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SHORT COMMUNICATIONS

New Synthesis of 3-Aroylcyclopropane-1,1,2,2-tetracarbonitriles

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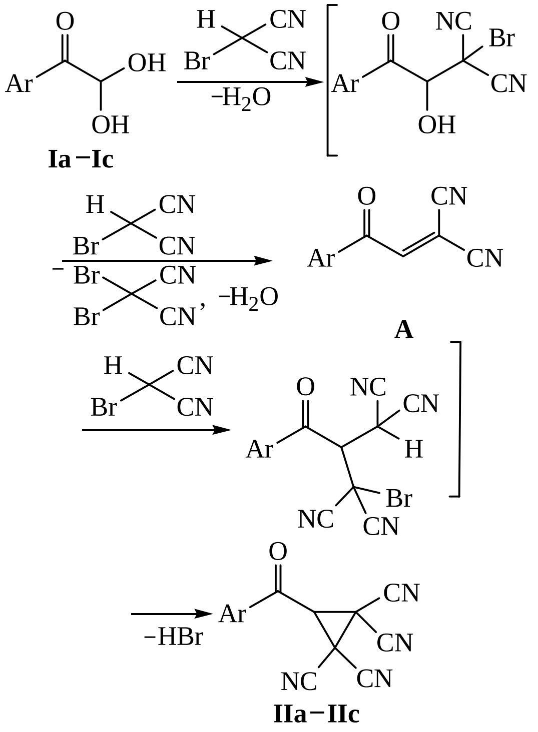
Many 1,1,2,2-tetracyanocyclopropanes were successfully prepared by Wideqvist reaction. The process consists in treating carbonyl compounds with monobromomalonodinitrile in ethanol or water at room temperature for 0.5–12 h in the presence of potassium iodide as reductant [1, 2].

We developed a new synthesis method for 3-aroylcyclopropane-1,1,2,2-tetracarbonitriles **IIa–IIc** based on Wideqvist reaction but without potassium iodide. The latter was excluded from the reaction to avoid side processes since the cyclopropanes containing five and six electron-withdrawing substituents were known to actively react with iodides [3–6].



Ar = C_6H_5 (**a**), p-BrC_6H_4 (**b**), *p*-$CH_3OC_6H_4$ (**c**).

Our synthesis of 3-aroylcyclopropane-1,1,2,2-tetracarbonitriles involves a treatment of substituted phenylglyoxal monohydrates in 2-propanol solution with an excess of monobromomalonodinitrile which simultaneously acts as a reductant converting into dibromomalonodinitrile.

We assume the following reaction scheme: The formed dicyanomethylene derivatives of phenylglyoxal **A** react with the second monobromomalonodinitrile molecule leading to compounds **IIa–IIc**.

Compounds analogous to cyclopropanes **IIa–IIc** were formerly obtained by the reaction of ω-chlorinated acetophenones with tetracyanoethylene in dioxane medium [7]. Hence the method we developed is a new procedure for preparation of 3-aroylcyclopropane-1,1,2,2-tetracarbonitriles.

The structure of synthesized cyclopropanes **IIa–IIc** was confirmed by IR, ^{1}H NMR, and mass spectra.

3-Benzoylcyclopropane-1,1,2,2-tetracarbonitrile (IIa). To a solution of 1.52 g (0.01 mol) of phenylglyoxal monohydrate (**Ia**) in 20 ml of 2-propanol was added at stirring in one portion 4.35 g (0.03 mol) of monobromomalonodinitrile. The mixture was stirred for 15 min, the separated precipitate was filtered off and washed in succession with small portions of 2-propanol and water. Yield 1.96 g (80%), mp 211–212°C (decomp.). IR spectrum ν, cm^{-1}: 1692.31 (C=O), 2264.03 (C≡N), 3033.24 (CH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.25 d, 7.8 t, 7.6 t (5H, $C_6\underline{H}_5$), 5.65 s (1H, CH of cyclopropane). Mass spectrum, *m/z* (I_{rel}, %): 246 (15) $[M]^+$, 105 (100) $[M – 141]^+$, 77 (60), 51 (40), 38 (10).

Compounds **IIb** and **IIc** were prepared similarly.

3-(4-Bromobenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (IIb). Yield 2.76 g (85%), mp 214–215°C (decomp.). IR spectrum, ν, cm^{-1}: 1691.97 (C=O), 2261.30 (C≡N), 3052.48 (C–H). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.15 d, 7.85 d (4H, 4-$BrC_6\underline{H}_4$), 5.6 s (1H, CH of cyclopropane). Mass spectrum, *m/z* (I_{rel}, %): 324 (10) $[M]^+$, 183 (100) $[M-141]^+$, 155 (50), 105 (30), 76 (75), 50 (80), 38 (25).

3-(4-Methoxybenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (IIc). Yield 2.20 g (80%), mp 204–205°C (decomp.). IR spectrum, ν, cm^{-1}: 1670.90 (C=O), 2260.63 (C≡N), 3023.30 (CH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.2 d, 7.15 d (4H, *4*-$CH_3OC_6\underline{H}_4$), 3.9 s (3H, $C\underline{H}_3O$), 5.65 s (1H, CH of cyclopropane). Mass spectrum, *m/z* (I_{rel}, %): 276 (25) $[M]^+$, 171 (50) $[M-105]^+$, 135 (100) $[M-141]^+$, 107 (10), 92 (25), 77 (30), 64 (20), 38 (10).

The purity of compounds synthesized was checked by TLC on Silufol UV-254 plates, development under UV irradiation, with iodine vapor, or by thermal decomposition. IR spectra were recorded on a Fourier spectrometer FSM-1202 from thin film of mulls in mineral oil. ^{1}H NMR spectra were registered on a spectrometer Bruker DRX-500, operating frequency 500.13 MHz, solvent DMSO-d_6, internal reference TMS. Mass spectra were measured on Finnigan MAT-INCOS 50 instrument (electron impact 70 eV).

REFERENCES

1. Hart, H. and Freeman, F., *J. Org. Chem.*, 1963, vol. 28, p. 1220.
2. Freeman, F. *Synthesis*., 1981, p. 925.
3. Yashkanova, O.V., Nasakin, O.E., Urman, Ya.G., Khrustalev, V.N., Nesterov, V.N., Antipin, M.Yu., and Lukin, P.M., *Zh. Org. Khim.*, 1997, vol. 33, p. 533.
4. Nasakin, O.E., Lukin, P.M., Lyshchikov, A.N., Vershinin, E.V., Kayukova, O.V., and Urman, Ya.G., *Zh. Org. Khim.*, 1996, vol. 32, p. 381.
5. Siaka, S., Kayukova, O.V., Kayukov, Ya.S., Lukin, P.M., Khrustalev, V.N., Nesterov, V.N., Nasakin, O.E., and Antipin, M.Yu., *Zh. Org. Khim.*, 1998, vol. 34, p. 1330.
6. Kayukova, O.V., Kayukova, Ya.S., Nikolaev, A.N., Tafeenko, V.A., Ershov, O.V., and Nasakin, O.E., *Zh. Org. Khim.*, 2005, vol. 41, p. 535.
7. Sheverdov, V.P., Ershov, O.V., Nasakin, O.E., Selyunina, E.V., Tikhonova, I.G., Chernushkin, A.N., and Khrustalev, V.N. *Zh. Obshch. Khim.*, 2000, vol. 70, p. 1334.