

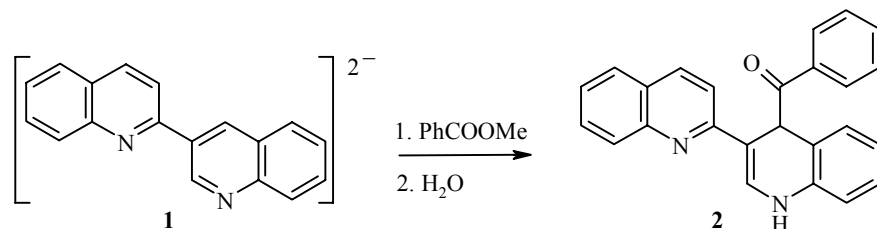
REACTION OF THE 2,3'-BIQUINOLYL DIANION WITH BENZOATE – A RARE CASE OF ACYLATION OF AROMATIC DIANIONS

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In a continuation of a study of the properties of the 2,3'-biquinolyl dianion (**1**), for which a convenient method of generation was proposed in our previous work [1], we investigated the acylation of this species by alkyl benzoates. As a rule, acylation products are not formed in the reactions of dianions of aromatic compounds [2].

We have shown that 2,3'-biquinolyl dianion obtained from 2,3'-biquinolyl and three equivalents of metallic lithium in absolute THF forms the benzoylation product at C_(4') upon stirring with a two-fold molar excess of methyl benzoate (dried by distillation over CaH₂) at room temperature for 2 h, namely, 4'-benzoyl-1',4'-dihydro-2,3'-biquinolyl (**2**), in 61% yield. This product was isolated analogously to the procedure used for the arylation products of this dianion [3].



The key step in this reaction is probably electron transfer from dianion **1** to methyl benzoate since the replacement of this ester by isopropyl benzoate or *tert*-butyl benzoate does not lead to a significant change in the yield or reaction time.

Dianion **1** acts as a base relative to ethyl acetate. The major product of this reaction is 1',4'-dihydro-2,3'-biquinolyl and ethyl acetoacetate. No acylation products were isolated in this case.

4'-Benzoyl-1',4'-dihydro-2,3'-biquinolyl (2) was obtained in 61% yield; mp 197-198°C (benzene). ¹H NMR spectrum at 200 MHz (acetone-d₆), δ, ppm, *J* (Hz): 6.43 (1H, s, 4'-H); 6.76 (1H, dd, *J*_{5'6'} = 7.96, *J*_{6'7'} = 7.52, 6'-H); 6.95 (1H, d, *J*_{7'8'} = 8.11, 8'-H); 7.06 (1H, d, *J*_{5'6'} = 7.96, 5'-H); 7.10 (1H, dd, *J*_{6'7'} = 7.52, *J*_{7'8'} = 8.11, 7'-H); 7.33 (1H, d, *J* = 7.78, 5-H); 7.45 (2H, m, 6-H, 4-Ph); 7.69 (1H, d, *J*₅₆ = 8.04, 5-H); 7.62 (3H, m, 8-H, 3,5-Ph); 7.71 (1H, dd, *J*₆₇ = 7.44, *J*₇₈ = 8.42, 7-H); 7.82 (1H, d, *J*₃₄ = 8.97, 3-H); 7.84 (1H, d, *J*_{NH-2H} = 5.97, NH); 8.38 (2H, d, *J*₇₈ = 7.68, 2,6-Ph). Mass spectrum, *m/z* (70 eV): 362 [M⁺] (18%). Found, %: C 82.96; H 4.98; N 7.68. C₂₅H₁₈N₂O. Calculated, %: C 82.85; H 5.01; N 7.73.

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REFERENCES

1. A. V. Aksenov, I. V. Aksenova, I. V. Voroblev, A. A. Bumber, A. F. Pozharskii, and Yu. I. Shmushkevich, *Khim. Geterotsikl. Soedin.*, 1391 (1996).
2. N. L. Holy, *Chem. Rev.*, 243 (1974).
3. A. V. Aksenov, I. V. Aksenova, I. V. Voroblev, and Yu. I. Shmushkevich, *Khim. Geterotsikl. Soedin.*, 1094 (1997).