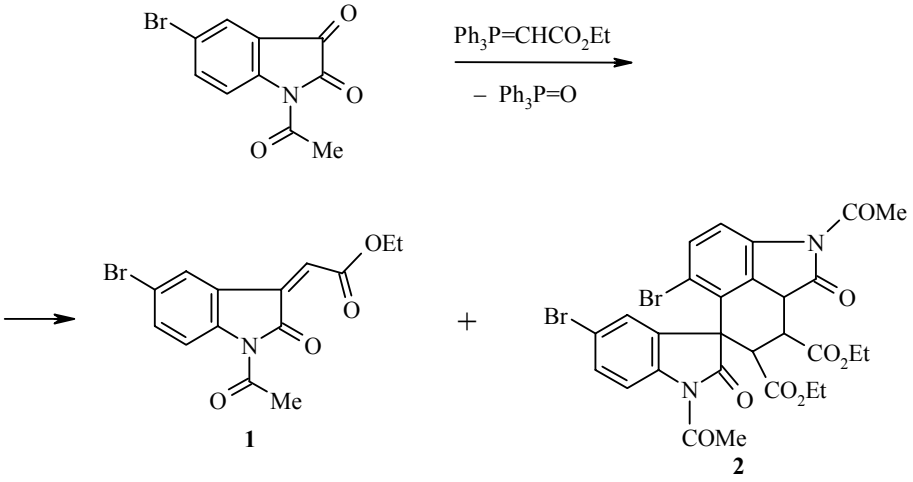
Chemistry of Heterocyclic Compounds, Vol. 40, No. 4, 2004

UNUSUAL REACTION OF 1-ACETYL-5-BROMO-1H-INDOLE-2,3-DIONE WITH ETHYL (TRIPHENYL-PHOSPHORANYLIDENE)ACETATE

V. O. Kozminykh, K. Sh. Lomidze, E. N. Kozminykh, and A. N. Berezin

Keywords: 1-acetyl-5-bromo-1H-indole-2,3-dione, diethyl ester of 2,1'-diacetyl-5,5'-dibromo-1,2'-dioxo-1,1',2,2',7,8,8a-heptahydrospiro{benzo[*cd*]indole-6,3'-indole}-7,8-dicarboxylic acid, ethyl (triphenylphosphoranylidene)acetate.

Isatins readily react with methylene triphenylphosphoranes to form 3-methylene-1,3-dihydro-2H-indol-2-ones, which are of practical importance [1-5]. As a result of reaction of 1-acetyl-5-bromo-1H-indole-2,3-dione with the ethyl ester of triphenylphosphoranylidene acetic acid (ethoxycarbonylmethylene triphenylphosphorane), in addition to the usual Wittig reaction product (the yellow ethyl ester of (2*Z*)-(2-oxo-1,2-dihydro-3H-indol-3-ylidene)acetic acid (**1**)), we unexpectedly isolated a colorless "dimer": the diethyl ester of 2,1'-diacetyl-5,5'-dibromo-1,2'-dioxo-1,1',2,2',7,8,8a-heptahydrospiro{benzo[*cd*]indole-6,3'-indole}-7,8-dicarboxylic acid (**2**).



Thus a mixture of 1-acetyl-5-bromo-1H-indole-2,3-dione (1.34 g, 5 mmol) and the ethyl ester of triphenylphosphoranylidene acetic acid (1.74 g, 5 mmol) was boiled in benzene (70 ml) for 2.5 h. The solvent was evaporated and the residue was recrystallized from alcohol (compound **1** was obtained) and dioxane (spiro compound **2** was obtained).

Perm State Pedagogical University, Perm 614990, Russia; e-mail: kvo@pi.ccl.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 619-620, April, 2004. Submitted January 3, 2004.

Ethyl Ester of (2*Z*)-(1-Acetyl-5-bromo-2-oxo-1,2-dihydro-3H-indol-3-ylidene)acetic Acid (1). Yield 0.96 g (57%); mp 150-151°C (ethanol). ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 1.37 (3H, t, $OCH_2\underline{CH_3}$); 2.63 (3H, s, $COCH_3$); 4.34 (2H, q, $O\underline{CH_2}CH_3$); 6.82 (1H, s, CH); 7.63 (1H, d, 7-H); 8.15 (1H, d, 6-H); 8.78 (1H, s, 4-H). Found, %: C 50.11; H 3.30; Br 23.37; N 3.85. $C_{14}H_{12}BrNO_4$. Calculated, %: C 49.73; H 3.58; Br 23.63; N 4.14.

Diethyl Ester of 2,1'-Diacetyl-5,5'-dibromo-1,2'-dioxo-1,1',2,2',7,8,8a-heptahydrospiro{benzo[*cd*]-indole-6,3'-indole}-7,8-dicarboxylic Acid (2). Yield 0.50 g (30%); mp 236-237°C (dioxane). ^{1}H NMR spectrum (500 MHz, DMSO-d_6), δ, ppm: 0.83 (3H, t, $OCH_2\underline{CH_3}$); 1.28 (3H, t, $OCH_2\underline{CH_3}$); 2.60 (3H, s, $COCH_3$); 2.67 (3H, s, $CO\underline{CH_3}$); 3.60 (2H, q, $O\underline{CH_2}CH_3$); 3.63 (1H, t, 8-H); 3.68 (1H, d, 7-H); 4.19 (2H, q, $O\underline{CH_2}CH_3$); 4.30 (1H, d, 8*a*-H); 7.47 (1H, d, 3-H); 7.52 (1H, s, 4'-H); 7.56 (1H, d, 7'-H); 7.87 (1H, d, 4-H); 8.02 (1H, d, 6'-H). Mass spectrum, *m/z* (I_{rel}, %): 676 $[M]^+$ (11), 632 $[M - CO_2]^+$ or $[M - CH_3CO - H]^+$ (2), 602 $[M - CO_2Et - H]^+$ (8), 588 $[M - 2CO_2]^+$ or $[M - 2CH_3CO - 2H]^+$ (2), 560 (4), 538 (3), 517 (3), 500 (2), 471 (3), 444 (7), 427 (2), 409 (3), 382 (2), 366 (8), 337 $[1/2\ M - H]^+$ (5), 309 (3), 284 (5), 269 (3), 243 (3), 229 (6), 214 (8), 201 (5), 188 (3), 164 (2), 140 (2), 115 (2), 82 (5), 55 (3), 43 $[CH_3CO]^+$ (100). Found, %: C 49.56; H 3.24; Br 23.82; N 4.33. $C_{28}H_{24}Br_2N_2O_8$. Calculated, %: C 49.73; H 3.58; Br 23.63; N 4.14.

REFERENCES

1. H. A. Brandman, *J. Heterocycl. Chem.,* **10**, 383 (1973).
2. G. Tacconi, A. G. Invernizzi, and G. Desimoni, *J. Chem. Soc., Perkin Trans. 1*, 1872 (1976).
3. E. N. Kozminykh, E. S. Berezina, and V. O. Kozminykh, *Zh. Obshch. Khim.*, **66**, 1128 (1996).
4. E. N. Kozminykh, E. S. Berezina, V. E. Kolla, S. A. Shelenkova, E. V. Voronina, and V. O. Kozminykh, *Khim.-Farm. Zh.*, **31**, No. 2, 31 (1997).
5. F. H. Osman and F. A. El-Samahy, *Phosphorus, Sulfur, Silicon Relat. Elem.,* **134/135**, 437 (1998).