless crystals (0.58 g., m.p. 205°) which were identified by m.p., mixed m.p. and color reaction with sulfuric acid.

*Anal.* Calcd. for C<sub>26</sub>H<sub>21</sub>O<sub>3</sub>NS: C, 72.3; H, 5.1; N, 3.4; S, 7.7; active H, 0.48; mol. wt., 415. Found: C, 72.4; H, 4.9; N, 3.3; S, 7.5; active H, 0.44; mol. wt., 410.

(c) 2-Phenylsulfonyl-1,2-benzisothiazol-3-one (VIIIa).—A solution of VIIIa<sup>34</sup> in 30 ml. of benzene was treated with an ethereal solution of phenyllithium (prepared as above). The ether-benzene solution of the organic matter was extracted with cold aqueous sodium hydroxide solution (8%, ca. 27 ml.), washed with water, dried and evaporated. The oily residue was washed twice with cold light petroleum (b.p. below 40°, 60 ml.) and crystallized from petroleum ether as colorless crystals (0.41 g., m.p. 140°) which were identified as VIIIb<sup>35</sup> (m.p. and mixed m.p.).

*Anal.* Calcd. for C<sub>26</sub>H<sub>20</sub>O<sub>2</sub>S: C, 81.5; H, 5.4; S, 8.7; active H, 0.27; mol. wt., 368. Found: C, 81.4; H, 5.4; S, 8.6; active H, 0.26; mol. wt., 345.

The alkaline extract was acidified with dilute hydrochloric acid, extracted with ether, dried and evaporated; the solid residue (0.29 g.) was crystallized from benzene and identified as benzenesulfonamide.

(d) N-Benzenesulfonylphthalimide (IXa).—A solution of 2 g. of IXa<sup>36</sup> in 50 ml. of benzene was treated with phenyllithium as described for VIa (R = C<sub>6</sub>H<sub>5</sub>). The ethereal layer was extracted with cold aqueous sodium hydroxide solution, washed with water, dried and evaporated. The oily residue, which solidified after washing with cold light petroleum (b.p. below 40°), was crystallized from petroleum ether. Colorless crystals were obtained which were identified as IXb<sup>36</sup> (m.p. and mixed m.p.); yield 1.1 g., m.p. 201°.

*Anal.* Calcd. for C<sub>32</sub>H<sub>26</sub>O<sub>2</sub>: C, 86.9; H, 5.9; active H (two atoms), 0.45; mol. wt., 442. Found: C, 86.7; H, 5.8; active H, 0.44; mol. wt., 431.

After slow evaporation the light petroleum washings gave 0.31 g. of diphenyl.

The aqueous alkaline extract was acidified with dilute hydrochloric acid, extracted with ether, dried and evaporated; colorless crystals of benzenesulfonamide (0.48 g.) were obtained.

(e) 1,8-Naphthosultone (I).—I<sup>36</sup> (2 g.) was treated with phenyllithium and 30 ml. of benzene added; a yellow precipitate formed at once. The reaction mixture was kept for 30 minutes at 25° and then decomposed. The ethereal solution was washed with cold aqueous sodium hydroxide (8%, ca. 60 ml.) and the alkaline extract acidified, extracted with ether, dried and evaporated; the solid residue was crystallized from benzene-light petroleum to give II, m.p. 140° (identification by m.p. and mixed m.p.). In alcoholic solution it gives a green color with ferric chloride solution.

*Anal.* Calcd. for C<sub>16</sub>H<sub>12</sub>O<sub>3</sub>S: C, 67.6; H, 4.2; S, 11.3; active H, 0.35. Found: C, 67.5; H, 4.0; S, 11.2; active H, 0.32.

(f) N-Arylsulfonyl and N-Aroyl Derivatives.—IIIa, IIIb, IVa, Va, Vb and IVb were treated with phenyllithium as described for VIIa. The reaction products, worked up as in the corresponding experiments with phenylmagnesium bromide, were the same as in those experiments; there was no marked difference in yield.

Action of Lithium Aluminum Hydride on: (a) N-Arylsulfonyl and N-Aroyl Derivatives IIIa, IVb, Vb.—Solvents dried over sodium were used. To 0.7 g. of lithium aluminum hydride (New Metals and Chemicals, Ltd., London) was added 50 ml. of ether. After 15 minutes a benzene solution (30 ml.) containing 1 g. of IIIa, IVb or Vb was added in

(33) E. W. McClelland and A. J. Gait, *J. Chem. Soc.*, 921 (1926).

(34) E. W. Bartlett, L. E. Hart and E. W. McClelland, *ibid.*, 760 (1939).

(35) T. W. Evans and W. M. Dehn, *THIS JOURNAL*, **51**, 3651 (1929).

(36) H. Erdmann, *Ann.*, **247**, 306 (1888).

portions. The reaction mixture was refluxed for three hours and then kept overnight at room temperature. After treatment with cold dilute hydrochloric acid, the ethereal solution was dried and evaporated. The reaction products were worked up as follows: The oily residue, obtained in the case of IIIa, was washed several times with light petroleum (*ca.* 50 ml.); the resultant solid powder was crystallized from petroleum ether to give benzenesulfonamide (0.34 g.).

Evaporation of the light petroleum washings gave an oil which, on treatment with benzoyl chloride in the presence of aqueous sodium hydroxide and crystallization from ethyl alcohol, yielded 0.22 g. of phenylthiobenzoate; identification by m.p. and mixed m.p.

*Anal.* Calcd. for  $C_{13}H_{10}OS$ : C, 72.9; H, 4.7; S, 14.9. Found: C, 72.8; H, 4.5; S, 14.5.

The solid residues, which were obtained in the case of IVb and Vb after the washing with light petroleum, were crystallized to yield carbazole (0.42 g.) and benzanilide (0.38 g.), respectively. The light petroleum washings, on evaporation, gave benzyl alcohol which was identified as the  $\alpha$ -naphthylurethan (m.p. and mixed m.p.<sup>37</sup>).

(b) **1,8-Naphthosultone I and Derivatives (Ib-d).**—One gram each of I, Ib', Ic and Id was treated with lithium aluminum hydride as described above and the reaction mixture refluxed for two hours. After treatment with cold aqueous ammonium chloride solution the ethereal benzene solution was dried and evaporated.

The oily residue from I was washed with light petroleum (b.p. below 40°, *ca.* 40 ml.). On slow evaporation of the washings pale yellow crystals (0.1 g.) separated, which were recrystallized from light petroleum (b.p. below 40°) as 1-hydroxy-8-thionaphthol.

(37) A. I. Vogel, "A Text-book of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 775.

The residue from the light petroleum washings (b.p. below 40°) was crystallized from benzene-light petroleum (b.p. 50–60°), as yellow crystals of Xa, yield 0.45 g.

The solid residue, in the case of Ib, Ic and Id, was crystallized from benzene-light petroleum (b.p. 50–60°) to yield pale yellow crystals which proved in every case to be Xb; the yields were 65, 72 and 78%, respectively.

**Action of Benzoyl Chloride on Xa and Xb.**—Benzoyl chloride (2 ml.) was added to a solution of 0.4 g. of Xa in 20 ml. of aqueous sodium hydroxide (8%) and the mixture shaken for about 30 minutes. The resulting solid was filtered, washed thoroughly with water, dried and crystallized from benzene to give colorless crystals of the dibenzoyl derivative Xc, in an almost quantitative yield. The dibenzoyl derivative of Xb (Xd) was similarly prepared in almost quantitative yield.

(c) **N-Phenylsulfonylnaphthosultam (XI).**—XI<sup>15</sup> (1 g.) was treated with lithium aluminum hydride as described above. The solid residue was crystallized from benzene as colorless crystals of Xe, yield 0.52 g. The analytical values for 1-hydroxy-8-thionaphthol and Xa-e are given in Table II.

**Action of Phenyllithium on: (a) Phenanthraquinone Monoxime (XIII).**—A solution of 1 g. of XIII<sup>18</sup> in 40 ml. of dry benzene was treated with phenyllithium. The ether-benzene solution of the organic matter was dried and evaporated. The solid residue, upon crystallization from benzene, gave colorless crystals (m.p. 162°, yield 71%) which were identified as XIV by m.p. and mixed m.p.<sup>21</sup> and color reaction with sulfuric acid.

(b)  **$\alpha$ -Benzil Monoxime (XV).**—XV treated as above yielded colorless crystals (m.p. 153–154°) which were proved to be XVI by m.p. and mixed m.p. with an authentic specimen.<sup>22</sup> The yield is almost quantitative.

(38) H. Goldschmit, *Ber.*, **16**, 2176 (1883).

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### Studies in Mixed Ester Condensations. III

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A comparative study has been made of the use of sodium methoxide, sodium hydride, diethylaminomagnesium bromide and diisopropylaminomagnesium bromide as condensing agents for acylation of aliphatic esters with methyl benzoate and methyl 2-furoate. Diisopropylaminomagnesium bromide proved an excellent condensing agent for this purpose. Ethyl benzoylacetate, methyl  $\alpha$ -benzoylpropionate, methyl  $\alpha$ -benzoyl-*n*-butyrate and methyl 2-furoylpropionate have been prepared in yields of 44–51%, by appropriate mixed ester condensations using diisopropylaminomagnesium bromide as condensing agent and an equimolar ratio of acylating and acetylated ester; self-condensation of the aliphatic ester is virtually absent, obviating the necessity for an excess of this reagent. Sodium hydride has afforded good yields of mixed condensation products, but offers certain experimental difficulties in this use.

It has been shown previously<sup>1</sup> that various aliphatic esters may be acylated successfully by means of methyl benzoate, methyl furoate, methyl isobutyrate and methyl isovalerate using sodium methoxide as condensing agent and forcing conditions. Since considerable self-condensation of the aliphatic ester occurs under these experimental conditions, it is necessary to use an excess of this reactant for maximum conversion of the acylating ester to the mixed condensation product. Relatively few mixed ester condensations have been reported using basic condensing agents stronger than alkoxides. Ethyl formate, ethyl oxalate and ethyl benzoate have been condensed with ethyl isobutyrate by means of triphenylmethylsodium to afford the mixed condensation products in 16, 61 and 20% yields, respectively.<sup>2</sup> Ethyl nicotinate and cer-

tain phenyl esters have been used to acylate ethyl phenylacetate and several isopropyl and *t*-butyl esters in good yields with sodium amide as condensing agent.<sup>3</sup> Several successful mixed ester condensations have been effected using sodium hydride as condensing agent<sup>4</sup>; methyl and ethyl *n*-butyrate, ethyl laurate and ethyl isovalerate were the only aliphatic esters acylated in this work. Although diisopropylaminomagnesium bromide has been shown<sup>5</sup> to be an excellent reagent for the self-condensation of esters, no mixed ester condensations using this reagent have been reported.

We have investigated the use of several strong bases as catalysts for the acylations of aliphatic esters with methyl benzoate and methyl 2-furoate. Procedures have been developed whereby aliphatic esters may be acylated by means of these two acyl-

(1) E. E. Royals, *THIS JOURNAL*, **70**, 489 (1948); E. E. Royals, J. C. Hoppe, A. D. Jordan and A. G. Robinson, *ibid.*, **73**, 5857 (1951).

(2) B. E. Hudson and C. R. Hauser, *ibid.*, **63**, 3156 (1941); W. B. Rentrrow and C. R. Hauser, *ibid.*, **60**, 363 (1938).

(3) J. C. Shivers, M. L. Dillon and C. R. Hauser, *ibid.*, **69**, 119 (1947).

(4) F. W. Swamer and C. R. Hauser, *ibid.*, **72**, 1352 (1950).

(5) F. C. Frostick and C. R. Hauser, *ibid.*, **71**, 1350 (1949).