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Synthesis and Reactivity of 1-N,N-Diethylcarbamoyl-1,3-Butadiene.[1]

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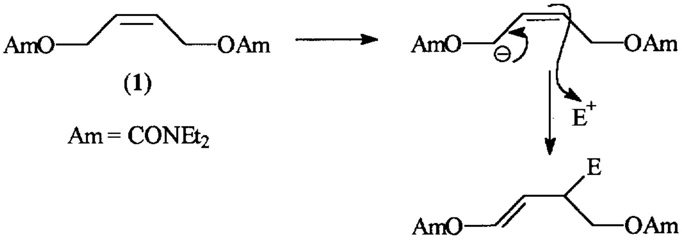
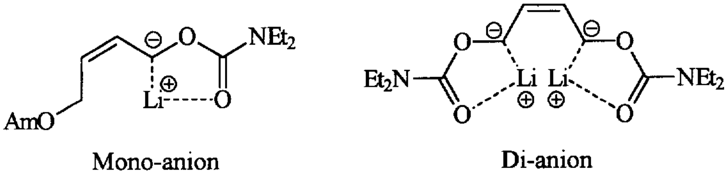
Abstract: 1-N,N-Diethylcarbamoyl-1,3-butadiene is easily prepared from *cis*-1,4-di-(N, N-diethylcarbamoyl)but-2-ene and reacts, as the vinyl anion, with various electrophiles. The preparation of the diene demonstrates the leaving ability of the N, N-dialkylcarbamoyl group.

The N, N-dialkyl carbamate group has been shown to be effective in stabilising anions in the allylic and benzylic positions[2], and as part of our studies involving such systems, it was decided that dicarbamates might afford better stabilisation. As a model system, *cis*-1,4-di-(N, N-diethylcarbamoyl)but-2-ene (**1**) was prepared. It was envisioned that (**1**) would react in a similar manner to other allylic carbamates, in that the allylic anion would react with electrophiles in the position β to the carbamate group, as shown in Scheme 1.



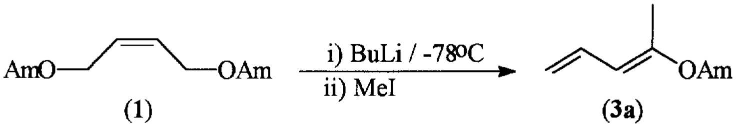
Scheme 1

We also thought that it may be possible to form a dianion in the presence of two equivalents of base. (Scheme 2).



Scheme 2

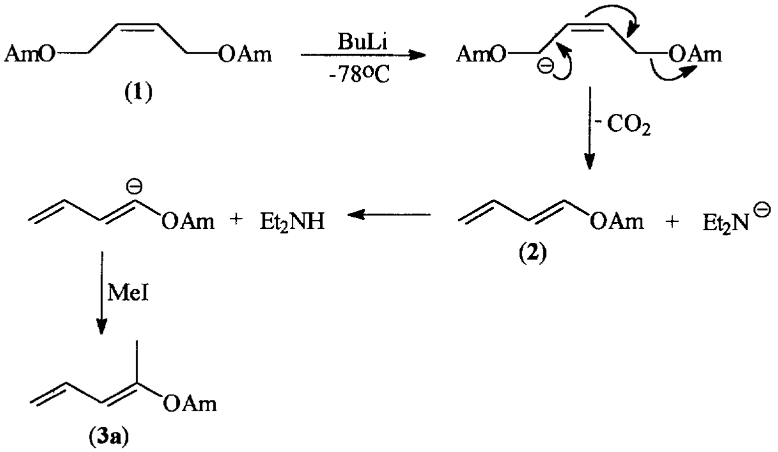
It was found, however, that on reaction with methyl iodide, the 1-methyl-1,3-butadienecarbamate (**3a**) was isolated in fair yield (Scheme 3), and none of the expected product (Scheme 1) was observed.



Scheme 3

The only way this could be accounted for was the initial elimination of one of the carbamate groups, which decarboxylates to yield the strong base, N, N-diethylamide. Abstraction of the vinyl proton, leads to the observed product (**3a**), as outlined in Scheme 4. Treatment of (**1**) with two equivalents of butyllithium and methyl iodide also results on the 1-methyl-1,3-butadienecarbamate (**3a**), and not the product from the expected dianion (Scheme 2), indicating that elimination of the carbamate group is rapid.

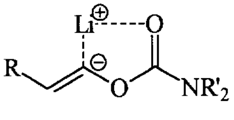
We have found that the best results were obtained by a two-pot reaction, with initial preparation and purification of the 1,3-butadiene carbamate, followed by reaction with electrophiles. Generation of the so-called "vinyl anion"[3,4,5] was most conveniently carried out using a slight excess of n-butyllithium in THF, followed by addition of the electrophile. Other bases, such as LDA and sec-BuLi/TMEDA, did not appear to be any more effective.



Scheme 4

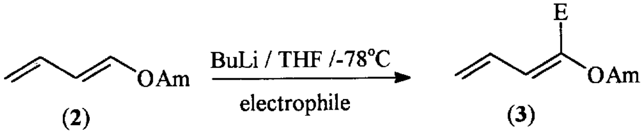
Apart from the obvious synthetic utility of this reaction for carrying out vinyl substitution reactions, this reaction highlights an unusual reaction of N, N-dialkylcarbamoyl groups, namely that they are very efficient leaving groups. Other studies in our laboratories[6] have shown the S_N2' elimination of the carbamate group by nucleophiles to be a fairly general reaction. We have not, however, observed any instance of a direct S_N2 reaction involving similar carbamates.

Treatment of (**1**) with butyllithium yields the unsubstituted diene (**2**) which, on further treatment with butyllithium, undergoes reaction in the 1-position. Two systems similar to (**2**) has been reported recently. Snieckus[3] prepared N, N-diethyl and N, N-diisopropyl vinyl carbamate which, after abstraction of the vinyl proton, reacted with various electrophiles. Hoppe[4,5] prepared allenes with a vinyl carbamate group and, on abstraction of the α-proton, reacted it with electrophiles to give substituted allenes. In both cases, Hoppe and Snieckus propose that the vinyl anion is stabilised by the carbamate group, *via* a five-membered transition state (4), shown below.



(4)

The vinyl anion thus generated has been found to be relatively unreactive, and only very reactive electrophiles react with any degree of success. Alkyl, benzyl and allyl halides, especially primary alkyl iodides, were expected to react readily, but we found that only methyl iodide reacted. Other alkyl halides were unreactive, while benzyl bromide, allyl bromide, benzaldehyde and benzophenone gave complex reaction mixtures of no synthetic use. The more reactive TMSCl reacts readily, but the more bulky TBDMSCl did not react. Acid chlorides, chloroformates and carbamoyl chlorides proved to be the most successful electrophiles, as shown in Scheme 5 and Table.



Scheme 5

Table: Yields of substituted dienes.

(3)	**Electrophile**	**% Yield**	**(3)**	**Electrophile**	**% Yield**
a	Methyl iodide	85	g	Allyl chloroformate	61
b	Ethyl iodide	0[a]	h	Ethyl chloroformate	58
c	TMSCl	69	i	Diethyl carbamoyl chloride	43
d	TBDMSCl	0[a]	j	Other alkyl halides[b]	0[a]
e	PhCOCl	55	k	Benzyl and allyl bromide	0[c]
f	$PhCO_2Et$	0[a]	l	Benzaldehyde, benzophenone	0[c]

[a] Starting material recovered quantitatively.

[b] Ethyl bromide, 1-bromopropane, 2-bromopropane and octyl bromide. Unreactive, only starting material isolated.

[c] Complex mixture of products.

As can be seen from the results, the 1-N,N-diethylcarbamoyl-1,3-butadiene is a very selective nucleophile, and even though it reacts with a limited range of electrophiles, the fact that most alkyl halides and esters are inert should allow one to prepare α,β,γ,δ-unsaturated carbonyl compounds in the presence of the less reactive esters and halides.

Experimental.

The tetrahydrofuran was dried using $LiAlH_4$ and distilled before use. N.M.R. spectra were recorded on a Varian Gemini 200 instrument. All chemical shifts are reported in ppm downfield from TMS as internal standard, using $CDCl_3$ as solvent. Mass spectra were recorded on a Hewlett-Packard gas chromatographic-mass spectrometer (HP5988A). Elemental analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyser.

Cis-1,4-di-(N,N-diethylcarbamoyl)-but-2-ene (1).

A solution of cis-1,4-dihydroxybut-2-ene (10.000 g, 0.1135 mol) in dry THF (50 ml) was added to a cooled (0°C), stirred suspension of NaH (8.514 g, 80 %, 0.2838 mol) in dry THF (100 ml). The mixture was allowed to warm to room temperature and stirred for 30 minutes. The reaction mixture was cooled again and a solution of N,N-diethylcarbamoylchloride (32,327 g, 0.2384 mol) in dry THF (50 ml) was added drop-wise. The reaction was warmed to room temperature and stirred for a further 4 hours. The reaction was quenched with water (100 ml) and the THF removed. The reaction mixture was diluted with diethylether (100 ml) and washed with 10% *aq.* $NaHCO_3$ (2 x 50 ml) and water (1 x 50 ml). The organic phase was separated and dried over anhydrous $MgSO_4$. The solvent was removed and the residue distilled to yield cis-1,4-di-(N,N-diethylcarbamoyl)-but-2-ene (30.301 g, 93 %). b.p. 165 °C / 5 mm Hg. δ_H (200 MHz) 1.12 (12H, t, 4 x $C\mathit{H}_3$), 3.28 (bq, 8H, 4 x $C\mathit{H}_2CH_3$), 4.70 (d, 4H, $C\mathit{H}_2$-CH=CH- $C\mathit{H}_2$), 5.76 (t, 2H, $C\mathit{H}$=$C\mathit{H}$). δ_C (50 MHz) 13.58 and 14.00 (2 x q, 2 x $\mathit{C}H_3$), 41.28 and 41.80 (2 x t, 2 x $\mathit{C}H_2CH_3$), 60.73 (t, $\mathit{C}H_2$-CH=CH-$\mathit{C}H_2$), 128.46(d, CH=CH), 155.63 (s, 2 x C=O). *m/z:* 286 (M^+, <1 %), 117 (19), 100 (100), 72 (85), 54 (21), 44 (24). (Anal. Calcd. for $C_{14}H_{26}N_2O_4$: C, 58.72; H, 9.15, N, 9.78. Found : C, 58.58; H, 9.21, N, 9.63 %).

Trans-1-N,N-diethylcarbamoyl-1,3-butadiene (2).

Cis-1,4-di-(N,N-diethylcarbamoyl)-but-2-ene (5.000 g, 0.0175 mol) was dissolved in dry THF (75 ml) and cooled to -78°C (acetone / solid CO_2) under nitrogen with stirring. ^{n}BuLi in hexane (0.0210 mol) was added drop-wise and the mixture was stirred at -78°C for 2.5 hours. The reaction was quenched with saturated *aq.* NH_4Cl and the THF removed. The residue was dissolved in diethylether (100 ml) and washed with water (2 x 50 ml). The organic phase was separated, dried over anhydrous $MgSO_4$ and the solvent removed. The residue was distilled to yield trans-1-N,N-diethylcarbamoyl-1,3-butadiene. (2.697 g, 91 %). b.p. 77°C / 0.25 mm Hg. δ_H (200 MHz) 1.15 (t, 6H, 2 x $C\mathit{H}_3$), 3.33 (q, 4H, 2 x $C\mathit{H}_2CH_3$), 5.05 (dd, 2H, $C\mathit{H}_2$=CH), 5.96 (t, 1H, $C\mathit{H}$=CH-O), 6.28 (dt, 1H, CH_2=$C\mathit{H}$), 7.38 (d, 1H, CH=$C\mathit{H}$-O). δ_C (50 MHz) 13.30 and 14.18 (2 x q, $CH_2\mathit{C}H_3$), 41.57 and 42.20 (2 x t, $\mathit{C}H_2CH_3$), 113.72 (d, CH_2=CH), 115.40 (t, $\mathit{C}H_2$=CH), 132.29 (d, CH=CH-O), 140.52 (d, CH-O), 152.77 (s, C=O). *m/z:* 169 (M^+, 13 %), 100 (99), 72 (100), 56 (23). Calcd. for $C_9H_{15}NO_2$: C, 63.88; H, 8.93, N, 8.28. Found : C, 63.81; H, 8.99, N, 8.08 %).

*General procedure for the preparation of 1-substituted dienes (***3***).*

A solution of 1-N,N-diethylcarbamoyl-1,3-butadiene (0.250 g, 0.00148 mol) in dry THF (10 ml) was cooled to -78°C (acetone / solid CO_2) under an atmosphere of nitrogen with stirring. ^{n}BuLi (0.00163 mol) was added dropwise and the mixture stirred for 1 hour. A solution of electrophile (a = MeI, c = TMSCl, e = PhCOCl, g = allyl chloroformate, h = ethyl chloroformate and i = N,N-diethylcarbamoylchloride) (0.00163 mol) in dry THF (5 ml) was added dropwise and the mixture stirred for a further 3 hours. The reaction was quenched with sat. *aq.* NH_4Cl, diluted with diethylether (50 ml) and washed with water (2x 50 ml). The organic phase was dried (anhydrous $MgSO_4$), the solvent removed and then purified by column chromatography.

(**3a**) Oil; 85 %; δ_H (200 MHz) 1.16 (6H, t, $N(CH_2C\mathit{H_3})_2$), 2.02 (3H, s, $C\text{-}C\mathit{H_3}$), 3.31 (4H, q, $N(C\mathit{H_2}CH_3)_2$), 5.08 (2H, dd, $C\mathit{H_2}{=}CH$), 5.83 (1H, d, $C\mathit{H}{=}C\text{-}CH_3$), 6.40 (1H, dt, $CH_2{=}C\mathit{H}$). δ_C (50 MHz) 13.31 and 14.00 (2x q, $N(CH_2\mathit{C}H_3)_2$), 15.99 (q, $C\text{-}\mathit{C}H_3$), 41.73 and 41.78 (2x t, $N(\mathit{C}H_2CH_3)_2$), 116.34 (t, $\mathit{C}H_2{=}CH$), 118.39 (d, $\mathit{C}H{=}C\text{-}CH_3$), 131.14 (d, $CH_2{=}\mathit{C}H$), 148.56 (s, $CH{=}\mathit{C}\text{-}CH_3$), 153.83(s, $\mathit{C}{=}O$). *m/z:* 183 (M^+, 3 %), 100 (100), 72 (45), 44 (12). Calcd. for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35, N, 7.64. Found : C, 65.77; H, 9,09, N, 7.55 %).

(**3c**) Oil; 69 %; δ_H (200 MHz) 0.25 (9H, s, $Si(C\mathit{H_3})_3$), 1.16 (6H, m, $N(CH_2C\mathit{H_3})_2$), 3.32 (4H, q, $N(C\mathit{H_2}CH_3)_2$), 5.18 and 6.50 (4H, m, vinyl-*H*). δ_C (50 MHz) 0.00 (q, $Si(\mathit{C}H_3)_3$), 14.04 and 14.74 (2x q, $N(CH_2\mathit{C}H_3)_2$), 42.36 and 42.53 (2x t, $N(\mathit{C}H_2CH_3)_2$), 119.18 (t, $\mathit{C}H_2{=}CH$), 132.12 (d, $CH_2{=}\mathit{C}H$), 133.76 (d, $\mathit{C}H{=}C\text{-}SiMe_3$), 155.75 (s, $\mathit{C}\text{-}SiMe_3$), 160.09 (s, $\mathit{C}{=}O$). *m/z:* 241 (M^+, <1 %), 174 (11), 100 (100), 73 (46), 72 (78), 44 (29). Calcd. for $C_{12}H_{23}NO_2Si$: C, 59.70, H, 9.60, N, 5.80. Found : C, 59.84; H, 9.32, N, 5.59 %).

(**3e**) Oil; 55 %; δ_H (200 MHz) 0.96 and 1.18 (6H, 2x t, $N(CH_2C\mathit{H_3})_2$), 3.18 and 3.33 (4H, 2x q, $N(C\mathit{H_2}CH_3)_2$), 5.10 - 5.50 (2H, dd, $C\mathit{H_2}{=}CH$), 6.30 - 6.60 (2H, m, $C\mathit{H}\text{-}C\mathit{H}$), 7.30 - 8.00 (5H, m, Ar-*H*). δ_C (50 MHz) 12.86 and 13.88 (2x q, $N(CH_2\mathit{C}H_3)_2$), 41.74 and 41.90 (2x t, $N(\mathit{C}H_2CH_3)_2$), 122.33 (t, $\mathit{C}H_2{=}CH$), 125.47, 128.18 and 129.05 (3x d, Ar-*C*), 130.21 (d, $CH_2{=}\mathit{C}H$), 132.58 (d, $CH_2{=}CH\text{-}\mathit{C}H$), 137.19 (s, *C*-COPh), 144.64 (s, Ar-*C*), 153.30(s, $\mathit{C}ONEt_2$), 190.19 (s, *C*OPh). *m/z:* 273 (M^+, 4 %), 105 (7), 101 (7), 100 (100), 77 (8), 72 (33), 44 (5). Calcd. for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01, N, 5.12. Found : C, 70.16; H, 7.11, N, 5.14 %).

(**3g**) Oil; 61 %; δ_H (200 MHz) 1.23 (6H, m, $N(CH_2C\mathit{H_3})_2$), 3.36 (4H, m, $N(C\mathit{H_2}CH_3)_2$), 4.74 (2H, d, $OC\mathit{H_2}CH{=}CH_2$), 5.20 - 5.60 (4H, m, 2x $C\mathit{H_2}{=}CH$), 5.80 - 6.10 (1H, m, $OCH_2C\mathit{H}{=}CH_2$), 6.41 (1H, d, $CH_2{=}C\mathit{H}\text{-}CH$). δ_C (50 MHz) 13.32 and 14.00 (2x q, $N(CH_2\mathit{C}H_3)_2$), 42.02 and 42.27 (2x t, $N(\mathit{C}H_2CH_3)_2$), 65.68 (t, $O\mathit{C}H_2CH{=}CH_2$), 118.42 (t, $CH_2CH{=}\mathit{C}H_2$), 124.82 (t, $\mathit{C}H_2{=}CH\text{-}CH$), 130.94 (d, $CH_2\mathit{C}H{=}CH_2$), 130.98 (d, $CH_2{=}\mathit{C}H\text{-}CH$), 131.66 (d, $CH_2{=}CH\text{-}\mathit{C}H$), 137.32 (s, $CH{=}\mathit{C}\text{-}C{=}O$), 153.98 (s, $N\mathit{C}{=}O$), 161.98 (s, $O\mathit{C}{=}O$). *m/z:* 253 (M^+, 1 %), 100 (100), 72 (35), 44 (4). Calcd. for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56, N, 5.53. Found : C, 61.78; H, 7.51, N, 5.69 %).

(3h) Oil; 58 %; δ_H (200 MHz) 1.20 (6H, m, $N(CH_2CH_3)_2$), 1.31 (3H, t, OCH_2CH_3), 3.34 (4H, m, $N(CH_2CH_3)_2$), 4.29 (2H, q, OCH_2CH_3), 5.44 (2H, dd, CH_2=CH-CH), 6.39 (1H, d, CH_2=CH-CH), 6.20 - 6.50 (1H, m, CH_2=CH-CH). δ_C (50 MHz) 13.34 and 13.99 (2x q, $N(CH_2CH_3)_2$), 14.09 (q, OCH_2CH_3), 42.03 and 42.28 (2x t, $N(CH_2CH_3)_2$), 61.16 (t, OCH_2CH_3), 124.54 (t, CH_2=CH), 130.54 (d, CH_2=CH), 130.99 (d, CH_2=CH-CH), 137.61 (s, CH_2=CH-CH=C), 154.01 (s, NC=O), 162.32 (s, OC=O). *m/z:* 241 (M^+, 17 %), 196 (8), 100 (100), 72 (28), 44 (7). Calcd. for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94, N, 5.81. Found : C, 59.84; H, 7.88, N, 5.87 %).

(3i) Oil; 43 %; δ_H (200 MHz) 1.23 (12H, m, 2x $N(CH_2CH_3)_2$), 3.20 - 3.70 (8H, 2x m, 2x $N(CH_2CH_3)_2$), 5.10 - 5.40 (2H, dd, CH_2=CH), 6.07 (1H, d, CH_2=CH-CH), 6.20 - 6.50 (1H, dt, CH_2=CH). δ_C (50 MHz) 13.13, 13.27, 13.96 and 14.11 (4x q, 2x $N(CH_2CH_3)_2$), 28.29, 41.97, 42.11 and 43.01 (4x t, 2x $N(CH_2CH_3)_2$), 118.75 (d, CH_2=CH), 119.78 (t, CH_2=CH), 130.01 (d, CH_2=CH-CH), 142.99 (s, CH_2=CH-CH=C), 153.08 (s, NC=O), 164.18 (s, OC=O). *m/z:* 268 (M^+, 1%), 100 (100), 72 (51), 44 (12). Calcd. for $C_{14}H_{24}N_2O_4$: C, 62.66; H, 9.01, N, 10.44. Found : C, 62.40; H, 8.89, N, 10.52 %).

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