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Reaction of the Nitrile of 3,3-Diphenyl-2-propenic Acid with the Carbanions of Some α-Branched Nitriles

Short Communication

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Reaction of the nitrile of 3,3-diphenyl-2-propenic acid with α-branched nitriles in the presence of lithium amide in liquid ammonia does not give the corresponding *Michael* adducts but the β,γ-unsaturated nitriles **6**. Conc. sulfuric acid transforms these nitriles into the γ-lactones **7**.

(Keywords: Addition-Elimination; γ-Lactones; Nitriles)

Reaktion von 3,3-Diphenyl-2-propensäurenitril mit den Carbanionen einiger α-verzweigter Nitrile (Kurze Mitteilung)

Die Reaktion von 3,3-Diphenyl-2-propensäurenitril mit α-verzweigten Nitrilen in Gegenwart von Lithiumamid in flüssigem Ammoniak führt nicht zu den entsprechenden *Michael*-Addukten, sondern zu den β,γ-ungesättigten Nitrilen **6**. Durch Einwirkung von konz. Schwefelsäure entstehen aus diesen Nitrilen die γ-Lactone **7**.

It was recently shown[1] that reaction of acetonitrile with the nitrile of 3,3-diphenyl-2-propenic acid (3-phenylcinnamonitrile, **5**) in the presence of lithium amide in liquid ammonia gives two products, namely the dinitrile of 3,3-diphenylglutaric acid (**1**) and 4,4-diphenylvinylacetonitrile (**2**); the amounts of **1** or **2** depend on the amount of the amide used.

Under the same reaction conditions reaction of **5** with *p*-tolunitrile affords 1,1-diphenyl-3-[*p*-cyanophenyl]-1-propene (**3**) and 1,3-di[*p*-cyanophenyl]-2-[diphenylmethyl]-1-propene (**4**)[1]. The absence of a *Michael* adduct (analogous to **1**) may in this case be ascribed to a possible steric hindrance.

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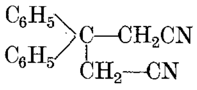
In order to test this assumption we have examined the behaviour of **5** towards the carbanions of α-branched nitriles.



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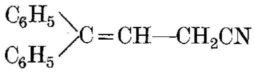

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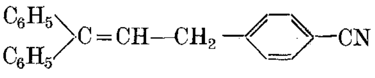

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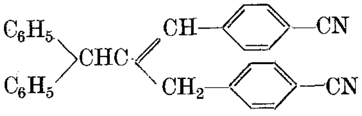

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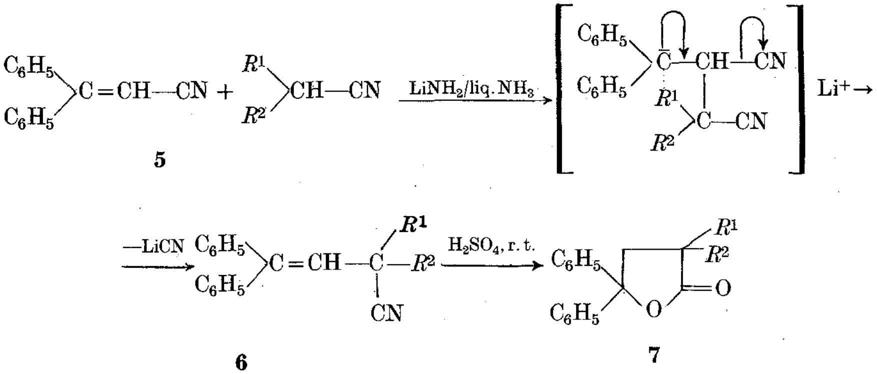
The experiments were carried out with the nitriles of 2-methyl- and 2-phenyl-propionic, cyclopentanecarboxylic and cyclohexanecarboxylic acids. With the exeption of 2-phenylpropionitrile under the action of lithium amide in liquid ammonia all other nitriles gave with high yields (72–88%) the expected β,γ-unsaturated α,α-disubstituted nitriles **6**, i.e. the nitrile of 4,4-diphenyl-2,2-dimethyl-3-butenic acid (**6a**), 1,1-diphenyl-2-[1-cyanocyclopentyl]-ethylene (**6b**) and 1,1-diphenyl-2-[1-cyanocyclohexyl]-ethylene (**6c**). From the nitrile of 2-phenylpropionic acid only the dimer of **5** was formed. This result is most probably due to the weaker nucleophilicity of the corresponding carbanion.



6 and **7**, resp.	R^1	R^2
a	CH_3	CH_3
b	$-(CH_2)_4-$	
c	$-(CH_2)_5-$	

The structures of the nitriles **6 a, 6 b,** and **6 c** (so far not described in the literature) were confirmed by analytical and spectral data. Treatment with conc. sulfuric acid at room temperature gave the γ-lactones **7** (yields 44–69%).

Experimental

The melting points were determined on a *Böetius* hot-stage microscope and are uncorrected. The IR-spectra were taken on a Specord 71-IR (Zeiss-Jena, DDR) in $CHCl_3$, the ^1H-NMR-spectra on a TESLA BS-487C (80 MHz), inner standard *HMDSO*, in $CDCl_3$.

Preparation of nitriles **6 a–c** *(General procedure):*

To a suspension of 0.35 g (50 mmol) of $LiNH_2$ in 300 ml liqu. NH_3[2], 25 mmol of the corresponding nitrile, dissolved in 10 ml of abs. ether were added during 5 min with stirring. After additional stirring for 5 min a solution of 5.10 g (25 mmol) of **5** in 10 ml abs. ether was added. The reaction mixture was then stirred for 1 h. After neutralization with 2.68 g (50 mmol) solid NH_4Cl, NH_3 was evaporated. Cold water (100 ml) was poured on to the residue and the isolated crystals were recrystallized from methanol.

Nitrile of 4,4-diphenyl-2,2-dimethyl-3-butenic acid (**6 a**)

Yield of crude product: 4.40 g (72%). M.p. 104–108°. After recrystallization colourless crystals, m.p. 106–108°.

IR: 2 240 cm^{-1} (C≡N), 1 630 cm^{-1} (C=C).

$C_{18}H_{17}N$ (247.32). Calcd. N 5.66. Found N 5.56.

1,1-Diphenyl-2-(1-cyanocyclopentyl)-ethylene (**6 b**)

Yield of crude product: 6.40 g (94%); M.p. 75–78°. After recrystallization: 6.00 g (88%); M.p. 78–79°.

IR: 2 240 cm^{-1} (C≡N), 2 800-3 000 (CH_2-groups from cyclopentanering).

^1H-NMR: 7.15–7.48 (m, 10 H, arom.), 5.95 (s, 1 H, CH=), 1.65–2.32 (m, 8 H, 4 CH_2-groups).

$C_{20}H_{19}N$ (273.0). Calcd. N 5.13. Found N 5.07.

1,1-Diphenyl-2-(1-cyanocyclohexyl)-ethylene (**6 c**)

Yield of colourless crystals: 6.00 g (84%); M.p. 90–91°.

IR: 2 240 cm^{-1} (C≡N), 2 800–3 000 cm^{-1} (CH_2-groups from cyclohexanering).

$C_{21}H_{21}N$ (287.4). Calcd. N 4.87. Found N 5.02.

Transformation of **6** *into Lactones* **7** *(General procedure):*

A solution of 1.00 g of the corresponding nitrile **6** in 10 ml conc. sulfuric acid was kept for 24 h at room temp. and then poured on to ice. The crystals were recrystallized from ethylacetate.

3,3-Dimethyl-5,5-diphenyl-1,4-butanolid (**7 a**)

Yield of crude product: 0.85 g (84%); M.p. 110-116°. After recrystallization: 0.70 g (69%) colourless crystals; M.p. 115-117°.

IR: 1760 cm^{-1} (C=O, γ-lactone).

^{1}H-NMR: 7.10-7.48 (m, 10 H, arom.), 2.88 (s, 2 H, —CH$_2$—), 1.09 (s, 6 H, 2 CH$_3$-groups).

$C_{18}H_{18}O_2$ (266.3). Calcd. C 81.17, H 6.81. Found C 81.18, H 6.91.

1-Oxo-3,3-diphenyl-2-oxaspiro[4,4]-nonane (**7 b**)

Yield of crude product: 0.45 g (44%); M.p. 108-110°. (Unchanged on recrystallization.)

IR: 1760 cm^{-1} (C=O, γ-lactone).

^{1}H-NMR: 7.08-7.58 (m, 10 H, arom.), 2.89 (s, 2 H, CH$_2$-lactone ring), 1.27-2.07 (m, 8 H, cyclopentane ring).

$C_{20}H_{20}O_2$ (292.4). Calcd. C 82.15, H 6.85. Found C 82.46, H 6.64.

1-Oxo-3,3-diphenyl-2-oxaspiro[4,5]-decane (**7 c**)

Yield of crude product: 0.60 g (59%); M.p. 117-118°. (Unchanged on recrystallization.)

IR: 1760 cm^{-1} (C=O, γ-lactone).

^{1}H-NMR: 7.10-7.48 (m, 10 H, arom.), 2.90 (s, 2 H, CH$_2$-lactone ring), 1.08-1.80 (m, 10 H, cyclohexane ring).

$C_{21}H_{22}O_2$ (306.4). Calcd. C 82.32, H 7.24. Found C 82.41, H 7.56.

References

[1] *Y. Anghelova, K. Popandova-Yambolieva* and *C. Ivanov*, Commun. Depart. Chem. Bulg. Acad. Sci. **10**, 126 (1977).

[2] *W. Dunnavant* and *C. R. Hauser*, J. Org. Chem. **25**, 503 (1960).