

## 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-arylcyclopropane-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].

Our synthesis of 3-arylcyclopropane-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.

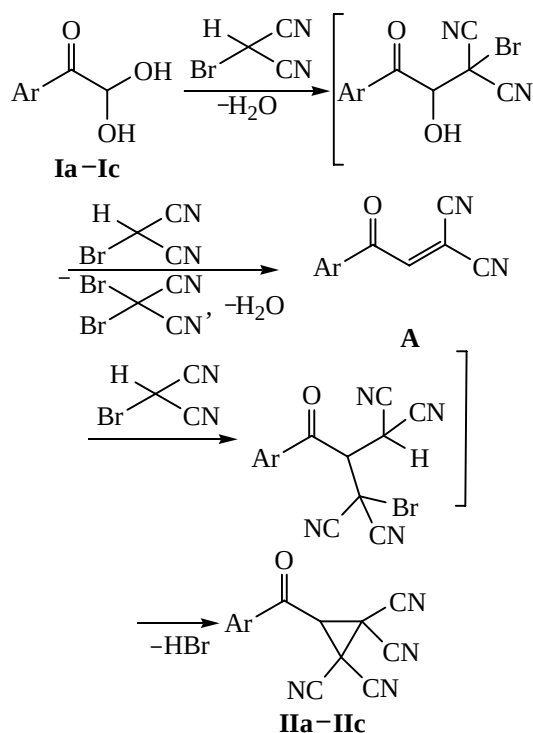
We assume the following reaction scheme: The formed dicyanomethylene derivatives of phenylglyoxal **A** react with the second monobromomalonodinitrile molecule leading to compounds **IIa–IIc**.

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

The structure of synthesized cyclopropanes **IIa–IIc** was confirmed by IR,  $^1\text{H}$  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  $\nu$ ,  $\text{cm}^{-1}$ : 1692.31 (C=O), 2264.03 (C $\equiv$ N), 3033.24 (CH).  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 8.25 d, 7.8 t, 7.6 t (5H, C $_6\text{H}_5$ ), 5.65 s (1H, CH of cyclopropane). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 246 (15) [ $M$ ] $^+$ , 105 (100) [ $M - 141$ ] $^+$ , 77 (60), 51 (40), 38 (10).

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



Ar = C $_6\text{H}_5$  (**a**), p-BrC $_6\text{H}_4$  (**b**), p-CH $_3$ OC $_6\text{H}_4$  (**c**).

**3-(4-Bromobenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (IIb).** Yield 2.76 g (85%), mp 214–215°C (decomp.). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1691.97 (C=O), 2261.30 (C $\equiv$ N), 3052.48 (C–H).  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 8.15 d, 7.85 d (4H, 4-BrC $_6$ H $_4$ ), 5.6 s (1H, CH of cyclopropane). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 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,  $\nu$ ,  $\text{cm}^{-1}$ : 1670.90 (C=O), 2260.63 (C $\equiv$ N), 3023.30 (CH).  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 8.2 d, 7.15 d (4H, 4-CH $_3$ OC $_6$ H $_4$ ), 3.9 s (3H, CH $_3$ O), 5.65 s (1H, CH of cyclopropane). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 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.  $^1\text{H}$  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).

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