Acenaphthene I. The preparation of derivatives of 4,5-diamino naphthalic anhydride[1]

Louis A. Jones,[2] Charles T. Joyner, Hong Ki Kim, and Robert A. Kyff[3]
Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27607

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The preparation of 5-nitroacenaphthene (**2**) using several nitrating agents resulted in a product which was found to be contaminated with 20–30% of the 3-nitro isomeride. Separation was accomplished by t.l.c. and the n.m.r. spectra of the isomers are now reported. A new synthesis of 4,5-dinitronaphthalic anhydride (**5**) and an improved preparation of the dimethyl and diethyl esters of 4-nitronaphthalic anhydride and **5** is described. The esters were converted to the corresponding diamino derivatives by high pressure hydrogen–Pd reduction.

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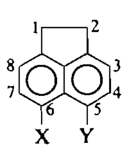
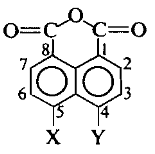
Acenaphthene (**1**) has been used as a convenient starting material for the preparation of 5-nitroacenaphthene (**2**) which can be oxidized to the 4-nitronaphthalic anhydride (**3**). It has been reported that the nitro group can be reduced to the amine although the literature is in conflict (1). For nitration, mixtures such as glacial acetic acid – nitric acid (2), concentrated sulfuric acid – nitric acid (2*d*, 3) and $UO_2(NO_3)_2 \cdot H_2O \cdot N_2O_4$ (4*a*) have been used successfully to prepare **2** in 75–85% yield. Oxidation to **3** using glacial acetic acid and sodium dichromate occurs in yields of 59% (2, 5). In our studies of the published methods of nitration, modification of Sachs and Mosebach's procedure (2*a*, *b*) gave superior results. However, in all methods used to prepare **2**, the n.m.r. spectra suggested that 20–30% of the 3-nitro isomer was present and extensive recrystallization failed to improve the melting point or the n.m.r. pattern. A search of the literature revealed that only **2** has been considered to be the product of nitration of acenaphthene using acetic acid – nitric acid. Use of benzoyl nitrate as the nitrating agent has been reported to produce 3-nitroacenaphthene (41%) while diacetylorthonitric acid gave a 22% yield (6). In our hands, attempts to resolve the mixture by column chromatography, sublimation, and zone refining were unsuccessful but t.l.c. afforded separation. Preparative t.l.c. gave two compounds, pure **2** and the 3-nitro isomeride and the n.m.r. spectra, when combined, gave the original spectrum of impure **2** (Fig. 1). Reduction of impure **2** to the amine gave the pure 5-amino derivative after two recrystallizations from ethanol as indicated by comparison with the product derived from the t.l.c. purified compound.



1 X = Y = H
2 X = H; Y = NO_2
4 X = NO_2; Y = NO_2



3 X = H; Y = NO_2
5 X = NO_2; Y = NO_2

Attempts to oxidize impure **2** to **3** by neutral sodium dichromate under high pressure (7) and also by the Cornforth reagent (8) resulted in complete degradation in the former case and less than 10% yield in the latter. Although it has been reported (2*b*, 4*b*) that 4-nitronaphthalic acid is the original product of oxidation which then dehydrates to **3**, only **3** was obtained on acetic acid – sodium dichromate oxidation and t.l.c. indicated no 3-nitro isomer survived the oxidation. Attempted reduction (1) of **3** to the amine gave only an amorphous yellow–orange powder of an indefinite m.p., and the i.r. and n.m.r. spectra suggested some polymerization had occurred as indicated by diffuse N—H and poorly defined anhydride carbonyl absorptions.

The preparation of 4,5-dinitronaphthalic anhydride (**5**) has been accomplished with acetic anhydride – nitric acid and oxidation was carried out as previously described (2*b*). However, the extensive length of time required for stepwise preparation of **5** prompted an investigation into quicker methods of nitration and oxidation.

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[2] To whom inquiries should be sent.

[3] Present address: IBM Research Laboratories, Essex Junction, Vermont.

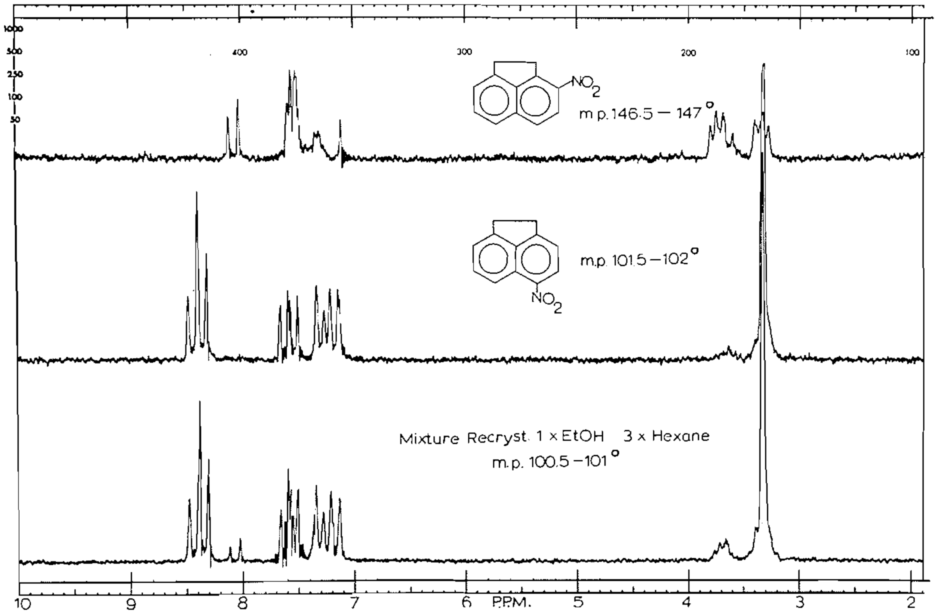
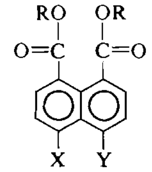


FIG. 1. Nitration products of acenaphthene. Run on an HA-100 in $CDCl_3$ with 1% TMS.

Oxidation with concentrated nitric acid under reflux conditions overnight showed that **4** → **5** occurred in 24% yield and **2** → **5** gave a 22% yield. Starting with **1** and refluxing for 16–18 h gave *ca.* 25% yield of pure **5** and it seems reasonable therefore that the pathway follows **1** → **2** → **4** → **5** under the *in situ* nitrating–oxidizing conditions. It should be noted that no nitrated product other than **5** was found nor was there any evidence for the formation of any of the corresponding acid, contrary to published results (2*b*). Attempts to reduce the nitro groups to amines using Pd–H_2 under pressure or $SnCl_2$–HCl (2*b*, 5) resulted in a brown powder of indeterminate m.p. and an i.r. spectrum completely lacking in the two carbonyl stretching vibrations characteristic of anhydrides.

It was considered desirable to determine if the esters of **3** and **5** could be successfully reduced to give the corresponding amines. Several methods of esterification were investigated including the formation of the acid chlorides but yields were too low to be practicable. The procedure of Bickoff *et al.* (9) (*i.e.*, refluxing an acetone solution of **3** or **5** with dialkylsulfate and potassium carbonate) resulted in low yields of the desired esters. However, when the corresponding alcohol was used as the solvent and the anhydride refluxed overnight with the dialkylsulfate and potassium carbonate, yields were considerably improved. In this manner, a 76% yield of 4-nitronaphthalic-1,8-dimethyl ester (**4**), 69% of 4-nitronaphthalic-1,8-diethyl ester (**7**), 90% of 4,5-dinitronaphthalic-1,8-dimethyl ester (**8**), and 51% of 4,5-dinitronaphthalic-1,8-diethyl ester (**9**) was obtained. An 18.4% yield of **6** has been previously reported from refluxing the potassium salt of **3** with dimethylsulfate (2*b*).



6 R = Me; X = H; Y = NO_2	6*a* Y = NH_2
7 R = Et; X = H; Y = NO_2	7*a* Y = NH_2
8 R = Me; X = Y = NO_2	8*a* X = Y = NH_2
9 R = Et; X = Y = NO_2	9*a* X = Y = NH_2

Reduction was attempted via $SnCl_2$–HCl (5), Fe–HCl (1*a*), and PtO_2–H_2 in ethanol (10), and in the latter case a blue precipitate was formed which was not investigated further. However, in all cases, the yield was small. Successful conversion of **6**, **7**, **8**, and **9** to the corresponding amines occurred by the Pd–H_2 reduction of the heterogeneous nitronaphthalic ester–benzene system under high pressure and moderate temperature.

Experimental[4]

Acenaphthene (**1**) (practical, Aldrich Chemical Co., Inc.) was conveniently purified by batch chromatography on alumina using hexane as the elutant. Approximately 750 g of alumina slurried in hexane was added to a column 9.5 × 80 cm and on this was placed 2 kg of practical **1**. Hexane was continuously run through the bed until all of **1** disappeared and the collected elutant stripped off under vacuum; m.p. 95 °C, n.m.r. δ 3.18 (4H, s, cycloaliphatic H), 6.53–8.00 (6H, m, aromatic H).

5-Nitroacenaphthene (2)

The procedure used was similar to that of previous workers (2*a*, *b*). A mixture of 400 g of **1** and acetic acid (3.2 l) was cooled to 15 °C in an ice bath and nitric acid (180 g, $d = 1.42$) was added with stirring at such a rate as to maintain a temperature of 15–20 °C. After 1 h, the precipitate was filtered, washed with acetic acid, and recrystallized from hexane. This gave 340 g (66%) of impure (*ca.* 20% of 3-nitroacenaphthene) 5-nitroacenaphthene (**2**). A portion of this was successively recrystallized from ethanol and hexane to give yellow–green needles, m.p. 101–105 °C, lit. m.p. 101–102 °C (2*b*). Qualitative t.l.c. (Barkerflex Silica Gel 1 B, hexane:ether 3:1 v/v) showed the 3-nitro isomer to have the larger R_f and preparative t.l.c. (silica gel HF, 40 × 20 cm glass plates, hexane:ether, 3:1 v/v) separated the two bands. The n.m.r. spectra are shown in Fig. 1 and integrate correctly; 3-nitroacenaphthene m.p. 146.5–147 °C, lit. m.p. 151.5 °C (6).

Anal. Calcd. for $C_{12}H_9NO_2$ (mol. wt. 199.14): C, 72.36; H, 4.52; N, 7.04. Found: C, 72.21; H, 4.58; N, 6.94.

Impure **2** (0.5 g) was refluxed with 2 ml of hydrazine hydrate and 0.05 g of 10% Pd on carbon in 50 ml of ethanol for 2 h, and filtration, followed by evaporation, gave impure 5-aminoacenaphthene. This was recrystallized twice from ethanol to give 0.3 g (71%) of pure compound, m.p. 106 °C, lit. m.p. 104 °C (11). The t.l.c. purified **2** was treated similarly and the product melted at 106.5 °C; mixed m.p. showed no depression. The n.m.r. and i.r. spectra were identical and t.l.c. showed no impurities present; i.r. 1330 (NO_2 sym. stretch) and 1520 cm^{-1} (NO_2 asym. stretch); n.m.r. δ 3.30 (4H, s, methylene H), 3.65 (2H, s, amine H), 6.60–7.60 (5H, m, aromatic H).

4-Nitronaphthalic Anhydride (3)

The solid from above was added to acetic acid (5.2 l) containing technical sodium dichromate (3200 g) and the mixture was heated on a boiling water bath for 5 h. The solution was poured into water and the orange crystals were filtered and dissolved in 3% potassium carbonate solution. This was filtered and the filtrate was acidified with hydrochloric acid, producing a light tan precipitate. After filtration, water washes, and drying, a total of 301 g of **3** (48%), m.p. 228–229 °C, was obtained, lit. m.p. 228–229 °C (2*b*). No 2-nitro compound was indicated by t.l.c.; i.r. (KBr) 1300 (NO_2 sym. stretch), 1525 (NO_2 asym. stretch), 1760 (C=O sym. stretch), and 1790 cm^{-1} (C=O asym. stretch).

5,6-Dinitroacenaphthene (4)

Compound **1** (90.5 g) was added slowly to 700 ml of nitric acid – acetic anhydride (2:5 v/v). The mixture was stirred for two h (28.0–68.5 °C) and then heated to 93.0 °C for 1 h, and then diluted with water and filtered. The resulting precipitate was recrystallized from glacial acetic acid and toluene, yielding 32 g of **4** (20%), reddish-brown needles, m.p. 213–214 °C; lit. m.p. 210–212 °C (11). Qualitative t.l.c. indicated only one compound; i.r. (KBr) 1325 (NO_2), 1515 (NO_2) cm^{-1}; n.m.r. (DMSO) δ 3.55 (4H, s, methylene H) and 6.75–7.63, (4H, AB pattern, aromatic H).

4,5-Dinitronaphthalic Anhydride (5)

To a vigorously stirred sample of 150 g of **1** in cold acetic acid (900 ml, 15 °C) was added 405 ml of nitric acid ($d = 1.5$) slowly in small portions such that the temperature did not rise above 20 °C. The yellow mixture was stirred for 1 h at 15–20 °C and heated to 80 °C for an additional 20 min. Nitric acid (2.5 l, $d = 1.42$) was then added and the mixture refluxed for 16–18 h, cooled, and filtered. The light yellow crystals obtained were washed with water until neutral and then dried. A 73.5 g sample (26%) of **5**, m.p. 324–326 °C, was obtained, lit. m.p. 323–324 °C (2*b*), i.r. (KBr) 1330 (NO_2), 1530 (NO_2), 1750 (C=O), and 1780 cm^{-1} (C=O).

4-Nitronaphthalic-1,8-dimethylester (6)

A 146 g sample of **3** was added to methanol (2.5 l) and 114 ml of dimethylsulfate. The mixture was refluxed, 91 g of potassium carbonate added, and refluxing continued overnight. The addition of water caused a tan precipitate to form and, following filtration, the solid was washed and dried to give 131.4 g of **6** (76%), m.p. 125–126 °C, i.r. (KBr) 1280 (C—O), 1345 (NO_2), 1525 (NO_2) and 1725 cm^{-1} (C=O); n.m.r., δ 3.85 (6H, s, methyl), 7.30–8.60 (5H, m, aromatic H).

Anal. Calcd. for $C_{14}H_{11}NO_6$ (289.26): C, 58.13; H, 3.84; N, 4.84. Found: C, 58.27; H, 3.76; N, 4.76.

4-Aminonaphthalic-1,8-dimethylester (6a)

A mixture of 131.4 g of **6**, benzene (1 l), and 6.5 g of Pd catalyst was placed in a 2 l high pressure apparatus which was sealed, flushed three times with 200 p.s.i. hydrogen, and then filled to 1100 p.s.i. hydrogen. Stirring and heating to 75 °C initiated the reaction which continued for 5 min. The maximum temperature reached was 110 °C, at which point the mixture was cooled to room temperature, excess hydrogen released, and the mixture was filtered to recover catalyst. The filtrate was stripped of benzene and the gum-like yellow–brown product dissolved in 600 ml of methanol. Concentrated hydrochloric acid (300 ml) was added and the precipitated white salt was filtered and washed twice with acetone. After drying, 94.2 g of the salt was obtained. This was dissolved in water and the solution made basic and exhaustively extracted with ether. The ether was partially evaporated in air, cooled in an acetone – Dry Ice bath, and filtered to give 64.9 g (55%) of **6*a***, m.p. 86–90 °C;

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[4] Melting points were determined on a Thomas Hoover capillary melting point apparatus and elemental analyses, by Galbraith Laboratories, Inc., Knoxville, Tennessee. The u.v. spectra were determined on a Perkin–Elmer Model 202 ultraviolet-visible spectrophotometer. The n.m.r. spectra of all the compounds were run in deuterochloroform with TMS as an internal standard on a Varian T-60 n.m.r. spectrophotometer except where otherwise noted. The i.r. spectra were run on a Perkin–Elmer 521 i.r. spectrophotometer.

i.r. (Nujol) 1250 (C—O), 1725 (C═O), and 3340 cm^{-1} (NH_2); n.m.r. δ 3.80 (6H, s, methyl H), 4.38 (2H, s, amine H), 6.50–7.90 (5H, m, aromatic H).

Anal. Calcd. for $C_{14}H_{13}NO_4$ (259.28): C, 64.84; H, 5.06; N, 5.40. Found: C, 64.90; H, 5.03; N, 5.35.

4-Nitronaphthalic-1,8-diethyl Ester (7)

Compound **3** (24.4 g), 500 ml of ethanol, 13.4 ml of diethyl sulfate, were refluxed, and potassium carbonate (7.6 g) added. Refluxing was continued for 2 h and then an additional 13.4 ml of diethyl sulfate and 7.6 g of potassium carbonate was added and refluxing continued for an additional 3 h after which the hot mixture was filtered. The filtrate was diluted with water and the precipitate was filtered, washed, and dried to give 21.8 g (69%) of yellow-green crystals, m.p. 83.0 °C; i.r. (KBr) 1275 (C—O), 1335 (NO_2), 1530 (NO_2), and 1715 cm^{-1} (C═O); n.m.r., δ 1.50 (6H, t, methyl H), 4.50 (4H, q, methylene H), 7.58–8.56 (5H, m, aromatic H).

Anal. Calcd. for $C_{16}H_{15}NO_6$ (317.30): C, 60.56; H, 4.77; N, 4.42. Found: C, 60.41; H, 4.66; N, 4.54.

4-Aminonaphthalic-1,8-diethyl Ester (7a)

A mixture of 100 g of **7**, benzene (1 l), and 5 g of Pd catalyst was placed in a prepared high pressure apparatus (*vide ante*). The mixture was stirred constantly and heated at 125 °C for 1 h, cooled to room temperature, and treated as previously described. The filtrate, stripped of benzene, produced a brown gummy substance which dissolved in 700 ml carbon tetrachloride and resulted in the formation of a yellow precipitate when cooled to 0 °C. Filtration yielded 72 g (80%) of yellow crystals, m.p. 127–130 °C. Recrystallization from EtOH–H_2O (1:1) yielded 64.8 g (72%) of **7***a*, m.p. 132–132.5 °C; i.r. (Nujol) 1260 (C—O), 1740 (C═O), and 3380 cm^{-1} (NH_2); n.m.r. δ 1.38 (6H, t, methyl H), 4.38 (4H, q, methylene H), 4.60 (2H, s, amine H), 7.20–8.08 (5H, m, aromatic H).

Anal. Calcd. for $C_{16}H_{17}NO_4$ (287.34): C, 66.85; H, 5.96; N, 4.87. Found: C, 66.72; H, 5.96; N, 4.84.

4,5-Dinitronaphthalic-1,8-dimethyl Ester (8)

Methanol (3 l) containing 172.4 g of **5**, and dimethyl sulfate (114 ml) were refluxed and 91.2 g of potassium carbonate was added. After refluxing for 2 h, 22.8 g of potassium carbonate and 28.5 ml of dimethyl sulfate was added and the mixture refluxed for an additional 3 h and filtered while hot. The precipitate was washed once with methanol and 3 times with water and dried, yielding 180 g (90%), m.p. 247–249 °C; lit. m.p. 236–240 °C (2*b*); i.r. (KBr) 1270 (C—O), 1340 (NO_2), 1540 (NO_2), and 1715 cm^{-1} (C═O); n.m.r. δ 3.99 (6H, s, methyl), 8.28 (4H, AB pattern, aromatic H).

Anal. Calcd. for $C_{14}H_{10}N_2O_8$ (334.26): C, 50.30; H, 3.02; N, 8.38. Found: C, 50.20; H, 3.11; N, 8.33.

4,5-Diaminonaphthalic-1,8-dimethyl Ester (8a)

A mixture of 100 g of **8**, benzene (1 l), and 10 g of Pd catalyst was placed in a high pressure reaction apparatus and reduced as previously described. The reaction proceeded for 15 min at 75 °C. After cooling, the mixture was filtered and the dark green precipitate boiled in methanol, filtered hot, and the filtrate cooled to −4 °C. Filtration gave 45.5 g (55%) of light yellow-green crystals of 4,5-diaminonaphthalic-1,8-dimethyl ester (**8***a*) m.p. 213.5–215.0 °C; i.r. (Nujol) 1250 (C—O), 1680 (C═O), 3370 (NH_2), and 3400 cm^{-1} (NH_2); n.m.r. (on a HA-100, in DMSO-d_6): δ 3.68 (6H, s, methyl H), 6.38 (4H, s, amine H), 7.15 (4H, AB pattern, aromatic H).

Anal. Calcd. for $C_{14}H_{14}N_2O_4$ (274.30): C, 61.30; H, 5.15; N, 10.22. Found: C, 61.42; H, 4.97; N, 10.09.

4,5-Dinitronaphthalic-1,8-diethyl Ester (9)

Ethanol (250 ml), 17.3 g of **5**, and diethyl sulfate (9 ml) were refluxed and 5.25 g of potassium carbonate added and refluxed for 2 h. An additional 5.25 g of potassium carbonate and 9 ml of diethyl sulfate was added after a 2 h reflux, refluxing continued for an additional 3 h and filtered while hot. The light tan crystalline precipitate was washed several times with water and dried, yielding 11 g (50.7%) of 4,5-dinitronaphthalic-1,8-diethyl ester (**9**) m.p. 155–157 °C, lit. m.p. 156.5–157 °C (2*b*); i.r. (KBr) 1260 (C—O), 1350 (NO_2), 1545 (NO_2) and 1725 cm^{-1} (C═O); n.m.r. δ 2.48 (6H, t, methyl H), 4.42 (4H, q, methylene H), 8.28 (4H, AB pattern, aromatic H).

Anal. Calcd. for $C_{16}H_{14}N_2O_8$ (362.32): C, 53.04; H, 3.90; N, 7.73. Found: C, 52.96; H, 3.91; N, 7.56.

4,5-Diaminonaphthalic-1,8-diethyl Ester (9a)

A mixture of 50 g of **9**, 500 ml of benzene, and 5 g of Pd catalyst was reduced as previously described at 100 °C overnight. After filtering the mixture, the precipitate was dissolved in 700 ml of boiling ethanol and filtered for catalyst removal. Upon cooling, brown crystals were obtained which were dried to yield 15.9 g (39%), m.p. 166–167 °C, lit. m.p. 167.0–167.5 °C (2*b*); i.r. (Nujol), 1240 (C—O), 1690 (C═O), 3380 cm^{-1} (NH_2); n.m.r. δ 1.36 (6H, t, methyl H), 4.30 (4H, q, methylene H), 4.83 (4H, s, amine H), 7.10 (4H, AB pattern, aromatic H).

1. (*a*) F. ANSELM and F. ZUCKMAYER. Ber. **32**, 3283 (1899). (*b*) C. GRAEBE. Ann. **327**, 84 (1903). (*c*) M. OKAZAKI and N. ISHIKAWA. Yûki Gôsei Kagaku Kyôkai Shi, **14**, 398 (1956).
2. (*a*) F. SACHS and G. MOSEBACH. Ber. **44**, 2852 (1911). (*b*) I. HONDA and M. OKAZAKI. J. Soc. Org. Syn. Chem. Japan, **7**, 25 (1950). (*c*) M. OKAZAKI, T. TANAKA, and S. TANIGUCHI. Yûki Gôsei Kagaku Kyôkai Shi, **14**, 344 (1956). (*d*) M. M. DASHEVSKI. Zhur. Priklad Khim. **32**, 2749 (1959).
3. T. ISHII and Y. YAMAZAKI. Mem. Fac. Technol. Tokyo Metropol. Univ. **1**, 21 (1951).
4. (*a*) J. R. LACHER, K. ENSLEY, and A. TENGE. J. Org. Chem. **24**, 1347 (1959). (*b*) M. OKAZAKI, Y. SUHARA, and M. FUJIYAMA. Yûki Gôsei Kagaku Kyôkai Shi, **14**, 394 (1956).
5. M. OKAZAKI and I. ISHIKAWA. Yûki Gôsei Kagaku Kyôkai Shi, **14**, 398 (1956).
6. G. T. MORGAN and H. A. HARRISON. J. Soc. Chem. Ind. 413T (1930).
7. (*a*) S. KATO, H. HASHIMOTO, and H. SUGIYAMA. Yûki Gôsei Kagaku Kyôkai Shi, **14**, 723 (1956). (*b*) L. FRIEDMAN, D. L. FISHEL, and H. SCHECTER. J. Org. Chem. **30**, 1453 (1965).
8. R. H. CORNFORTH, J. W. CORNFORTH, and G. POPJÁK. Tetrahedron, **18**, 1351 (1962).
9. E. M. BICKOFF, R. L. LYMAN, A. L. LIVINGSTON, and A. N. BOOTH. J. Amer. Chem. Soc. **80**, 3969 (1958).
10. R. ADAMS and F. L. COHEN. Org. Syn. Coll. Vol. **1**, 240 (1944).
11. M. P. CAVA, K. E. MERKEL, and R. H. SCHLESSINGER. Tetrahedron, **21**, 3059 (1965).
12. H. J. RICHTER. J. Org. Chem. **21**, 619 (1956).