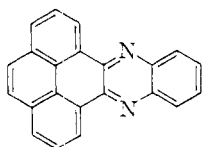
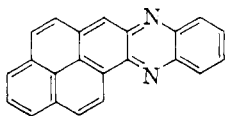


pyrene-4',5',2,3-quinoxaline, m.p. ca. 272°. Recrystallization from chlorobenzene yielded golden yellow needles, m.p. 276.8–277.4° (lit. m.p. 262°). Further evidence that this compound was the azine of pyrene-4,5-quinone rather than the azine of the unknown pyrene-1,2-quinone (VIII) was furnished by the infrared spectrum. Three major absorption bands were observed in the region of out-of-plane CH deformation vibrations at 832, 765, and 717 cm^{-1} . These may be assigned to 2,3, and 4 adjacent free H atoms, respectively. Since no absorption was observed in the 900–860 cm^{-1} region for one adjacent free H atom, structure VIII is excluded. Other major absorption peaks of the infra-



VII



VIII

red spectrum were observed at 3040, 1484, 1433, 1426, 1362, 1337, 1294, 1175, and 1097 cm^{-1} .

Anal. Calcd. for $\text{C}_{22}\text{H}_{12}\text{N}_2$: N, 9.21. Found: N, 8.99.

4-Formyl-5-carbomethoxyphenanthrene. The aldehyde-ester, m.p. 113–114° (lit. m.p. 111–112°) was prepared by the method of Badger and coworkers⁵ in 45% yield from the lactol of 4-formylphenanthrene-5-carboxylic acid isolated from the preceding periodate oxidations of pyrene. The infrared spectrum confirmed the structure of the free aldehyde-ester by the presence of two strong carbonyl peaks at 1720 and 1683 cm^{-1} . Other major absorption peaks in the infrared spectrum were observed at 3040, 2950, 2830, 2740, 1437, 1286, 1266, 1241, 1198, 1137, 1034, 842, 817, 806, 763, and 719 cm^{-1} .

Acknowledgment: The authors express their appreciation to the American Petroleum Institute for the grant which made this research possible.

UNIVERSITY PARK, PA.

[CONTRIBUTION NO. 890 FROM THE CHEMISTRY LABORATORIES OF INDIANA UNIVERSITY]

Thiocarbonyls. VII. Studies on *p*-Substituted Acetophenones¹

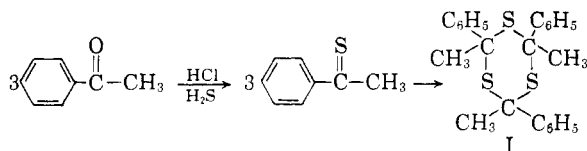
E. CAMPAIGNE, WM. BRADLEY REID, JR., AND JOHN D. PERA²

Received February 23, 1959

Several *p*-substituted acetophenones have been subjected to conditions under which acetophenone is known to give trithioacetophenone. *p*-Fluoro-, *p*-chloro-, *p*-bromo-, *p*-iodo-, and *p*-methylacetophenone all formed trimeric thiones. Trimers could not be obtained from *p*-ethyl- or *p*-phenylacetophenone. Compounds of unknown structure related to "anhydrotriacetophenone disulfide" were obtained from *p*-fluoro-, *p*-chloro-, *p*-bromo-, *p*-iodo-, and *p*-phenylacetophenone. *p*-Methyl- and *p*-ethylacetophenone on treatment with hydrogen sulfide produced oils which on distillation were converted to the corresponding 2,4-diarylthiophenes, a reaction characteristic of "anhydrotriacetophenone disulfide."

Although the reaction of acetophenone with hydrogen sulfide and hydrogen chloride was described more than sixty years ago by Baumann and Fromm,³ no work has appeared in the literature describing the reactions of substituted acetophenones. The work herein described is concerned with the reaction of some *p*-substituted acetophenones with hydrogen sulfide utilizing hydrogen chloride as catalyst. Baumann and Fromm³ allowed acetophenone to react with dry hydrogen sulfide and dry hydrogen chloride at 0° in alcoholic solution and obtained two compounds. Initially the

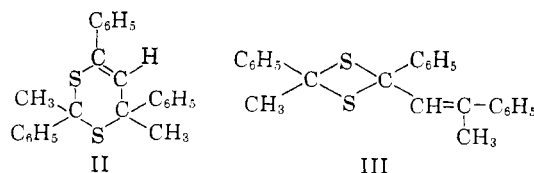
reaction formed a blue violet solution of monomeric thioacetophenone which rapidly faded to yield white crystalline trimer (I). Although theoretically there should be geometrical isomers of trithioacetophenone,⁴ only one isomer has been reported and no evidence was found for the existence of a second isomer in this work. When the mother liquor from the acetophenone reaction was allowed to stand at room temperature, Baumann and Fromm³ were able to isolate a white crystalline compound of formula $\text{C}_{24}\text{H}_{22}\text{S}_2$ which differed from the formula for trithioacetophenone by the elements of hydrogen sulfide. They proposed the structure II or III and called the compound "anhydrotriacetophenone disulfide."



(1) Presented before the Organic Division at the 134th meeting of the American Chemical Society, Chicago, Ill., September 1958. For paper VI of this series, see E. Campaigne and R. D. Moss, *J. Am. Chem. Soc.*, **76**, 1269 (1954).

(2) Taken in part from a thesis to be submitted by John D. Pera to Indiana University in partial fulfillment of the degree, Doctor of Philosophy, and in part from the thesis of Wm. Bradley Reid, Jr., submitted to Indiana University in partial fulfillment of the degree, Doctor of Philosophy, June 1946.

(3) E. Baumann and E. Fromm, *Ber.*, **28**, 895 (1895).

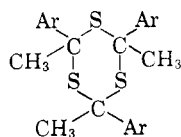


Campaigne⁵ was able to prepare the "anhydrotriacetophenone disulfide" in 57% yield by increasing the reaction temperature to room tem-

(4) E. Campaigne, *Chem. Revs.*, **39**, 31 (1946).

(5) E. Campaigne, *J. Am. Chem. Soc.*, **66**, 684 (1944).

TABLE I
PROPERTIES OF SUBSTITUTED TRITHIOACETOPHENONES



| Ar | M.P. | Yield, % | Formula | % S | | Mol. Wt. | |
|---|-----------|-------------|--|--------|-------------------|----------|--------------------|
| | | | | Calcd. | Found | Calcd. | Found ^a |
| <i>p</i> -FC ₆ H ₄ | 151-152 | 44 | C ₂₄ H ₂₁ F ₃ S ₃ | 20.8 | 21.0 ^b | 463 | 462 |
| <i>p</i> -ClC ₆ H ₄ | 165-166 | 56 | C ₂₄ H ₂₁ Cl ₃ S ₃ | 18.8 | 19.3 | 512 | 514 |
| <i>p</i> -BrC ₆ H ₄ | 193-193.5 | 54 | C ₂₄ H ₂₁ Br ₃ S ₃ | 14.9 | 14.5 | 645 | 640 |
| <i>p</i> -IC ₆ H ₄ | 186.5-188 | 47 | C ₂₄ H ₂₁ I ₃ S ₃ | — | — ^c | 786 | 788 |
| <i>p</i> -CH ₃ C ₆ H ₄ | 122-122.5 | 37 | C ₂₇ H ₃₀ S ₃ | 21.3 | 21.2 | 451 | 448 |

^a Cryoscopically in benzene. ^b Calcd.: C, 62.3; H, 4.6. Found: C, 61.7; H, 4.7. ^c Calcd.: C, 36.7; H, 2.7. Found: C, 36.9; H, 2.9.

TABLE II
PROPERTIES OF THE "ANHYDRO" COMPOUNDS
(*p*-XC₆H₄)₃C₆H₇S₂

| <i>p</i> -X | M.P. | Yield, ^a % | Formula | Analysis, % S | |
|---|-------------|--------------------------|--|---------------|-------------------|
| | | | | Calcd. | Found |
| <i>p</i> -F | 132-133.5 | 43 | C ₂₄ H ₁₉ F ₃ S ₂ | 15.0 | 15.1 ^b |
| <i>p</i> -Cl | 161.5-162.5 | 21 | C ₂₄ H ₁₉ Cl ₃ S ₂ | 13.6 | 13.1 |
| <i>p</i> -Br | 166.5-167.5 | 17 | C ₂₄ H ₁₉ Br ₃ S ₂ | 10.6 | 10.2 |
| <i>p</i> -I | 163-165 | 10 | C ₂₄ H ₁₉ I ₃ S ₂ | — | — ^c |
| <i>p</i> -C ₆ H ₅ | 172 dec. | 81 | C ₄₂ H ₃₄ S ₂ | 10.6 | 10.9 |

^a By reaction conditions B. ^b Calcd. for C, 67.3; H, 4.5. Found: C, 68.1; H, 4.9. ^c Calcd. for C, 38.2; H, 2.6. Found: C 38.5; H, 2.8.

perature. He also showed that the compound could be converted to 2,4-diphenylthiophene by reaction with copper chromite, as well as by pyrolysis as had been described earlier.³ The "anhydro" compound melted to a blue liquid, a characteristic which holds for all the "anhydro" type compounds prepared in this work. The trimeric acetophenones dissociate to the purple monomers when heated above their melting points.

The acid catalyzed reactions of the *p*-haloacetophenones with hydrogen sulfide proceeded in the same manner as acetophenone, so that the trimers as well as the "anhydro" compounds have been isolated. At 4-5°, the yield of *p*-chloro and *p*-bromo trimers exceeded that of the "anhydro" compounds but when the reactions were allowed to proceed at room temperature, the amounts of "anhydro" compound obtained exceeded that of the trimers. The "anhydro" derivatives of the *p*-haloacetophenones were all readily converted to the corresponding 2,4-dihalophenylthiophenes by the method previously described.⁵

With *p*-methylacetophenone, the trimer was obtained in 31% yield, but the "anhydro" compound was not isolated. The oily product of the reaction yielded a tar after distillation from which could be isolated 2,4-di-*p*-tolylthiophene, undoubtedly formed by the pyrolysis of the "anhydrotri-*p*-methylacetophenone disulfide."⁵ In the case of *p*-ethylacetophenone, neither the trimer nor

the "anhydro" compound was isolated. Here again, however, the residue of a distillation of an oily product yielded a tar from which was isolated 2,4-di-(*p*-ethylphenyl)thiophene.

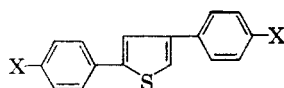
With *p*-phenylacetophenone, the trimer was not isolated, but an 81% yield of the "anhydrotri-*p*-phenylacetophenone disulfide" was obtained. This compound was converted to the 2,4-*p*-xenylthiophene with copper chromite using the method described by Campaigne.⁵

The new substituted trithioacetophenones and their properties are listed in Table I.

The properties of the anomalous "anhydro" compounds obtained along with the trithioacetophenones are listed in Table II.

The 2,4-diarylthiophenes were identified by analysis, conversion to characteristic mercuri-chloride adducts, and ultraviolet spectroscopy. 2,4-Diarylthiophenes exhibit a characteristic strong peak at about 260 mμ.⁵ The absorption spectra of the 2,4-diarylthiophenes reported in Table III were determined in ethanol on a Beckman DK1 double beam recording spectrograph, using 1.00 cm. silica cells.

The principal, λ_{max} and ε_{max} of the substituted compounds, illustrates nicely the effects of substituents on a conjugated aromatic system. For example, in the series where X = F (λ_{max} 256), H (λ_{max} 259), alkyl (λ_{max} 262), the bathochromic shift of 3 mμ for each change of substituent undoubtedly

TABLE III
 PROPERTIES OF 2,4-DIARYLTHIOPHENES


| X | M.P. | Yield, % | Formula | λ_{\max} | | Analysis, % S | |
|-------------------------------|-------------|-------------|-------------------------------------|------------------|-------------------|---------------|-------------------|
| | | | | Millimicrons | ϵ_{\max} | Calcd. | Found |
| H | 120-121.5 | 83 | C ₁₆ H ₁₂ S | 259 | 31,700 | 13.6 | 13.5 |
| F | 124-124.5 | 82 | C ₁₆ H ₁₀ FS | 256 | 30,800 | 11.8 | 11.7 ^a |
| Cl | 139-140 | 80 | C ₁₆ H ₁₀ ClS | 264 | 38,300 | 10.5 | 10.2 |
| Br | 173.5-174.5 | 50 | C ₁₆ H ₁₀ BrS | 266 | 45,000 | 8.1 | 8.1 |
| I | 250-251 | 72 | C ₁₆ H ₁₀ IS | 272 | 45,800 | 6.6 | 6.3 ^b |
| CH ₃ | 145-145.5 | — | C ₁₅ H ₁₆ S | 262 | 35,100 | 12.1 | 12.1 |
| C ₂ H ₅ | 109-110 | — | C ₂₀ H ₂₀ S | 262 | 28,300 | 11.0 | 11.3 |
| C ₆ H ₅ | 295-296 | — | C ₂₆ H ₂₀ S | 289 | — ^c | 10.6 | 10.9 |

^a Calcd. for C, 70.6; H, 3.7. Found: C, 70.7; H, 3.8. ^b Calcd. for C, 39.4; H, 2.1. Found: C, 39.9; H, 2.2. ^c Slightly soluble in ethanol.

reflects the influence of I effects on the spectrum. The relatively small hypsochromic shift of the fluoro-derivative from the unsubstituted system is due to the counterbalancing bathochromic effects of halogens,⁶ attributed to interaction between unshared electrons of the substituent and the aromatic system. This is clearly shown in the series where X = F (λ_{\max} 256), Cl (λ_{\max} 264), Br (λ_{\max} 266), I (λ_{\max} 272). The ϵ_{\max} values also show a decreasing transition energy. The $\Delta\lambda$ values compare quite closely to similar values in the halogenated benzene series.⁶ The pair X = CH₃ (ϵ_{\max} 35,100), C₂H₅ (ϵ_{\max} 28,300) shows the expected decrease in ϵ_{\max} on increasing the size of the alkyl group.⁷

EXPERIMENTAL

The *p*-methyl-, *p*-phenyl-, *p*-chloro-, and *p*-bromoacetophenones were purchased from Distillation Products Industries. Hydrogen sulfide (purified) and hydrogen chloride were obtained from cylinders purchased from The Matheson Co., Inc.

p-Ethylacetophenone was synthesized by the method described by Allen⁸ for the synthesis of aceto-*p*-cymene. *p*-Ethylacetophenone had a b.p. of 133-134° at 21 mm. and was obtained in 46.7% yield. *p*-Iodoacetophenone was also synthesized by a Friedel-Craft reaction but in order to minimize the decomposition of the iodo compounds to free iodine the modification of Kimura⁹ was used in which a mixture of acetyl chloride and iodobenzene was added to finely divided aluminum chloride suspended in carbon disulfide. The yield of *p*-iodoacetophenone, m.p. 86-87°, was 61% of theoretical.

p-Fluoroacetophenone.¹⁰ A 1-l. flask equipped with condenser and drying tube, stirrer and dropping funnel was charged with 47.1 g. (0.49 mole) of fluorobenzene (Distillation Products Industries), 295 ml. of dry carbon disulfide, and 195.5 g. (1.5 moles) of pulverized anhydrous aluminum chloride. The mixture was treated with 42.1 g. (0.41 mole) of acetic anhydride added dropwise over a period of 20 min.

with cooling. The reaction was then refluxed for 2 hr. while hydrogen chloride gas was evolved. The carbon disulfide was removed by distillation and the residue added to cracked ice. After extraction of the water-oil mixture and drying of the ether solution, 42.3 g. (68% yield) of *p*-fluoroacetophenone, b.p. 73° at 4 mm., was obtained by vacuum distillation.

Examination of the literature revealed conflicting reports concerning the boiling point of *p*-fluoroacetophenone,¹¹ so to insure the purity of the product, the fraction above was distilled through a column and the bulk of the liquid distilled at 199°, n_D^{25} 1.5090. The column was 24 in. long, 0.5 in. in diameter and packed with glass helices. It was provided with an electrically heated jacket and the still head was of the total condensation variable take-off type. Cooling curves of this fraction and lower boiling fractions were obtained using a copper-constantan two-junction thermocouple and a Brown recorder. The fraction boiling at 199° had a freezing point of 4.0° and did not contain any isomers.

Reactions of p-haloacetophenones with hydrogen sulfide. All of the *p*-haloacetophenones were treated in a similar manner. The reaction of *p*-chloroacetophenone is characteristic.

A. A stirred solution of 15 g. (0.097 mole) of *p*-chloroacetophenone in 100 ml. of 95% ethanol was treated with dry hydrogen chloride gas added at the rate of 30 g. per hr. for 1 hr. while cooling with an ice bath. The temperature was then lowered to 5° and dry hydrogen sulfide and hydrogen chloride gases were passed into the solution at rates of 15 g. and 30 g. per hr., respectively. The solution immediately acquired a purple color which deepened as the reaction continued. After 45 min. a white precipitate appeared and the amount of solid increased during the course of the reaction. After 3 hr., the reaction was stopped and 9.2 g. (56%) of purple-tinged tri-*p*-chlorothioacetophenone was obtained by filtration. On standing in the refrigerator for 2 days, the mother liquor precipitated an additional 1.63 g. of white solid. When this solid was fractionally crystallized from acetone, a small amount of "anhydrotri-*p*-chloroacetophenone disulfide" was obtained in addition to the tri-*p*-chlorothioacetophenone. An additional small amount of the "anhydro" compound was isolated from the original mother liquor after several days standing at room temperature. The tri-*p*-chlorothioacetophenone was recrystal-

(6) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

(7) E. A. Braude, *Ann. Rept. Prog. Chem.*, **42**, 105-30 (1945).

(8) C. F. H. Allen, *Org. Syntheses, Coll. Vol. 2*, 3 (1943).

(9) W. Kimura, *Ber.*, **67B**, 394 (1934).

(10) R. E. Lutz *et al.*, *J. Org. Chem.*, **12**, 617 (1947).

(11) (a) G. Schiemann and R. Pillarsky, *Ber.*, **64**, 1340 (1931); (b) D. P. Evans, V. G. Morgan, and F. B. Watson, *J. Chem. Soc.*, 1167 (1935); (c) M. W. Renoll, *J. Am. Chem. Soc.*, **68**, 1159 (1946); (d) N. P. Buu-Hoï, N. Hoan, and P. Jacquignon, *Rec. trav. chim.*, **68**, 781 (1949); (e) W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **35**, 488 (1957).

lized three times from cyclohexane and three times from acetone to yield fine white needles, m.p. 165–166°. The melted liquid turned purple at 185°.

The "anhydrotri-*p*-chloroacetophenone disulfide" was recrystallized twice from cyclohexane to white blocky crystals. The solid turned blue on melting.

B. A stirred solution of 25 g. (0.16 mole) of *p*-chloroacetophenone in 250 ml. of 95% ethanol was treated with dry hydrogen chloride and dry hydrogen sulfide gases at rates of 30 g. and 15 g. per hr., respectively, with the temperature maintained between 10 and 15°. After 30 min. the reaction became purple and after 3.5 hr. a white solid appeared. The reaction was continued for an additional 1.5 hr. and then was filtered. A yield of 5.3 g. of solid was obtained. When this solid was fractionally crystallized from acetone, 2.98 g. (11%) of tri-*p*-chlorothioacetophenone, m.p. 165–166°, was obtained.

After standing at room temperature, the original mother liquor had become red-brown in color and had precipitated 11.2 g. of solid. When this material was fractionally crystallized from acetone, 5.47 g. (21%) of "anhydrotri-*p*-chloroacetophenone disulfide" melting at 161.5–162.5° was obtained.

The mixture of products obtained with *p*-iodoacetophenone would not separate by fractional crystallization and it was necessary to extract the trimer from the mixture with cold benzene for several hours. Both the trimer and the "anhydro" compound were purified by crystallization from dimethyl formamide-ethanol solution.

Tri-p-methylthioacetophenone. A stirred solution of 26.8 g. (0.20 mole) of *p*-methylacetophenone in 300 ml. of 95% ethanol was treated with dry hydrogen sulfide and dry hydrogen chloride gases added at rates of 94 and 27 g. per hr., respectively. The temperature was maintained below –5° and after 30 min. the reaction became purple. The color intensified to a purple-black and after 5 hr. a purple, vile-smelling resin had collected on the stirrer shaft. The solvent was decanted and after the resin was triturated with 50 ml. of 95% ethanol while intermittently warming and cooling, 16.5 g. (54%) of white powder was obtained. After recrystallizing twice from a 1:1 acetone-ethanol mixture, 11 g. (37%) of the tri-*p*-methylthioacetophenone was obtained.

2,4-Di-p-tolylthiophene. A stirred solution of 67 g. (0.5 mole) of *p*-methylacetophenone in 400 ml. of 95% ethanol was treated with dry hydrogen sulfide and dry hydrogen chloride gases added at rates of 94 and 36 g. per hr., respectively. The temperature was maintained between –5° and –1°. After 1 hr., the solution became purple and in 5 hr. a deep purple resin had deposited on the stirring shaft. After the solvent had been removed by decantation, the resinous material was triturated with alcohol, but crystallization could not be effected. Attempted crystallization from acetone gave a yellow oil which upon distillation yielded a purple oil, b.p. 97–100° at 2 mm., which was probably the monomeric *p*-methylthioacetophenone. The residue from the distillation, a deep brown tar, was repeatedly recrystallized from benzene and 95% ethanol and finally yielded micalike plates of 2,4-di-*p*-tolylthiophene.

The 2,4-di-*p*-tolylthiophene was converted to 2,4-di-*p*-

tolyl-5-chloromercurithiophene by the method of Bogert and Herrera.¹² The compound crystallized from alcohol as white, silky needles, m.p. 212–214°.

Anal. Calcd. for C₁₈H₁₅HgS₂Cl: S, 6.42. Found: S, 6.39.

Reaction of p-ethylacetophenone with hydrogen sulfide. A stirred solution of 37 g. (0.25 mole) of *p*-ethylacetophenone in 300 ml. of 95% ethanol was treated at –10° with dry hydrogen sulfide and dry hydrogen chloride gases added at rates of 94 g. and 22 to 27 g. per hr., respectively. After 16 hr., the purple resinous material that had collected in the reaction flask was separated by decantation. Since crystallization could not be effected the yellow oil resulting from treatment with acetone-alcohol, mixture was vacuum distilled. The bulk of the yellow oil decomposed to a dark brown tar and hydrogen sulfide was evolved. Repeated fractional crystallization of the tar from benzene-alcohol mixture yielded 2 g. (7.7%) of yellow powder. When this was treated with Norit and further recrystallized, 1.2 g. (4.6%) of a white crystalline 2,4-di(*p*-ethylphenyl)thiophene was obtained.

The 2,4-di(*p*-ethylphenyl)thiophene was converted to 2,4-di(*p*-ethylphenyl)-5-chloromercurithiophene by the method of Bogert and Herrera,¹² m.p. 185–186°.

Anal. Calcd. for C₂₀H₁₅HgS₂Cl: S, 6.08. Found: S, 6.00.

"Anhydrotri-p-phenylacetophenone disulfide." A suspension of 4.9 g. (0.025 mole) of *p*-phenylacetophenone in 300 ml. of 95% ethanol was cooled to –12° and then treated with dry hydrogen sulfide at the rate of 68 g. per hr. and with dry hydrogen chloride at such a rate as to maintain the temperature of the suspension below –5°. After 2 hr., the reaction was faintly purple; after 5 hr., deep purple; and at the end of 5.75 hr. there was an instantaneous solution of the suspended material. The solution, which was now purple-black, was treated an additional 3 hr. during which time a white precipitate appeared. The precipitate, after filtration, washing with alcohol and drying, amounted to 4.07 g. (81%), m.p. 157–160°. After recrystallization twice from benzene-alcohol mixture, 1 g. (20%) of white powdery "anhydrotri-*p*-phenylacetophenone disulfide" was obtained, m.p. 172° dec.

2,4-Diarythiophenes. All of the "anhydro" compounds have been converted to the 2,4-diarythiophenes using the method described by Campaigne.⁸ The reaction of "anhydrotri-*p*-chloroacetophenone disulfide" is typical.

Three grams of "anhydrotri-*p*-chloroacetophenone disulfide" was mixed with 40 ml. of dry xylene and 10 g. of finely ground copper chromite. After 3 hr. refluxing, the mixture was suction filtered and the residue washed twice with 15 ml. portions of xylene heated to about 60°. The combined filtrate and washings were evaporated *in vacuo* and the brown, crystalline solid was decolorized with Darco and recrystallized twice from ethyl alcohol. The yield of white, micalike plates of 2,4-di-*p*-chlorophenylthiophene was 1.52 g. (80%), m.p. 139–140°.

BLOOMINGTON, IND.

(12) M. T. Bogert and P. P. Herrera, *J. Am. Chem. Soc.*, **45**, 238 (1923).