

TABLE V  
 PHYSICAL CONSTANTS OF DIELS-ALDER ADDUCTS

| Diene-<br>ophile <sup>a</sup> | Mp or bp of<br>butadiene adduct,<br>°C (mm) | Mp or bp of<br>isoprene adduct,<br>°C (mm) | Mp or bp of<br>2-CF <sub>3</sub> -butadiene<br>adduct, °C (mm) |
|-------------------------------|---------------------------------------------|--------------------------------------------|----------------------------------------------------------------|
| 1                             | 201.5-202 <sup>b</sup>                      | 115-116 <sup>c</sup>                       |                                                                |
| 4                             | 100-105 (9) <sup>d</sup>                    | 114 (10) <sup>e</sup>                      |                                                                |
| 5                             | 99 <sup>f</sup>                             | 63.5-64 <sup>g</sup>                       | 106 <sup>h</sup>                                               |
|                               | 116.5-118 (5)                               | 125-127.5 (5)                              |                                                                |
| 6                             | 94.5 (3) <sup>i</sup>                       | 127-129.5 (6) <sup>j</sup>                 | 114.5 (5) <sup>e</sup>                                         |
| 7                             | 100.5-102<br>(2.5) <sup>k</sup>             | 132-134 (5) <sup>l</sup>                   |                                                                |
| 8                             | 73-73.5 (20) <sup>m</sup>                   | 90-93 (20) <sup>n</sup>                    | 112 (30) <sup>e</sup>                                          |
| 9                             | 76 (19) <sup>o</sup>                        | 93 (20) <sup>p</sup>                       |                                                                |
| 10                            | 110.5 (5) <sup>q</sup>                      | 121.5-121.7 (6) <sup>r</sup>               | 119-120 (5) <sup>e</sup>                                       |

<sup>a</sup> Dienophile number corresponds to the set number of Table I.  
<sup>b</sup> Literature mp 201-202°: W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Amer. Chem. Soc.*, **80**, 2783 (1958). <sup>c</sup> Literature mp 114-116°: C. A. Stewert, Jr., *J. Org. Chem.*, **28**, 3320 (1963). <sup>d</sup> Literature bp 114° (10 mm): ref 31. <sup>e</sup> New compound; see text for identification. <sup>f</sup> Literature mp 101-102°: L. F. Fieser and R. C. Novello, *J. Amer. Chem. Soc.*, **64**, 802 (1942); <sup>g</sup> Literature mp 63-64°: O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **470**, 101 (1929). <sup>h</sup> Literature mp 107-107.5°: A. L. Henne and P. E. Hinkamp, *J. Amer. Chem. Soc.*, **76**, 5147 (1954). <sup>i</sup> Literature bp 137° (20 mm): I. N. Nazarov and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 329 (1954); *Chem. Abstr.*, **49**, 5329 (1955). <sup>j</sup> Literature bp 149-149.5° (20 mm): A. A. Petrov and N. P. Sopov, *Sb. Statei Obshch. Khim.*, **2**, 853 (1953); *Chem. Abstr.*, **49**, 5329 (1955). <sup>k</sup> Literature bp 138.5-139.5° (10 mm): N. P. Sopov and V. S. Milkashevskaya, *Zh. Obshch. Khim.*, **26**, 1914 (1956); *Chem. Abstr.*, **51**, 4968 (1957); <sup>l</sup> Literature bp 151.5-152.5° (10 mm): footnote k. <sup>m</sup> Literature bp 80-82° (23 mm): E. D. Bergmann and D. F. Hermann, *J. Appl. Chem. (London)*, **3**, 42 (1953). <sup>n</sup> Literature bp 85-86° (15 mm): H. E. Hennis, *J. Org. Chem.*, **28**, 2570 (1963). <sup>o</sup> Literature bp 83° (20 mm): A. A. Petrov and N. P. Sopov, *J. Gen. Chem. USSR*, **17**, 2228 (1947); *Chem. Abstr.*, **42**, 4957 (1948). <sup>p</sup> Literature bp 102-104° (25 mm): I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1412 (1959); *Chem. Abstr.*, **54**, 1409 (1960). <sup>q</sup> Literature bp 114-115° (5 mm): footnote i. <sup>r</sup> Literature bp 149.5-150° (20 mm): footnote j.

The 2-trifluoromethylbutadiene-dimethyl maleate adduct gave the following nmr data:  $\tau$  3.62 (m, 1 H), 6.27 (s, 6 H), 6.72-7.18 (m, 2 H), and 7.18-7.61 (m, 4 H).

*Anal.* Calcd for C<sub>11</sub>H<sub>13</sub>F<sub>3</sub>O<sub>4</sub>: C, 49.6; H, 4.9. Found: C, 49.5; H, 5.0.

**Competitive Experiments.**—The reaction conditions are shown in Tables I and II. With no solvent runs the reactions were carried out in thick-wall, sealed tubes. The method of analysis of the relative rate is similar to that reported previously,<sup>3</sup> except that in runs with fumaryl chloride the product was converted into the dimethyl ester by treatment with absolute methanol before glpc analysis. Carbowax 6000 (10 wt %) on Diasolid M (Nihon Chromato Industries Co., Ltd.) was used for analyses in sets 1, 1', 3, 3', and 6-15 (Tables I and II). For sets 4, 4', 5, and 5', Silicon DC 550 on Diasolid M (the same supplier) was employed.

**Kinetic experiments** were carried out in a conventional way in a thermostat, with a known amount of dimethyl *trans*-4-cyclohexene-1,2-dicarboxylate added as the internal standard for glpc analysis (silicon DC 550 column) of the product formed by appropriate intervals of reaction period.

**Rate Constant of MA-AlCl<sub>3</sub>-Cyclopentadiene Reaction in Benzene.**—This reaction is too fast to measure directly in the usual way. The relative rate, cyclopentadiene *vs.* isoprene, in benzene at 20° toward MA-AlCl<sub>3</sub> was determined to be 646:1 by the competitive experiments similar to those described above (silicon DC 550 column). Since  $k^i/k^b$  is 12.1 (Table I) and  $k^b = 1.15 \times 10^{-8}$  l/mol sec,<sup>1</sup> the desired rate constant is calculated to be 8.99 l/mol sec.

**Proof of Kinetic Control of the Product Ratio.**—The Diels-Alder adduct from butadiene (or isoprene) was treated with a large excess of isoprene (or butadiene) at room temperature for a period longer than that of the corresponding competitive experiment. It was ascertained by glpc that no cross-adduct was formed under the experimental conditions.

**Registry No.**—Butadiene, 106-99-0; isoprene, 78-79-5; 2-(trifluoromethyl)butadiene, 381-81-7; isoprene-vinylidene cyanide adduct, 23884-89-1; 2-(trifluoromethyl)-butadiene-dimethyl fumarate adduct, 23884-90-4; 2-(trifluoromethyl)butadiene-methyl acrylate adduct, 23884-91-5; 2-(trifluoromethyl)butadiene-dimethyl maleate adduct, 23884-92-6.

## Preparation of Di- and Triaroylamides by Means of *n*-Butyllithium and Aroyl Halides. Influence of Lewis Bases<sup>1</sup>

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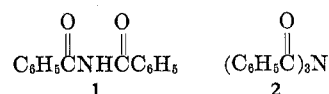
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Aroylations of the N-lithio salts of various amides, amines, and phthalimide have been accomplished by aroyl halides in the presence of Lewis bases such as 1,4-diazabicyclo[2.2.2]octane (dabco) to afford conveniently di- and triaroylamides in good to excellent yield. Presumably, the Lewis bases coordinate with the lithium cations and perhaps with the acid halides, resulting in enhanced reactivities of the nitrogen anions toward electrophiles, and of the carbonyl group of the acid chlorides toward nucleophiles.

Aroylation of amides and related organic nitrogen compounds to afford di- and triaroylamides such as **1** and **2**, respectively, has been accomplished under a variety of conditions, but there does not appear to be a general method for synthesizing such compounds. For example, benzamide has been benzoylated by benzoyl chloride to afford dibenzamide (**1**) in some cases,<sup>2</sup> and tribenzamide (**2**) in others.<sup>3</sup> An especially

interesting method of preparing amide **2** involves tribenzoylation of lithium nitride.<sup>4</sup> Although good yields of di- and triaroylamides have often been reported,<sup>2-4</sup> reaction times and conditions have usually been inconvenient. In addition, certain aroylations of amides have been limited to primary ones.<sup>3</sup>



(1) Supported by the Petroleum Research Fund, administered by the American Chemical Society, on Grant PRF 959-G.

(2) A. W. Titherly, *J. Chem. Soc.*, **85**, 1678 (1904).

(3) Q. E. Thompson, *J. Amer. Chem. Soc.*, **73**, 5841 (1951).

(4) F. P. Baldwin, E. J. Blanchard, and P. E. Koenig, *J. Org. Chem.*, **30**, 671 (1965).



Finally, lithium nitride was tribenzoylated in THF in the presence of dabco to afford tribenzamide (2) in 44% yield after only a 5-hr reflux period; in the absence of dabco, 2 was obtained in only 18% yield under similar conditions. Lithium nitride has previously been benzoylated in diglyme for 48 hr to give 2 in 61% yield.<sup>4</sup>

### Discussion

The aroylations of certain organic nitrogen anions described above represent a convenient and useful method for the preparation of various amides in which all of the ionizable hydrogen atoms on the nitrogen atom have been replaced by aroyl groups. In most cases, the yields of the desired products are at least doubled by the presence of dabco or other Lewis bases. The presumably quite general reactions are clean and the products are purified without difficulty.

The structures of the products which appear to be new, 4-6, were supported by elemental analyses and by infrared and nmr spectroscopy (see Experimental Section).

Certain entries in Table I deserve special comment. In the benzoylations of N,N-dilithiobenzamide (3) the yields of tribenzamide (2) were highly dependent on the choice of solvent, but not on the choice of added Lewis base. Thus, in the absence of added Lewis base, 2 was obtained in 71% yield in diglyme-hexane, but only in 33% yield in THF-hexane. In the presence of added Lewis base in THF-hexane, comparable yields of 2 were obtained regardless of whether dabco, diglyme, or TMEDA were employed. Ethyl ether-hexane, though, proved to be a less satisfactory solvent for the preparation of 2, even in the presence of dabco. With the exception of the benzoylation of 3 in THF-hexane, all diaroylations of N,N-dilithioamides were accomplished in higher yields after 5-hr rather than 1-hr reflux periods.

There appear to be at least three explanations for the positive effect of Lewis bases on these aroylations: (A) the reactivity of the *n*-butyllithium is enhanced<sup>5</sup> so that more extensive reaction with the original nitrogen compounds is realized; (B) the reactivity of the respective nitrogen anions is enhanced;<sup>6</sup> (C) the reactivity of the aroyl halides is enhanced.<sup>6</sup>

The first possibility was eliminated by gas-measurement experiments. For example, treatment of a refluxing mixture of phthalimide and dabco in THF with 1 equiv of *n*-butyllithium in hexane caused the same amount of gas to be evolved as in the absence of dabco.

Regarding the other two possibilities, it is generally recognized that Lewis bases like dabco coordinate with cations<sup>5</sup> even at relatively high temperatures<sup>5a</sup> to increase the reactivity of the counteranion toward electrophiles. However, similar molecular complexes of tertiary amines with acid chlorides appear to be stable only at relatively low temperatures.<sup>3,6,8</sup> Diglyme and other polyethers are also known to coordinate effectively with cations,<sup>9</sup> but similar coordination of these ethers with aroyl halides should be minimal.

Thus, we favor explanation B, although C cannot be unequivocally eliminated.

Finally, it is interesting that such high yields of N-aroil derivatives of the amides and phthalimide are obtained, since the corresponding O-aroil derivatives were also possible. Incidentally, the 1,3-dibenzoylation of dilithiothiourea (13) is also interesting, since such 1,3 dianions usually undergo only a single condensation with electrophiles.<sup>10</sup>

### Experimental Section<sup>11</sup>

**Aroylation of Amides.**—In Table I are summarized the results obtained by adding certain acid chlorides to N-lithioamides under various conditions; particulars are listed below.

**A. General Method Illustrated by Benzamide and Benzoyl Chloride.**—To a solution of 6.05 g (0.05 mol) of benzamide and 0.1 mol of the appropriate Lewis base (Table I) in 75 ml of anhydrous THF under nitrogen was added, during 3 min 70.3 ml (0.1125 mol) of 1.6 *M* *n*-butyllithium in hexane.<sup>12</sup> The mixture was refluxed for 20 min and then treated (without the heating mantle) with a solution of 16.1 g (0.1125 mol) of benzoyl chloride in 50 ml of THF added at such a rate (60 min) that the mixture continued to reflux gently. When the addition was completed, the reaction mixture was heated and maintained at reflux for 0.5-5 hr (Table I) and then it was cooled to 0° by an ice bath. After 100 ml of water had been added the resulting precipitate was collected, washed with water and ether, and air dried to afford tribenzamide (2), mp 206-208°; recrystallization of the product gave the pure product, mp 211-212° (lit.<sup>13</sup> mp 207-208°). Concentration of the original organic phase and that obtained from three extractions by ether of the aqueous phase gave small additional amounts of product 2.

**B. Benzamide and *p*-Toluoyl Chloride.**—Addition of 17.5 g (0.1125 mol) of *p*-toluoyl chloride in 50 ml of THF to 0.05 mol of N,N-dilithiobenzamide (3) and 11.2 g (0.1 mol) of dabco in 75 ml of THF as above afforded, after recrystallization from benzene, 11.0 g (62%) of benzdi-*p*-toluamide (4): mp 215-216°; ir (Nujol) 1670 (C=O), 825, 747, and 680 cm<sup>-1</sup> (ArH); nmr (CDCl<sub>3</sub>) δ 7.47 (m, 13, ArH) and 2.15 (s, 6, CH<sub>3</sub>).

*Anal.* Calcd for C<sub>23</sub>H<sub>19</sub>NO<sub>2</sub>: C, 77.31; H, 5.32; N, 3.92. Found: C, 77.59; H, 5.49; N, 3.90.

**C. Benzamide and Anisoyl Chloride.**—This reaction was accomplished essentially as above employing 19.3 g (0.1125 mol) of anisoyl chloride in THF for 5 hr to give 11.4 g (59%) of benzdianisamide (5): mp 166-168°; ir (Nujol) 1668 (C=O), 838, 742, and 685 cm<sup>-1</sup> (ArH); nmr (CDCl<sub>3</sub>) δ 7.68 (m, 13, ArH) and 4.6 (s, 6, CH<sub>3</sub>).

*Anal.* Calcd for C<sub>23</sub>H<sub>19</sub>NO<sub>2</sub>: N, 3.56. Found: N, 3.34.

**D. Benzamide and Cinnamoyl Chloride.**—This reaction was effected as above using 18.33 g (0.11 mol) of cinnamoyl chloride in THF for 1 hr to afford 12.8 g (67%) of benzdicinnamamide (6): mp 176-179°; ir (Nujol) 1650 (C=O), 1300, 962 (C=C), 730, and 690 cm<sup>-1</sup> (ArH); nmr (CF<sub>3</sub>CO<sub>2</sub>H) δ 7.42 (m, 15, ArH) and 6.1 (m, 4, CH).

*Anal.* Calcd for C<sub>25</sub>H<sub>19</sub>NO<sub>2</sub>: C, 78.74; H, 4.98; N, 3.67. Found: C, 78.65; H, 5.00; N, 3.48.

**E. *p*-Toluamide and *p*-Toluoyl Chloride.**—As above, 6.8 g (0.05 mol) of *p*-toluamide and 11.2 g (0.1 mol) of dabco in 75 ml of THF, 70.3 ml (0.1125 mol) of 1.6 *M* *n*-butyllithium in hexane,<sup>12</sup> and 17.5 g (0.1125 mol) of *p*-toluoyl chloride in THF, refluxed for 5 hr and recrystallized from 95% ethanol, gave 13.3 g (71%) of tri-*p*-toluamide (7), mp 250.5-251° (lit.<sup>3</sup> mp 246 ± 2°). Compound 7 was also obtained in 45% yield when the reflux period was diminished from 5 to 1 hr.

(10) E. M. Kaiser and C. R. Hauser, *Tetrahedron Lett.*, 3341 (1967); E. M. Kaiser and R. D. Beard, *ibid.*, 2583 (1968).

(11) Melting points were taken on a Thomas-Hoover capillary melting point apparatus in open capillary tubes and are uncorrected. Infrared spectra were determined on a Perkin-Elmer Infracord Model 137 as Nujol mulls. Nmr spectra were obtained with a Varian Associates A-60 spectrometer using tetramethylsilane as internal standard. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(12) Supplied by the Foote Mineral Co., Exton, Pa.

(13) C. Blacher, *Chem. Ber.*, 28, 435 (1895).

(8) For example, see H. Adkins and Q. E. Thompson, *J. Amer. Chem. Soc.*, 71, 2242 (1949).

(9) See H. D. Zook, T. J. Russo, E. F. Ferrand, and D. S. Stotz, *J. Org. Chem.*, 33, 2222 (1968), and references cited therein.

**F. Anisamide and Anisoyl Chloride.**—Anisamide (7.6 g, 0.05 mol) and 11.2 g (0.1 mol) of dabco in 75 ml of THF, 70.3 ml (0.1125 mol) of 1.6 *M* *n*-butyllithium in hexane,<sup>12</sup> and 19.3 g (0.1125 mol) of anisoyl chloride in THF gave, after recrystallization from 95% ethanol, 11.35 g (54%) of trianisamide (8), mp 195–196° (lit.<sup>3</sup> mp 197.5–198°). When the reaction was repeated for 1 hr instead of 5 hr, compound 8 was obtained in 58% yield.

**Benzoylation of Lithiobenzanilide.**—Lithiobenzanilide (0.05 mol), prepared in 75 ml of THF from 9.85 g (0.05 mol) of benz-anilide, 11.2 g (0.1 mol) of dabco, and 40 ml (0.064 mol) of 1.6 *M* *n*-butyllithium in hexane<sup>12</sup> by heating for 1 hr, was treated in the usual fashion during 15 min with a solution of 8.05 g (0.056 mol) of benzoyl chloride in 50 ml of THF. After refluxing for 1 hr, the resulting solution was worked up to give, after recrystallization from 95% ethanol, 11.35 g (75%) of *N,N*-dibenzoyl-aniline (11), mp 161–162.5° (lit.<sup>14</sup> mp 160–162°). When the reaction was repeated in the absence of dabco, 11 was obtained in 68% yield.

**Benzoylation of Lithio-*N*-methylbenzamide.**—*N*-Methylbenzamide (6.75 g, 0.05 mol) was lithiated during 20 min in 75 ml of THF by 35 ml (0.056 mol) of 1.6 *M* *n*-butyllithium in hexane<sup>12</sup> in the presence of 5.6 g (0.05 mol) of dabco. The resulting suspension was treated during 30 min with a solution of 8.05 g (0.056 mol) of benzoyl chloride in 50 ml of THF, refluxed for 1 hr, and then worked up as usual. Recrystallization of the crude product from methanol afforded 7.85 g (66%) of *N,N*-dibenzoylmethylamine (12), mp 97–99° (lit.<sup>15</sup> mp 94–95°).

**Dibenzoylation of Diphenylthiourea.**—*N,N'*-Dilithiodiphenylthiourea (13, 0.025 mol) was prepared in 75 ml of THF from 5.7 g (0.025 mol) of diphenylthiourea, 5.6 g (0.05 mol) of dabco, and 39 ml (0.06 mol) of 1.6 *M* *n*-butyllithium in hexane<sup>12</sup> as above. The resulting yellow solution was treated during 15 min with a solution of 8.05 g (0.056 mol) of benzoyl chloride in 50 ml of THF and the mixture was refluxed for 1 hr. After the usual work-up, the crude product was recrystallized from 95% ethanol to give 5.3 g (51%) of *N,N'*-dibenzoyl-*N,N'*-diphenylthiourea (14), mp 159–162° (lit.<sup>16</sup> mp 160.5°).

**Benzoylation of Phthalimide.**—As above, 7.35 g (0.05 mol) of phthalimide and 5.6 g (0.05 mol) of dabco in 75 ml of THF was treated with 35 ml (0.055 mol) of 1.6 *M* *n*-butyllithium in hexane.<sup>12</sup> After 30 min, the resulting white suspension was treated during 10 min with a solution of 8.05 g (0.056 mol) of benzoyl chloride in 50 ml of THF; heat was applied for 5 hr. Work-up followed by recrystallization of the crude product from 95% ethanol gave 9.94 g (80%) of *N*-benzoylphthalimide (15), mp 167–168° (lit.<sup>17</sup> mp 168°). When the reaction was repeated with-

out dabco, 6.56 g (52%) of compound 15 was obtained, mp 167–168°.

**Aroylations of *N,N*-Dilithioaniline. A. With Benzoyl Chloride.**—A solution of 4.65 g (0.05 mol) of aniline and 11.2 g (0.1 mol) of dabco in 75 ml of THF was treated with 70.3 ml (0.1125 mol) of 1.6 *M* *n*-butyllithium in hexane<sup>12</sup> and the mixture was refluxed for 10 min. Subsequent addition to the mixture of a solution of 16.1 g (0.1125 mol) of benzoyl chloride in 50 ml of THF followed by a 1-hr reflux period afforded, after recrystallization from ethanol, 12.21 g (81%) of 11, mp and mmp 161–162.5°; the yield of 11 was only 40% in the absence of dabco.

**B. With *o*-Phthaloyl Chloride.**—Dilithioaniline (0.05 mol), prepared as in part A above, was treated during 1 hr with a solution of 10.1 g (0.05 mol) of *o*-phthaloyl chloride in 100 ml of THF. After the resulting mixture had been heated for 5 hr, it was worked up in the usual fashion. The crude product was recrystallized from ethanol to give 8.08 g (73%) of phthalanil (16), mp 209–210° (lit.<sup>18</sup> mp 203°).

**Benzoylation of Dibenzylamine.**—*N*-Lithiodibenzylamine was prepared in 75 ml of THF from 9.85 g (0.05 mol) of dibenzylamine, 5.6 g (0.05 mol) of dabco, and 35 ml (0.055 mol) of 1.6 *M* *n*-butyllithium in hexane.<sup>12</sup> After stirring for 1 hr at 25°, the bright red mixture was treated during 5 min with a solution of 8.05 g (0.056 mol) of benzoyl chloride in 50 ml of THF. The resulting mixture was stirred for 3 hr at 25°, and then it was worked up in the usual fashion to afford, after recrystallization from ethanol, 12.4 g (83%) of *N*-benzoyldibenzylamine (17), mp 112–113° (lit.<sup>19</sup> mp 112–113°). When the reaction was repeated without dabco, 9.22 g (61%) of product 17 was obtained, mp and mmp 112–113°.

**Benzoylation of Lithium Nitride.**—To a red suspension of 1.75 g (0.05 mol) of lithium nitride and 16.8 g (0.15 mol) of dabco in 75 ml of THF was added during 30 min a solution of 24.6 g (0.175 mol) of benzoyl chloride. Heat was evolved and the suspension turned purple, gray, and then yellow. The mixture was heated and maintained at reflux for 5 hr, and then it was worked up in the usual fashion to give 7.2 g (44%) of tribenzamide 2, mp and mmp 211–212°. When the reaction was repeated in the absence of dabco, compound 2 was obtained in only 18% yield.

**Registry No.**—*n*-Butyllithium, 109-72-8; 2, 602-88-0; 4, 23825-26-5; 5, 23825-27-6; 6, 23825-28-7; 7, 23825-29-8; 8, 1107-48-8; 11, 3027-01-8; 12, 23825-32-3; 14, 23796-78-3; 15, 4583-50-0; 16, 520-03-6; 17, 23825-35-6.

(17) A. W. Titherly and W. L. Hicks, *J. Chem. Soc.*, **89**, 709 (1906).

(18) A. Laurent and C. Gerhardt, *Justus Liebig's Ann. Chem.*, **68**, 33 (1848).

(19) H. Franzen, *Chem. Ber.*, **42**, 2486 (1909).

(14) P. Kay, *Chem. Ber.*, **26**, 2855 (1893).

(15) O. Mumm, H. Hesse, and H. Volquartz, *ibid.*, **48**, 388 (1915).

(16) A. Deninger, *ibid.*, **28**, 1322 (1895).