| Compound *t*-alkyl phenols | M. p., °C. | B. p., °C. | Phenol coefficient | Analyses, % Calcd. C | Calcd. H | Found C | Found H |
|---|---|---|---|---|---|---|---|
| I *p*-(2,2,3-Trimethyl)propylphenol $(CH_3)_2CHC(CH_3)_2C_6H_4OH$ | 105 | | 45 | 80.85 | 10.16 | 80.72 | 10.02 |
| II *p*-*t*-Heptylphenol $(CH_3)_2(C_4H_9)CC_6H_4OH$ | | 280 (760 mm.) | | 81.18 | 10.49 | 81.35 | 10.70 |
| Cycloalkyl phenols | | | | | | | |
| III *p*-(2-Methyl)-cyclohexylphenol $CH_3C_6H_{10}C_6H_4OH(2)$ | 107 | | 50 | 82.04 | 9.54 | 82.37 | 9.71 |
| IV *p*-(3-Methyl)-cyclohexylphenol $CH_3C_6H_{10}C_6H_4OH(3)$ | 101 | | 105 | 82.04 | 9.54 | 82.22 | 9.60 |
| V *p*-(4-Methyl)-cyclohexylphenol[a] $CH_3C_6H_{10}C_6H_4OH(4)$ | 108 | | 70 | | | | |
| Alkyl-aryl phenols | | | | | | | |
| VI *p*-Benzylphenol[b] $C_6H_5CH_2C_6H_4OH$ | 82 | | | | | | |
| VII *p*-($\alpha$-Phenylethyl)phenol $C_6H_5CH(CH_3)C_6H_4OH$ | 64 | | 40 | | | | |
| VIII 2-Phenyl-2-(4-hydroxy)[c]phenylbutane $C_6H_5C(CH_3)(C_2H_5)C_6H_4OH$[6] | | 145–148 (2.5 mm.) | 33 | 84.90 | 8.02 | 85.00 | 8.22 |
| IX 2-Methyl-3-phenyl-3-(4-hydroxy)phenylbutane $C_6H_5C(CH_3)(CH(CH_3)_2)C_6H_4OH$[5] | | 157–160 (3 mm.) | | 84.94 | 8.39 | 85.12 | 8.51 |

[a] Meyer and Bernhauser, *Monatsh.*, **54**, 721 (1929). [b] Paternò, *Gazz. chim. ital.*, **2**, 1 (1872); Fileti, *ibid.*, **3**, 121 (1873); *Ber.*, **6**, 757 (1873); Rennie, *J. Chem. Soc.*, **41**, 34 (1882); Zincke and Walter, *Ann.*, **334**, 373 (1904); Perkin and Hodgkinson, *J. Chem. Soc.*, **37**, 725 (1880). [c] Pickard and Littlebury, *ibid.*, **89**, 469 (1906); Stoermer and Kippe, *Ber.*, **36**, 4012 (1903); Koenigs and Carl, *ibid.*, **24**, 3894 (1891).

solutions at 37°) using *Staphylococcus aureus*. The authors desire to thank Dr. Wm. A. Feirer of Sharp and Dohme, Philadelphia, for performing these determinations.

## Summary

1. The Liebmann method of condensing alcohols with phenols in the presence of zinc chloride has been extended to include *t*-hexyl, *t*-heptyl and *t*-octyl alcohols, giving in the first two cases the corresponding substituted phenols, while *p*-*t*-butylphenol was obtained from 2,2,4-trimethylpentanol-4.

2. Application of the same method to aromatic alcohols led to positive results in all cases, encountering a rearrangement in the case of $\beta$-phenylethyl alcohol.

3. Methylcyclohexanols also could be condensed with phenols by this method, with the *t*-octylcyclohexanol again giving *p*-*t*-butylphenol, instead of the expected *t*-octylcyclohexylphenol.

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[CONTRIBUTION FROM THE UNIVERSITY OF KANSAS]

# Some Alkyl Derivatives of Certain Aryl Substituted Thiazolidones[1]

BY JOHN A. DAVIS AND F. B. DAINS

In a recent paper by Eberly and Dains[2] it was shown that the alkylation of the mono-aryl thiazolidones, $\overset{1}{S}\!-\!\overset{2}{C}(NHR)\!=\!\overset{3}{N}\!-\!\overset{4}{C}O\!-\!\overset{5}{C}H_2$, gave two isomeric products, one of the 2-aryl-2-alkylthiazolidone and the other the 2-aryl-3-alkylthiazolidone; results not in harmony with the structure assigned by Beckurts and Frerich,[3] *viz.*, 2-alkyl-3-arylthiazolidone. This paper is a further study of nine aryl substituted thiazolidones in order to determine the structure of the alkylation products and to determine the effect both of the aryl groups and of different alkyl halides on the amount of the two possible isomers.

A. Two methods were used in preparing the thiazolidones.

(1) **From $RNHCOCH_2Cl$ and KSCN.**—Equal molecular quantities of the two were dissolved in alcohol and refluxed for one to five hours. In certain cases this method gave a tarry product and a poor yield.

(1) From a thesis presented to the Graduate School of the University of Kansas by John A. Davis in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Eberly and Dains, THIS JOURNAL, **55**, 3859 (1933).

(3) Beckurts and Frerich, *Arch. Pharm.*, **253**, 233–265 (1915).

(2) **From the Mono-aryl Thiourea.**—This when refluxed in alcohol for one to three hours with equal molecular quantities of pyridine and ethyl chloroacetate usually gave a product free from tar.

B. **Preparation of the Sodium Salt.**—The thiazolidones were soluble in hot 5% sodium hydroxide and on cooling the sodium salts crystallized from the solution.

C. **Alkylation** occurred when an alcohol solution of the sodium salt was heated with an alkyl halide. The 2-alkyl thiazolidone was separated from the 3-alkyl derivatives by the solubility of the former in dilute hydrochloric acid.

Hydrolysis of these alkyl substituted thiazolidones usually resulted in complete rupture of the ring, but it has been found that the 5-benzal derivatives are much more stable, hydrolysis usually yielding 5-benzal-2,4-thiazoledione or 5-benzal-3-alkyl-2,4-thiazoledione, thus affording a convenient method of determining the nature of the group at 2. Hydrolysis was carried out by boiling the benzal derivative in alcoholic hydrochloric acid for five to twenty-five hours.

The benzal derivatives were prepared by a few minutes of heating of a saturated alcohol solution of the thiazolidone and benzaldehyde with a trace of alkali.

## Experimental

Following the general methods outlined above, thiazolidones were prepared from the following amines: *o*- and *p*-phenetidines, *o*-, *m*- and *p*-anisidines, pseudocumidine, 2-amino-*p*-cymene, 2,4-diiodoaniline and *p*-iodoaniline. Each of these was then ethylated by heating an alcohol solution of the corresponding sodium salt with ethyl iodide for two or three hours. The alcohol and excess ethyl iodide were then removed with steam and the oily residue dissolved in ether and repeatedly extracted with dilute hydrochloric acid (5–10%). Neutralization of the acid solution caused the separation of the 2-alkyl-2-aryl compound, while evaporation of the ether solution yielded the isomeric 2-aryl-3-alkyl derivative. The latter derivative was also synthesized in each case by two to three hours of heating of an alcohol solution of equal molecular quantities of ethyl chloroacetate, pyridine and the corresponding N-alkyl-N'-aryl thiourea. Ethylation in each case, with the exception of the thiazolidones from pseudocumidine, 2-amino-*p*-cymene and 2,4-diiodoaniline produced two isomeric products: one the 2-ethyl-2-aryl-4-thiazolidone, and the other the 2-aryl-3-ethyl compound. With pseudocumidine and 2-amino-*p*-cymene only the 2-alkyl-2-aryl derivatives were isolated, while with 2,4-diiodoaniline, only the 2-aryl-3-ethyl derivative was isolated.

The following table gives the percentage yields of the isomers obtained on ethylation of the thiazolidones.

| Thiazolidone from | % Yield of 2-ethyl-2-aryl compound | % Yield of 3-ethyl-2-aryl compound |
|---|---|---|
| *o*-Phenetidine | 68 | 1 |
| *p*-Phenetidine | 50 | 1 |
| *o*-Anisidine | 65 | 0.6 |
| *m*-Anisidine | 46 | 6 |
| *p*-Anisidine | 55 | 1 |
| Pseudocumidine | 56 | 0.0 |
| 2-Amino-*p*-cymene | 65 | 0.0 |
| *p*-Iodoaniline | 74 | 16 |
| 2,4-Diiodoaniline | 0 | 85 |

The 2-ethyl-2-aryl compounds obtained from *o*- and *p*-anisidine, *p*-phenetidine and pseudocumidine were identical with the corresponding compounds obtained by Beckurts and Frerich[3] and to which they assigned the erroneous structure, 2-ethyl-imino-3-aryl-4-thiazolidones. However, Beckurts and Frerich in their investigation had overlooked the occurrence of the 2-aryl-3-ethyl isomers.

The sodium salt of the thiazolidone from *p*-iodoaniline was treated with various alkyl halides and the following percentage yields of isomers were obtained.

| Alkyl halide | % Yield of 2-alkyl-2-aryl compound | % Yield of 3-alkyl-2-aryl compound |
|---|---|---|
| Methyl iodide | 60 | 7.5 |
| Ethyl iodide | 74 | 16 |
| Amyl iodide | 34 | 4 |
| Benzyl chloride | 60 | 4 |

Proof of structure was obtained in each case by acid hydrolysis of the corresponding 5-benzal derivative using a mixture of equal volumes of alcohol and concentrated hydrochloric acid. The 2-alkyl-2-aryl compounds gave 5-benzal-2,4-thiazoledione[4] and a secondary amine while the 2-aryl-3-alkyl compounds yielded a 5-benzal-3-alkyl-2,4-thiazoledione and the aryl amine. The thiazolediones separated during hydrolysis from the hot solutions, while the amines were obtained by neutralization of the acid after removal of the alcohol.

(4) Ref. 2, p. 3861.

The thiazolidones were also found to condense with *p*-nitrosodimethylaniline in the same manner as with benzaldehyde. A saturated alcohol solution of 2-ethyl-2-*p*-iodophenylamino-4-thiazolidone when heated with *p*-nitrosodimethylaniline and a trace of alkali gave a dark yellow crys-

PROPERTIES AND ANALYSES

| No. | Thioureas | Source | Formula | M. p., °C. | % Nitrogen Calcd. | Found |
|---|---|---|---|---|---|---|
| I | N-Ethyl-N′-*p*-ethoxyphenyl | [5] | $C_{11}H_{16}ON_2S$ | 112 | 12.50 | 12.42 |
| II | N-Ethyl-N′-*o*-ethoxyphenyl | [5] | $C_{11}H_{16}ON_2S$ | 88 | 12.50 | 12.45 |
| III | N-Ethyl-N′-pseudocumyl | [6] | $C_{12}H_{18}N_2S$ | 138 | 12.61 | 12.45 |
| IV | N-Methyl-N′-pseudocumyl | [7] | $C_{11}H_{16}N_2S$ | 179 | 13.46 | 13.40 |
| V | N-Ethyl-N′-*o*-methoxyphenyl | [5] | $C_{10}H_{14}ON_2S$ | 77 | 13.33 | 13.28 |
| VI | N-Ethyl-N′-*p*-methoxyphenyl | [5] | $C_{10}H_{14}ON_2S$ | 147 | 13.33 | 13.42 |
| VII | N-Ethyl-N′-*m*-methoxyphenyl | [5] | $C_{10}H_{14}ON_2S$ | 112 | 13.33 | 13.18 |
| VIII | Mono-*p*-cymyl | [8] | $C_{11}H_{16}N_2S$ | 152 | 13.46 | 13.40 |
| IX | N-Ethyl-N′-*p*-cymyl | [5] | $C_{13}H_{20}N_2S$ | 126 | 11.86 | 11.71 |
| X | N-Ethyl-N′-2,4-diiodophenyl | [9] | $C_9H_{10}I_2N_2S$ | 164 | 6.49 | 6.34 |
| XI. | N-Methyl-N′-*p*-iodophenyl | [10] | $C_8H_9IN_2S$ | 171 | 9.59 | 9.49 |
| XII | N-Ethyl-N′-*p*-iodophenyl | [5] | $C_9H_{11}IN_2S$ | 147.5 | 9.15 | 9.13 |
| XIII | N-Amyl-N′-*p*-iodophenyl | [11] | $C_{12}H_{17}IN_2S$ | 130 | 8.05 | 7.91 |
| XIV | N-Benzyl-N′-*p*-iodophenyl | [12] | $C_{14}H_{13}IN_2S$ | 149 | 7.61 | 7.52 |
| | 4-Thiazolidone | | | | | |
| XV | 2-*p*-Ethoxyphenylimino-3-ethyl- | | $C_{13}H_{16}O_2N_2S$ | 93 | 10.60 | 10.58 |
| XVI | 2-*o*-Ethoxyphenylamino-[13] | | $C_{11}H_{12}O_2N_2S$ | 172 | 11.86 | 11.80 |
| XVII | 2-Ethyl-2-*o*-ethoxyphenylamino- | | $C_{13}H_{16}O_2N_2S$ | 99 | 10.60 | 10.58 |
| XVIII | 2-*o*-Ethoxyphenylimino-3-ethyl- | | $C_{13}H_{16}O_2N_2S$ | 79 | 10.60 | 10.48 |
| XIX | 2-Pseudocumylimino-3-ethyl- | | $C_{14}H_{18}ON_2S$ | 77 | 10.68 | 10.53 |
| XX | 2-Pseudocumylimino-3-methyl-[14] | | $C_{13}H_{16}ON_2S$ | 91 | 11.29 | 11.27 |
| XXI | 2-*o*-Methoxyphenylimino-3-ethyl- | | $C_{12}H_{14}O_2N_2S$ | 114 | 11.20 | 11.10 |
| XXII | 2-*p*-Methoxyphenylimino-3-ethyl- | | $C_{12}H_{14}O_2N_2S$ | 83 | 11.20 | 11.26 |
| XXIII | 2-*m*-Methoxyphenylamino-[13] | | $C_{10}H_{10}O_2N_2S$ | 165 | 12.61 | 12.65 |
| XXIV | 2-Ethyl-2-*m*-methoxyphenylamino- | | $C_{12}H_{14}O_2N_2S$ | 112 | 11.20 | 10.89 |
| XXV | 2-*m*-Methoxyphenylimino-3-ethyl- | | $C_{12}H_{14}O_2N_2S$ | 65–66 | 11.20 | 11.22 |
| XXVI | 2-*p*-Cymylamino-[15] | | $C_{13}H_{16}ON_2S$ | 174 | 11.29 | 11.28 |
| XXVII | 2-Ethyl-2-*p*-cymylamino- | | $C_{15}H_{20}ON_2S$ | 85 | 10.14 | 10.04 |
| XXVIII | 2-*p*-Cymylimino-3-ethyl- | | $C_{15}H_{20}ON_2S$ | 64 | 10.14 | 10.01 |
| XXIX | 2-(2,4-Diiodophenylamino)-[16] | | $C_9H_6I_2ON_2S$ | 233 | 6.31 | 6.35 |
| XXX | 2-(2,4-Diiodophenylimino)-3-ethyl | | $C_{11}H_{10}I_2ON_2S$ | 173 | 5.94 | 5.90 |
| XXXI | 2-*p*-Iodophenylamino- | | $C_9H_7ION_2S$ | 226 | 8.81 | 8.78 |
| XXXII | 2-Methyl-2-*p*-iodophenylamino- | | $C_{10}H_9ION_2S$ | 207 | 8.44 | 8.42 |
| XXXIII | 2-*p*-Iodophenylimino-3-methyl- | | $C_{10}H_9ION_2S$ | 152 | 8.44 | 8.46 |
| XXXIV | 2-Ethyl-2-*p*-iodophenylamino- | | $C_{11}H_{11}ION_2S$ | 116 | 8.09 | 8.02 |
| XXXV | 2-*p*-Iodophenylimino-3-ethyl- | | $C_{11}H_{11}ION_2S$ | 103 | 8.09 | 8.15 |
| XXXVI | 2-Amyl-2-*p*-iodophenylamino- | | $C_{14}H_{17}ION_2S$ | 116 | 7.22 | 7.22 |
| XXXVII | 2-*p*-Iodophenylimino-3-amyl- | | $C_{14}H_{17}ION_2S$ | 57 | 7.22 | 7.17 |
| XXXVIII | 2-Phenylimino-3-amyl-[17] | | $C_{14}H_{18}ON_2S$ | Oil | 10.68 | 10.74 |
| XXXIX | 2-Benzyl-2-*p*-iodophenylamino- | | $C_{16}H_{13}ION_2S$ | 176 | 6.87 | 6.85 |
| XL | 2-*p*-Iodophenylimino-3-benzyl- | | $C_{16}H_{13}ION_2S$ | 137 | 6.87 | 6.82 |
| XLI | 2-Benzylimino-3-benzyl-[18] | | $C_{17}H_{16}ON_2S$ | 74 | 9.46 | 9.42 |

(5) Prepared from ethylamine and the corresponding substituted phenyl isothiocyanate.

(6) From ethyl isothiocyanate and pseudocumidine.

(7) From methyl isothiocyanate and pseudocumidine.

(8) Prepared by evaporation to dryness of a water solution of aminocymene hydrochloride and potassium thiocyanate.

(9) From ethyl isothiocyanate and 2,4-diiodoaniline.

(10) From methylamine and *p*-iodophenyl isothiocyanate.

(11) From amyl isothiocyanate and *p*-iodoaniline.

(12) From benzyl isothiocyanate and *p*-iodoaniline.

(13) Best prepared from the corresponding mono-thiourea and ethyl chloroacetate.

(14) Compound XIX first separated as an oil so the corresponding methyl derivative was prepared from IV for comparison.

(15) Best prepared from mono-*p*-cymyl thiourea and ethyl chloroacetate. Attempts to prepare this compound from ω-chloroacetoamino-*p*-cymene and chloroacetyl chloride led to the formation of a very tarry product. ω-Chloroacetoamino-*p*-cymene was prepared by treating an acetone solution of 2-amino-*p*-cymene with equal molecular quantities of chloroacetyl chloride and pyridine, m. p. 85°. *Anal.* Calcd. for $C_{12}H_{16}ClON$: N, 6.21. Found: N, 6.16.

(16) Chloroacetyl chloride added to an acetone solution of 2,4-diiodoaniline and pyridine gave 2,4-diiodo-ω-chloroacetanilide, m. p. 153°. *Anal.* Calcd. for $C_8H_5ClI_2ON$: N, 3.33. Found: N, 3.26. The latter when dissolved in alcohol and heated with KSCN yielded XXIX.

(17) Prepared from N-amyl-N′-phenyl thiourea and ethyl chloroacetate.

(18) Prepared from N-benzyl-N′-phenyl thiourea and ethyl chloroacetate.

| No. | 5-Benzal-4-thiazolidone | Hydrolysis products[19] | Formula | M. p., °C. | % Nitrogen Calcd. | Found |
|---|---|---|---|---|---|---|
| XLII | 2-Ethyl-2-*p*-ethoxyphenylamino- | A, ethyl-*p*-phenetidine[20] | $C_{20}H_{20}O_2N_2S$ | 210 | 7.95 | 7.94 |
| XLIII | 2-*p*-Ethoxyphenylimino-3-ethyl- | B, *p*-phenetidine | $C_{20}H_{20}O_2N_2S$ | 135 | 7.95 | 7.89 |
| XLIV | 2-*o*-Ethoxyphenylimino-3-ethyl- | B, *o*-phenetidine[21] | $C_{20}H_{20}O_2N_2S$ | 113 | 7.95 | 7.79 |
| XLV | 2-Ethyl-2-*o*-ethoxyphenylamino- | A, ethyl-*o*-phenetidine[22] | $C_{20}H_{20}O_2N_2S$ | 164 | 7.95 | 7.86 |
| XLVI | 2-Ethyl-2-pseudocumyl- | A | $C_{21}H_{22}ON_2S$ | 180 | 8.00 | 7.98 |
| XLVII | 2-Pseudocumylimino-3-ethyl- | B, pseudocumidine | $C_{21}H_{22}ON_2S$ | 141 | 8.00 | 7.95 |
| XLVIII | 2-Pseudocumylimino-3-methyl- | Not hydrolyzed | $C_{20}H_{20}ON_2S$ | 136 | 8.33 | 8.28 |
| XLIX | 2-Ethyl-2-*o*-methoxyphenylamino- | A, ethyl-*o*-anisidine[23] | $C_{19}H_{18}O_2N_2S$ | 149 | 8.28 | 8.28 |
| L | 2-*o*-Methoxyphenylimino-3-ethyl- | B, *o*-anisidine | $C_{19}H_{18}O_2N_2S$ | 99 | 8.28 | 8.27 |
| LI | 2-Ethyl-2-*p*-methoxyphenylamino- | A | $C_{19}H_{18}O_2N_2S$ | 198 | 8.28 | 8.26 |
| LII | 2-*p*-Methoxyphenylimino-3-ethyl- | B, *p*-anisidine | $C_{19}H_{18}O_2N_2S$ | 125 | 8.28 | 8.24 |
| LIII | 2-Ethyl-2-*m*-methoxyphenylamino- | A | $C_{19}H_{18}O_2N_2S$ | 135 | 8.28 | 8.25 |
| LIV | 2-*m*-Methoxyphenylimino-3-ethyl- | B, *m*-anisidine | $C_{19}H_{18}O_2N_2S$ | 109 | 8.28 | 8.13 |
| LV | 2-Ethyl-2-*p*-cymylamino- | A | $C_{22}H_{24}ON_2S$ | 169 | 7.69 | 7.66 |
| LVI | 2-*p*-Cymylimino-3-ethyl- | B, 2-amino-*p*-cymene | $C_{22}H_{24}ON_2S$ | 73 | 7.69 | 7.64 |
| LVII | 2-(2,4-Diiodophenylimino)-3-ethyl-[24] | Not hydrolyzed | $C_{18}H_{14}I_2ON_2S$ | 210–211 | 5.00 | 5.01 |
| LVIII | 2-Methyl-2-*p*-iodophenylamino- | A, methyl-*p*-iodoaniline[25] | $C_{17}H_{13}ION_2S$ | 246 | 6.67 | 6.70 |
| LIX | 2-*p*-Iodophenylimino-3-methyl- | 5-Benzal-3-methyl-2,4-thiazoledione,[2] *p*-iodoaniline | $C_{17}H_{13}ION_2S$ | 167 | 6.67 | 6.72 |
| LX | 2-Ethyl-2-*p*-iodophenylamino- | A | $C_{18}H_{15}ION_2S$ | 231 | 6.45 | 6.51 |
| LXI | 2-*p*-Iodophenylimino-3-ethyl- | B, *p*-iodoaniline | $C_{18}H_{15}ION_2S$ | 172 | 6.45 | 6.43 |
| LXII | 2-Amyl-2-*p*-iodophenylamino- | A | $C_{21}H_{21}ION_2S$ | 202 | 5.88 | 5.94 |
| LXIII | 2-*p*-Iodophenylimino-3-amyl- | 5-Benzal-3-amyl-2,4-thiazoledione,[26] *p*-iodoaniline | $C_{21}H_{21}ION_2S$ | 105 | 5.88 | 5.87 |
| LXIV | 2-Phenylimino-3-amyl- | 5-Benzal-3-amyl-2,4-thiazoledione[26] | $C_{21}H_{22}ON_2S$ | 78 | 8.00 | 7.95 |
| LXV | 2-Benzyl-2-*p*-iodophenylamino- | A, benzylaniline, $I_2$ | $C_{23}H_{17}ION_2S$ | 221 | 5.65 | 5.70 |
| LXVI | 2-*p*-Iodophenylimino-3-benzyl- | 5-Benzal-3-benzyl-2,4-thiazoledione,[27] *p*-iodoaniline | $C_{23}H_{17}ION_2S$ | 162 | 5.65 | 5.68 |
| LXVII | 2-Benzylimino-3-benzyl- | 5-Benzal-3-benzyl-2,4-thiazoledione,[27] benzyl amine | $C_{24}H_{20}ON_2S$ | 109 | 7.29 | 7.33 |

talline product which recrystallized from glacial acetic acid melted with decomposition at 246°.

*Anal.* Calcd. for $C_{19}H_{19}ION_4S$: N, 11.77. Found: N, 11.68.

Similar treatment of 2-*p*-iodophenylimino-3-ethyl-4-thiazolidone with *p*-nitrosodimethylaniline yielded a slightly soluble, red crystalline product, m. p. 212°.

*Anal.* Calcd. for $C_{19}H_{19}ION_4S$: N, 11.77. Found: N, 11.58. Hydrolysis of these derivatives with hydrochloric acid in alcohol solution caused complete rupture of the ring.

(19) "A" indicates 5-benzal-2,4-thiazoledione, m. p. 243° and "B," 5-benzal-3-ethyl-2,4-thiazoledione, m. p. 95°. Ref. 2.

(20) Identified by its reaction with phenyl isocyanate to give N-ethyl-N-*p*-ethoxy-phenyl-N'-phenyl urea, m. p. 93°. *Anal.* Calcd. for $C_{17}H_{20}O_2N_2$: N, 9.86. Found: N, 9.91.

(21) With *p*-nitrobenzoyl chloride yielded *p*-nitrobenzoyl-*o*-phenetidide, m. p. 155°. *Anal.* Calcd. for $C_{16}H_{14}O_4N_2$: N, 9.79. Found: N, 9.74. And with *p*-tolyl isocyanate gave N-*p*-tolyl-N'-*o*-ethoxyphenyl urea, m. p. 172°. *Anal.* Calcd. for $C_{16}H_{18}O_2N_2$: N, 10.37. Found: N, 10.31.

(22) With benzene sulfonyl chloride gave ethyl-*o*-phenetidyl-benzene sulfonate, m. p. 61°. *Anal.* Calcd. for $C_{16}H_{19}O_3NS$: N, 4.59. Found: N, 4.79.

(23) Ethyl-*o*-anisidyl-benzene sulfonate formed on addition of benzene sulfonyl chloride, m. p. 90°. *Anal.* Calcd. for $C_{15}H_{17}O_3NS$: N, 4.81. Found: N, 4.93.

(24) Attempts to prepare this compound in alcohol solution were unsuccessful. It was finally obtained by using pyridine as the solvent.

(25) M. p. of product obtained by reaction with benzene sulfonyl chloride was 78°. *Anal.* Calcd. for $C_{13}H_{12}IO_2NS$: N, 3.75. Found: N, 3.90.

(26) M. p. 74°. *Anal.* Calcd. for $C_{15}H_{17}O_2NS$: N, 5.09; S, 11.65. Found: N, 5.24. S, 11.81.

(27) M. p. 134°. *Anal.* Calcd. for $C_{17}H_{13}O_2NS$: N, 4.75. Found: N, 4.82.

## Summary

The alkylation of nine different aryl substituted thiazolidones has been studied. Certain of the compounds described by Beckurts and Frerich as 2-alkyl-3-aryl thiazolidones were shown, in fact, to be 2-alkyl-2-aryl thiazolidones, thus confirming the work of Eberly and Dains.

In most cases it was found that alkylation produced two isomeric alkyl derivatives: one, the 2-alkyl-2-aryl thiazolidone and the other the 2-aryl-3-alkyl compound. The effect of the aryl group on the amounts of isomers obtained was noted as was also the effect of various alkyl halides.

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