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LETTERS TO THE EDITOR

Synthesis of 3-Acetonyl-1,1,2,2-tetracyanocyclobutanes

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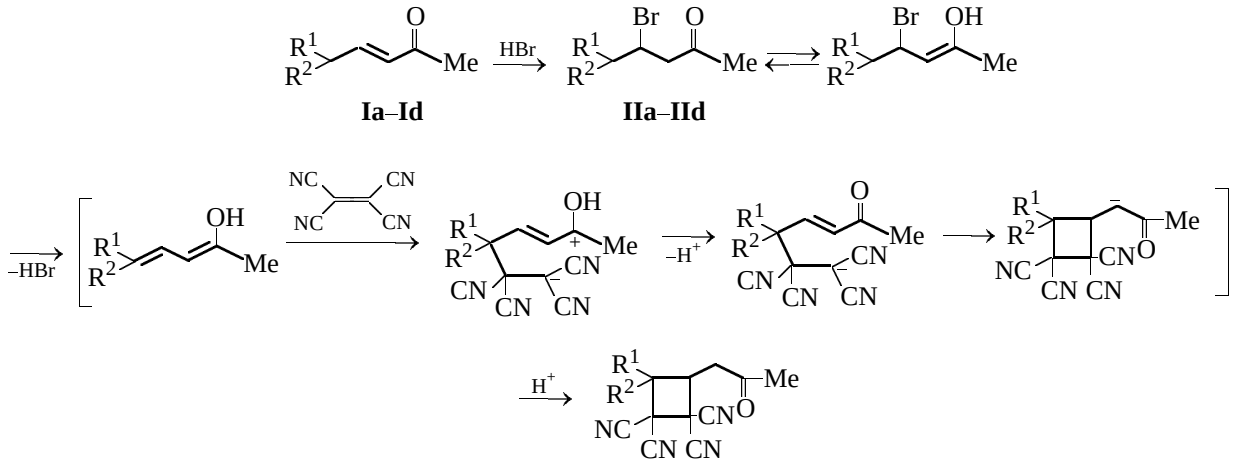
1,1,2,2-Tetracyanocyclobutanes are most frequently synthesized by a [2+2]-cycloaddition reaction [1–4]. The most facile reaction occurs between tetracyanoethylene and alkenes whose double bond is activated by electron-donor substituents. 1,1,2,2-tetracyanocyclobutanes are considered to be formed by a nonconcerted cycloaddition reaction involving a zwitterionic intermediate. The reactions of tetracyanoethylene with styrene [5] and vinyl ether [6] are assigned to this type of reactions. It is shown that first a charge-transfer complex is formed. Further, say, in the reaction of tetracyanoethylene with styrene, the zwitter ion $PhC^+HCH_2C(CN)_2C^-(CN)_2$ arises and then cyclizes into 1,1,2,2-tetracyano-3-phenylcyclobutane.

We have developed a new synthesis of 1,1,2,2-tetracyanocyclobutanes via reactions of tetracyanoethylene with α,β-unsaturated ketones **Ia**–**Id** (in the presence of HBr) or β-bromoketones **IIa**–**IId**. With α,β-unsaturated ketones **Ia**–**Id** in the presence of HBr, tetracyanoethylene reacts within 6–12 h, and the yields of cyclobutanes **IIIa**–**IIId** reach 56–71%. With β-bromoketones **IIa**–**IId**, tetracyanoethylene forms cyclobutanes **IIIa**–**IIId** within 2–3 min in 91–96% yields.



Ia–**Id** **IIa**–**IId** **IIIa**–**IIId**

R^1 = Et, R^2 = H (**a**); R^1 = Bu, R^2 = H (**b**); R^1 = R^2 = Me (**c**); R^1 = Ph, R^2 = H (**d**).

3-Ethyl-4-(2-oxopropyl)cyclobutane-1,1,2,2-tetracarbonitrile (IIIa). *a*. Tetracyanoethylene, 1.28 g, was dissolved with heating in 20 ml of dioxane and then 1.93 g of 4-bromoheptan-2-one was added. After 10 min, the reaction mixture was treated with 100 ml of water. The precipitate that formed was filtered off and washed with water and chloroform to obtain 96% of compound **IIIa**.

b. Tetracyanoethylene, 1.28 g, was added to a stirred and heated (40–50°C) mixture of 1.12 g 3-hepten-2-one in 20 ml of dioxane. When tetracyano-

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ethylene had completely dissolved, 1.6 g of 50% HBr was added. After 12 h, the reaction mixture was treated with 100 ml of water. The precipitate that formed was filtered off and washed with water, 2-propanol, and diethyl ether, and recrystallized from 2-propanol to obtain 71% of ketone **IIIa**, mp 204–205°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 2265 (C≡N), 1730 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.38 m (1H, C*H*CH_2CO), 3.25 m (1H, C*H*Et), 3.2 d.d (1H, CHC*H*$_2$CO, *J* 6.5, 8.5 Hz), 2.99 d.d (1H, CHC*H*$_2$CO, *J* 6.5, 8.5 Hz), 2.2 s (3H, COMe), 1.8 m (CHC*H*$_2$Me), 0.98 t (3H, CH_2C*H*$_3$, *J* 6.0 Hz). Found, %: C 65.12; H 4.97; N 23.39. $C_{13}H_{12}N_4O$. Calculated, %: C 64.99; H 5.03; N 23.32. X-ray diffraction analysis: space group *P*-1 at 20°C, *a* 7.9610(10), *b* 9.0580(10), *c* 9.8690(10) Å; α 101.570(10), β 104.810(10), γ 82.800(10)°; *V* 671.97(13) $Å^3$, *Z* 2.

Compounds **IIIb**–**IIId** were prepared in a similar way.

3-Butyl-4-(2-oxopropyl)cyclobutane-1,1,2,2-tetracarbonitrile (IIIb). Yield 93% (method *a*), 65% (method *b*), mp 198–199°C. IR spectrum, ν, cm^{-1}: 2270 (C≡N), 1720 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.49 m (1H, C*H*CH_2CO), 3.2 m (1H, C*H*Bu), 3.08 d.d (1H, CHC*H*$_2$CO, *J* 5.5, 8.0 Hz), 2.94 d.d (1H, CHC*H*$_2$CO, *J* 5.5, 8.5 Hz), 2.09 s (3H, COMe), 1.68–1.36 m (6H, C*H*$_2$C*H*$_2$C*H*$_2$Me), 0.98 t (3H, CH_2C*H*$_3$, *J* 7.0 Hz). Found, %: C 67.11; H 6.01; N 20.69. $C_{15}H_{16}N_4O$. Calculated, %: C 67.15; H 6.01; N 20.88.

3,3-Dimethyl-4-(2-oxopropyl)cyclobutane-1,1,2,2-tetracarbonitrile (IIIc). Yield 91% (method *a*), 78% (metod *b*), mp 153–154°C. IR spectrum, ν, cm^{-1}: 2265 (C≡N), 1720 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.53 d.d (1H, C*H*CH_2CO, *J* 7.5, 8.5 Hz), 3.15 d.d (1H, CHC*H*$_2$CO, *J* 6.5, 8.5 Hz), 2.95 d.d (1H, CHC*H*$_2$CO, *J* 6.5, 7.5 Hz), 2.22 s (3H, COMe), 1.5 s (3H, Me), 1.4 s (3H, Me). Found, %: C 64.82; H 5.07; N 23.22. $C_{13}H_{12}N_4O$. Calculated, %: C 64.99; H 5.03; N 23.32.

4-(2-Oxopropyl)-3-phenylcyclobutane-1,1,2,2-tetracarbonitrile (IIId). Yield 56% (method *b*), mp 187–188°C. IR spectrum, ν, cm^{-1}: 2275 (C≡N), 1725 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.43 s (5H, Ph), 4.88 d (1H, C*H*Ph, *J* 10.5 Hz), 4.21 m (1H, C*H*CH_2CO), 3.09 d.d (1H, CHC*H*$_2$CO, *J* 5.5, 8.0 Hz), 3.04 d.d (1H, CHC*H*$_2$CO, *J* 5.5, 7.5 Hz), 2.18 s (3H, COMe). Found, %: C 70.67; H 4.23; N 19.44. $C_{17}H_{12}N_4O$. Calculated, %: C 70.82; H 4.2; N 19.43.

The reaction progress and the purity of the synthesized compounds were controlled by TLC on Silufol UV-254 plates, development in iodine. The IR spectra were obtained on a UR-20 instrument in Vaseline oil. The ^{1}H NMR spectra were run on a Bruker AM-300 spectrometer in DMSO-d_6 at 300 MHz (internal reference TMS). The unit cell parameters and the reflection intensities for X-ray diffraction analysis were measured on a Siemens P3/PC four-circle diffractometer (λMoK_α radiation, graphite monochromator, θ/2θ scanning).

REFERENCES

1. Williams, J.K., Wiley, D., and McKusick, B.C., *J. Am. Chem. Soc.*, 1962, vol. 84, no. 11, p. 2210.
2. Huisgen, R. and Steiner, G., *J. Am. Chem. Soc.*, 1973, vol. 95, no. 1, p. 5054.
3. Huisgen, R. and Steiner, G., *Tetrahedron Lett.*, 1973, no. 39, p. 3763.
4. Karle, I., Flippen, J., Huisgen, R., and Schug, R., *J. Am. Chem. Soc.*, 1975, vol. 97, no. 18, p. 5285.
5. Nakahara, M., Tsuda, Y., Sasaki, M., and Osugi, J., *Chem. Lett.*, 1976, no. 7, p. 731.
6. Schug, R. and Huisgen, R., *Chem. Commun.*, 1975, no. 1, p. 60.