Cyanotrimethylammonium Methylid, Formation and Reaction with α,β-Unsaturated Carbonyl Compounds: Novel Cyclopropanation with an Ammonium Ylid

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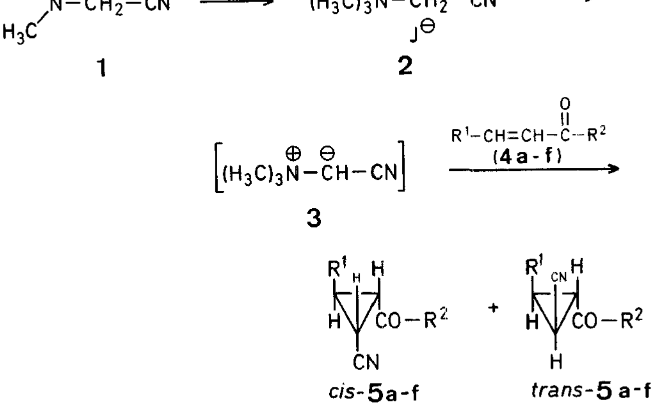
The nitrogen ylids, unlike their sulfur and phosphorus counterparts, behave more like classical carbanions in their chemical reactivity[1]. Their reactions with activated double bonds yield only Michael-type adducts rather than cyclopropane ring formation. Similarly with aldehydes and ketones, they are known to give only the corresponding aldol-type compounds. Much of the earlier work on nitrogen ylids was confined to the more stable immonium and cycloimmonium ylids and their synthetic applications[2]. There are only a few reports of stable ammonium ylids and their synthetic applications have virtually not been investigated[3]. We report here the preparation of cyanotrimethylammonium methylid, a novel ammonium ylid and its facile reaction with α,β-unsaturated carbonyl compounds to yield cyclopropanes. To our knowledge, this is the first report of cyclopropanation of an activated double bond with an ammonium ylid, except for a sole reference on the formation of tribenzoylcyclopropane as one of the products from the reaction of phenacylpyridinium methylid with phenacyl bromide[4,5].

The ylid **3** was generated by stirring a suspension of the readily available cyanomethyltrimethylammonium iodide[6] **(2)** and sodium hydride in dry tetrahydrofuran. When this ylid was reacted *in situ* with chalcone **4a**, work-up and column chromatography of the reaction mixture yielded the mixture of the *cis*- and *trans*-cyclopropane **5a** in 10% and 51% yield, respectively. The stereoisomeric cyclopropanes **5b, c** were similarly obtained by the reaction of respective chalcones **4b, c** with **3**. The reaction of chalcone **4d** with **3** gave only *trans*-**5d** in 34% yield, while *cis*-**5d** could not be isolated from the reaction mixture. Similarly, the reaction of ethyl cinnamate **(4e)** with **3** gave only *trans*-**5e** in 65% yield, while ethyl acrylate **(4f)** yielded the mixture of *cis*- and *trans*-**5f** in 21% yield. Reaction of **3** with 2-cyclohexen-1-one did not give any identifiable product. Similarly, reactions of **3** with acrylamide, cinnamanilide, cinnamaldehyde, and nitrostyrene yielded only polymeric mixtures.



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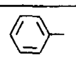
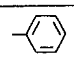
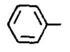
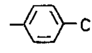
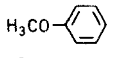
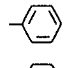
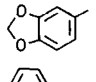
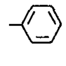
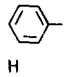
a		
b		
c		
d		
e		OC_2H_5
f	H	OC_2H_5

A Michael-type addition of the ylid carbon atom to the C=C bond of **4a-f** followed by ring closure with elimination of trimethylamine should account for cyclopropane formation. An alternative mechanism through decomposition of **3** to a cyanocarbene intermediate followed by its addition to the double bond is ruled out, since **3** does not add to unactivated double bonds such as those of cyclohexene or stilbene and no trace of 1,2,3-tricyanocyclopropane was obtained in any of the reactions.

The stereochemistry of **5a-e** was assigned by comparison of the N.M.R. chemical shifts and vicinal coupling constants with those of the known *cis*- and *trans*-**5a**[7].

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Table. 1,2-Disubstituted-3-cyanocyclopropanes **5a–f**

Product	Reaction time	Yield [%]	m.p. [°C] or b.p. [°C]/torr	Molecular formula[a] or Lit. data	I.R. (nujol) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]	M.S. m/e (M^+)
cis-**5a**	14 h	10	123–124°	123–124°[7]	2240 (CN); 1675 (CO)	2.30 (t, 1H, J=7 Hz); 3.45 (d, 2H, J=7 Hz); 7.0–7.8 (m, 8H_{arom}); 8.05 (m, 2H_{arom})	247
trans-**5a**	14 h	51	109–110°	109–110°[7]	2240 (CN); 1672 (CO)	2.62 (dd, 1H, J=8.5 and 4.5 Hz); 3.01 (dd, 1H, J=8.5 and 6.0 Hz); 3.61 (dd, 1H, J=6.0 and 4.5 Hz); 7.0–7.8 (m, 8H_{arom}); 8.05 (m, 2H_{arom})	247
cis-**5b**	16 h	32	133–134°	$C_{17}H_{12}ClNO$ (281.7)	2240 (CN); 1670 (CO)	2.36 (t, 1H, J=7 Hz); 3.36 (d, 2H, J=7 Hz); 6.8–7.7 (m, 8H_{arom}); 8.0 (m, 2H_{arom})	281.5
trans-**5b**	16 h	54	123–124°	$C_{17}H_{12}ClNO$ (281.7)	2236 (CN); 1672 (CO)	2.75 (dd, 1H, J=9 and 4.5 Hz); 3.02 (dd, J=9 and 6.0 Hz); 3.58 (dd, J=6 and 4.5 Hz); 6.9–7.7 (m, 7H_{arom}); 8.1 (m, 2H_{arom})	281.5
cis-**5c**	15 h	13	106–108°	$C_{18}H_{15}NO_2$ (277.3)	2238 (CN); 1668 (CO)	2.26 (t, 1H, J=7 Hz); 3.32 (d, 2H, J=7 Hz); 3.76 (t, 3H, $C\underline{H}_3O$); 7.01 (dd, 4H_{arom}); 7.6 (m, 3H_{arom}); 8.0 (m, 2H_{arom})	277
trans-**5c**	15 h	42	92–93°	$C_{18}H_{15}NO_2$ (277.3)	2240 (CN); 1670 (CO)	2.60 (dd, 1H, J=8.5 and 4.5 Hz); 2.92 (dd, 1H, J=8.5 and 6 Hz); 3.50 (dd, 1H, J=6 and 4.5 Hz); 3.72 (s, 3H, $C\underline{H}_3O$); 7.04 (dd, 4H_{arom}); 7.5 (m, 3H_{arom}); 8.0 (m, 2H_{arom})	277
trans-**5d**	16 h	34	102°	$C_{18}H_{13}NO_3$ (291.3)	2240 (CN); 1665 (CO)	2.60 (dd, 1H, J=9 and 4.5 Hz); 2.95 (dd, 1H, J=9 and 6 Hz); 3.52 (dd, J=6 and 4.5 Hz); 5.93 (s, 2H, $O{-}CH_2{-}O$); 6.80 (s, 3H_{arom}); 7.2–7.65 (m, 3H_{arom}); 8.02 (dd, 2H_{arom})	291
trans-**5e**	12 h	65	Yellow viscous liquid	$C_{13}H_{13}NO_2$ (215.2)	2240 (CN); 1730 (CO)[b]	1.30 (t, 3H, $C\underline{H}_3CH_2$); 2.40 (dd, 1H, J=8.5 and 6 Hz), 2.73 (t, 1H, J=6 Hz); 2.98 (dd, J=8.5 and 6 Hz); 4.24 (q, 2H, $CH_3C\underline{H}_2O$); 7.40 (br s, 5H_{arom})	215
cis/*trans*-**5f**	12 h	21	80–85°/3	80–82°/3 (*trans*); 80–87°/3 (*cis*)[8]	2240 (CN); 1738 (CO)[b]	1.1–1.8 (m, 5H, $C\underline{H}_3CH_2$ and two cyclopropyl protons); 1.8–2.55 (m, 2H, cyclopropyl proton); 4.18 (q, 2H, $CH_3C\underline{H}_2O$)	139

[a] Satisfactory microanalyses obtained: C ±0.44, H ±0.44, N ±0.42.

[b] I.R. of neat liquid.

Cyanomethyltrimethylammonium Iodide (2):

Prepared by the reported[6] procedure from *N,N*-dimethylaminoacetonitrile (**1**) and methyl iodide in dry ether at room temperature; yield: 90%; m.p. 210°C (dec) (Ref.[6], m.p. 210°C).

***cis*- and *trans*-1-Cyano-2,3-disubstituted Cyclopropanes 5a–f; General Procedure:**

A suspension of sodium hydride (0.025 mol, 50% suspension) and cyanomethyltrimethylammonium iodide (**2**; 0.02 mol) in dry tetrahydrofuran (25 ml) is stirred at room temperature for 1.5 h till the evolution of hydrogen is complete. A solution of **4a–f** (0.02 mol) in dry tetrahydrofuran (25 ml) is slowly added to the reaction mixture during 15 min with stirring and the temperature is slowly raised to 40–50°C, till the evolution of trimethylamine starts. The reaction mixture is stirred at 40–45°C for the stated time (Table) and the reaction is monitored by frequently checking the evolution of trimethylamine. When the evolution of trimethylamine is complete, the mixture is worked up by removing the solvent under reduced pressure, diluting with water (10–15 ml), neutralizing with dilute acetic acid, and extracting with ether (3 × 100 ml). The ether layer is dried with sodium sulfate, evaporated, and the residue is passed through a silica gel column; elution with benzene and hexane (1 : 1) gives first the *trans*-isomers of **5a–c**, while further elution with benzene and hexane (4 : 1) yields the *cis*-isomers of **5a–c**.

In the case of **4d**, only *trans*-**5d** was obtained on elution with benzene/hexane mixture (3 : 1) and no trace of *cis*-**5d** could be isolated.

Column chromatography of the reaction mixture obtained from **4e** and **3**, first yielded unreacted ethyl cinnamate (5%) on elution with benzene/hexane (1 : 1), while further elution with benzene/hexane (4 : 1) yielded *trans*-**5e**.

Column chromatography of the reaction mixture obtained from the reaction of **4f** and **3** gives a crude mixture of *cis*-**5f** and *trans*-**5f**, which on distillation (Vigreux column, 3 in) under reduced pressure gives a mixture of pure *cis*- and *trans*-**5f**; b.p. 80–83°C/3 torr[8].

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We are thankful to Prof. Barry M. Trost for sending us physical data, I.R. and N.M.R. spectral data for compounds *cis*-**5a** and *trans*-**5a**; see also, J. Adams, L. Hoffman, Jr., B. M. Trost, *J. Org. Chem.* **35,** 1600 (1970).

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