Table IX

Reactions of $CF_3CF_2CF_2I$ and of $(CF_3)_2CFI$ with 1,6-Heptadiene

Reaction time, hr	Reactants, M				% conversion to adducts			Adduct ratio	
	$CF_3CF_2CF_2I$	HPD	ABN[a]	R_FI[b]/HPD	I	IIIa,b	II	III/I	III/I + II
0.16	0.0050	0.0050	1.00	1.0/1.0	57.4	40.8	1.8	0.71	0.69
0.16	0.0050	0.0100	1.00	1.0/2.0	55.5	43.3	1.0	0.78	0.77
0.33	0.0100	0.0050	1.00	2.0/1.0	68.0	26.3	5.5	0.39	0.36
0.33	0.0050	0.0050	1.00	1.0/1.0	60.0	39.0	1.0	0.65	0.65
0.33	0.0050	0.0100	1.00	1.0/2.0	55.5	43.3	1.0	0.78	0.77
0.50	0.010	0.0050	1.00	2.0/1.0	62.5	23.8	13.7	0.38	0.31
0.50	0.0050	0.0050	1.00	1.0/1.0	57.0	37.4	5.7	0.66	0.60
0.50	0.0050	0.010	1.00	1.0/2.0	55.7	43.8	0.6	0.78	0.78
1.50	0.010	0.0050	1.00	2.0/1.0	57.5	25.7	16.8	0.45	0.35
1.50	0.0050	0.0050	1.00	1.0/1.0	56.4	37.4	6.3	0.66	0.60
4.00	0.010	0.0050	1.00	2.0/1.0	44.5	27.6	27.9	0.62	0.38
24.0	0.010	0.010	1.00	1.0/1.0	17.0	64.2	16.0	3.82	1.94
24.0	0.0050	0.010	1.00	1.0/2.0	8.6	84.5	4.0	9.85	6.70
24.0	0.0025	0.010	1.00	1.0/4.0	2.0	95.5	0.5	47.7	38.1
46.0	0.010	0.010	1.00	1.0/1.0	15.0	63.9	20.9	4.25	1.77
46.0	0.0050	0.010	1.00	1.0/2.0	4.06	92.95	1.3	23.2	17.5
46.0	0.0025	0.020	1.00	1.0/4.0	2.0	98.0	0.0	46.0	46.0
	$(CF_3)_2CFI$								
7.5	0.010	0.010	1.35	1.0/1.0	37.3	39.0	22.6	1.04	0.65
7.5	0.0050	0.010	1.10	1.0/2.0	32.2	58.0	9.74	1.80	1.38
7.5	0.0025	0.020	0.86	1.0/4.0	30.4	68.4	1.4	2.25	2.16
24.5	0.010	0.010	1.00	1.0/1.0	21.0	54.5	24.5	2.60	1.2
24.5	0.0050	0.010	1.00	1.0/2.0	6.70	90.0	3.3	13.3	9.0
24.5	0.0025	0.010	1.00	1.0/4.0	1.55	98.4	trace	61.1	61.1

[a] $M \times 10^{-4}$. [b] R_FI is either $CF_3CF_2CF_2I$ or $(CF_3)_2CFI$.

Isomerization of Propargylic Amines to Conjugated Dienes. 2-Dialkylamino-1,3-butadienes

M. L. Farmer, W. E. Billups, R. B. Greenlee, and A. N. Kurtz

Research Department, Union Carbide Corporation, Olefins Division, South Charleston, West Virginia

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A new class of reactive compounds, 2-dialkylamino-1,3-butadienes, may be obtained in good yield by the base-catalyzed isomerization of 3-dialkylamino-1-butynes.

Although base-catalyzed acetylene–allene and acetylene–acetylene interconversions have been reported frequently since the early work of Favorskii,[1-9] only recently have many examples of acetylene–allene–conjugated diene interconversions been reported. For instance Smadja has successfully isomerized 1-heptyne and 1-octyne to conjugated systems using potassium tertiary butoxide in dimethyl sulfoxide.[10] Subsequent investigations by Julia and Baillarge have shown that 1,1,4,4-tetraphenyl-1,2-butadiene gives 1,1,4,4-tetraphenyl-1,3-butadiene upon treatment with methanolic potassium hydroxide; 1,4-diphenoxy-2-butyne undergoes a similar rearrangement.[11] Recently an interesting example of an enyne system undergoing isomerization has been reported. The naturally occurring methyl crepenynate has been isomerized to *trans,cis,trans*- and *trans,cis,cis*-8,10,12-octadecatrienoic acids in 70% yield plus other conjugated trienes when heated with potassium hydroxide.[12] Sondheimer has converted cyclic polyynes and related compounds to fully conjugated ring systems with ease.[13] 1,2-Cyclodecadiene or cyclodecyne when heated with potassium hydroxide in diethyl "Carbitol" results in the formation of 69–73% *cis,cis*-1,3-cyclodecadiene.[14] Phenyl-substituted propargylic ethers and thio ethers have been easily isomerized to the allenes with potassium tertiary butoxide in dimethyl sulfoxide.[15] Under similar conditions, 1,3-diphenyl-3-dimethylamino-1-propyne and 1,3-diphenyl-3-dimethylamino-1,2-propadiene were equilibrated. However, in all cases when phenyl groups were replaced by alkyl groups, difficulties were reported.

We wish to report an example of a facile base-catalyzed isomerization of certain acetylenic compounds to 1,3-dienes; the reaction has been applied to propargylic amines and to hexynes, the former providing some heretofore unreported 3-dialkylamino-1,3-conjugated dienes. Since the propargylic amines are

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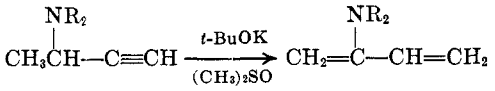
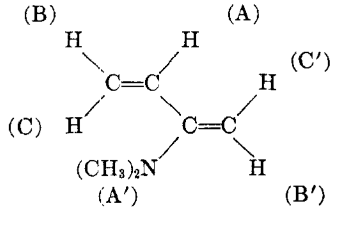
readily available from the reaction of acetylene with secondary amines in the presence of a Cu(I) catalyst at 80° and 200–300-psig pressure, the isomerization becomes a useful synthesis of 2-dialkylamino-1,3-butadienes and their derivatives.



$$CH_3\overset{NR_2}{\overset{|}{C}}H-C\equiv CH \xrightarrow[(CH_3)_2SO]{t\text{-BuOK}} CH_2=\overset{NR_2}{\overset{|}{C}}-CH=CH_2$$

The only previous isomerization of this type was claimed by Reppe and collaborators[16] several years ago when 3-amino-1-butynes were rearranged in the vapor phase over aluminum oxide activated with iron oxide, but few details of the reaction or products were given. In view of the instability of the 1,3-diene products it is improbable that any undecomposed 3-dialkylamino-1,3-dienes were ever isolated.

Using mild conditions, *i.e.*, 25–35° in dimethyl sulfoxide, the equilibrium is far on the side of the conjugated diene; thus 3-dialkylamino-1-butynes were converted to 2-dialkylaminobutadienes in 80% isolated yields with no starting butyne or allenic products ever observed in the isolated product. Distillation of the products gave a colorless liquid whose physical spectra all correlated well with a conjugated diene. Rapid decomposition of the compound in dilute solutions made determination of the ultraviolet spectrum uncertain, but λ_{max} 268 mμ (ϵ 2800) was recorded in the best run, with the maximum at 268 mμ decreasing rapidly with time. The bathochromic shift to longer wavelength (as compared with 1,3-butadiene) is in good accord with what is known about auxochromic groups involving π–p conjugation.[17] A mass spectrum (*m/e* 97) and neut equiv 103.9 confirmed the molecular weight. The proton nmr spectrum at 60 Mcps also supported the following structure.



The notation of Hobgood and Goldstein[18] is used to assign the parameters in Table I.

TABLE I

NMR SPECTRAL DATA ON 2-DIMETHYLAMINO-1,3-BUTADIENE

Proton	δ, ppm	Multiplicity (>0.5 cps)	*J*, cps
A	6.23	4	AB, 10.8; AC, 18.0
B	5.02	4	AB, 10.8; BB′, 0.4; BC, 2.7
B′	4.13	1	BB′, 0.4
C	5.41	4	AC, 18.0; BC, 2.7
C′	3.83	1	. . .
A′	2.52	1	. . .

The chemical shifts of 2-dimethylamino-1,3-butadiene are in excellent accord with those reported for 2-methoxy-1,3-butadiene published by Hobgood and Goldstein where protons B′ and C′ are shifted very far upfield.[19] The absence of coupling between protons A and B′ and A and C′ in that compound was attributed to cancellation of π–σ-electronic transmission of long-range coupling and may be operative also where the substituent is a dimethylamino group since in this case there is also no coupling between A and B′ and A and C′. In 2-dimethylamino-1,3-butadiene there is no coupling between B and C′, B′ and C, C and C′, and B′ and C′, but a small coupling constant between B and B′ (0.42 cps) was observed. 2-*t*-Butyl-1,3-butadiene similarly is reported to show no coupling between protons B and B′, B and C′, B′ and C, and C and C′. The only anomaly is the lack of coupling between protons B′ and C′; however, this absence of geminal coupling is reported not to be unusual.[20]

Additional support for the assigned structure comes from the hydrogenation of the compound over Adams catalyst at 50 psig and 25° in a quantitative yield to 2-dimethylaminobutane.

Several attempts were made to prepare the Diels–Alder adduct of 2-dimethylamino-1,3-butadiene, but all dienophiles reacted vigorously with the diene to give mixtures of unidentified products which were shown to contain no olefinic protons.

When the more sterically crowded 4-methyl-3-morpholino-1-phenyl-1-pentyne was treated with potassium *t*-butoxide in either dimethyl sulfoxide or dimethylformamide isomerization occurred within 3 hr at room temperature. Analysis of the crude reaction products by nmr showed that, in this case, quantitative conversion to the 4-methyl-3-morpholino-1-phenyl-1,2-pentadiene had occurred. Warming to approximately 80° failed to isomerize the molecule to the conjugated diene. The failure of this molecule to isomerize to the conjugated diene at moderate temperatures is apparently the result of the steric requirements of the *t*-butoxide anion as it approaches the hindered 4-position.

The dimethyl sulfoxide–potassium tertiary butoxide medium was also effective in the isomerization of 1-hexyne to conjugated dienes. After 92 hr at 72°, 8.2 g of 1-hexyne was isomerized to 8.0 g of a mixture of products containing 2.3% 1,3-hexadienes, 34.1% *trans,trans*-2,4-hexadiene, 52.0% *cis,trans*-2,4-hexadiene, and 10.2% 2-hexyne, as shown by vpc analysis. An identical run starting with 3-hexyne gave the same product distribution.

Experimental Section[21]

3-Dimethylamino-1-butyne.—A mixture of 225 g (5 moles) of dimethylamine, 250 ml of dimethylformamide (dried with Linde 5A Sieve), 24.7 g (0.25 mole) of cuprous chloride, and 15.3 g (0.187 mole) of dimethylamine hydrochloride was treated with 220 psig

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[18] R. T. Hobgood, Jr., and J. H. Goldstein, *J. Mol. Spectr.*, **12**, 76 (1964).

[19] A. H. Bothner-By and R. K. Harris, *J. Am. Chem. Soc.*, **87**, 3445 (1965).

[20] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p 85.

[21] Melting points were determined on a Fisher-Johns block. Refractive indexes were obtained in an Abbé refractometer (Bausch and Lomb). Infrared spectra were run directly or in CCl_4 and CS_2 solutions on a Beckman IR-5A spectrophotometer and the nmr spectra were determined neat or in CCl_4 solutions, containing TMS as internal standard, using a Varian A-60 spectrometer. Apparent chemical shifts are given in parts per million (δ). Glc analyses were accomplished on a Beckman GC-2 instrument.

of acetylene at 75° in a rocking 1-l. autoclave for 20.5 hr[22]; the reaction mixture was cooled under acetylene pressure without rocking. The cooled bomb was vented and the unreacted dimethylamine in the crude reaction mixture was allowed to escape. Gravity filtration gave 523 g of crude product which was distilled in a 12-in. Vigreux column. A distillation cut in the amount of 192 g and boiling at 44–155° at atmospheric pressure was taken. Vapor phase chromatography of this distillation cut on a 18-ft column of 5% Tergitol NP-27 + 1% benzidine on Floropak 80 showed 6.7% dimethylamine, 78.4% 3-dimethylamino-1-butyne, and 13.7% dimethylformamide.

Redistillation of combined crude products of a number of runs gave 99.86% pure (by vpc) of 3-dimethylamino-1-butyne: bp 93.4° (760 mm) (lit.[16] bp 96°); n^{20}D 1.4231; 2.7-min retention time at 130°; $\nu_{\max}^{\mathrm{neat}}$ 3320, 2225, 1460 cm^{-1}.

3-Diethylamino-1-butyne.—Similar runs with diethylamine were made. Redistillation of the combined crude products of a number of runs gave 99.47 % pure (vpc) of 3-diethylamino-1-butyne: bp 128.2–128.4° (760 mm) (lit.[16] bp 127–128°); n^{20}D 1.4300; 4.5-min retention time at 130°; $\nu_{\max}^{\mathrm{neat}}$ 3320, 2230, 1460 cm^{-1}.

2-Dimethylamino-1,3-butadiene.—In a typical experiment, 24.3 g (0.25 mole) of 3-dimethylamino-1-butyne was added slowly, with stirring at room temperature and under a nitrogen atmosphere, to a solution of 2.80 g (0.025 mole) of potassium tertiary butoxide in 24.3 g of dimethyl sulfoxide previously prepared in a drybox. The butyne was added at such a rate that the temperature remained below 35°. The reaction appeared complete (no longer exothermic) in 3 hr, but was allowed, in this case, to stand 2 days under a nitrogen atmosphere. Distillation of the crude reaction products was accomplished at *ca.* 0.5 mm of Hg and at approximately 0° through a 12-in. Vigreux column attached to a distillation head cooled by circulating acetone at −78° through the condenser. The distillate was collected in a trap maintained at −78° to yield 20.2 g of colorless liquid: $d^{25}{}_{25}$ 0.7882; n^{20}D 1.4638; $\nu_{\max}^{\mathrm{CCl_4}}$ 1830, 1600, 980, 920, 875 cm^{-1}; $\lambda_{\max}^{\mathrm{cyclohexane}}$ 268 mμ, ϵ 2800 (maximum rapidly decreased with time); nmr 6.23 (quartet, 0.9 H), 5.41 (quartet, 0.9 H), 5.02 (quartet, 0.9 H), 4.13 (singlet, 1.0 H), 3.83 (singlet, 1.0 H), 2.52 (singlet, 6.0 H); neut equiv 103.9; mass spectrum (*m/e* 97).

Anal. Calcd for $C_6H_{11}N$: C, 74.24; H, 11.42; N, 14.43. Found: C, 73.98; H, 11.15; N, 15.37.

The product, upon warming, evolves heat and darkens, especially if solvents are added, but the compound may be stored neat with no special precautions at −78° for a least a week. Attempts to form the Diels–Alder adduct at −50 to +25° failed with dimethylacetylene dicarboxylate, methyl propiolate, maleic anhydride, sulfur dioxide, tetracyanoethylene, and acrylonitrile. In all cases the addition of the dienophile caused rapid exothermic decomposition to products shown, by nmr, to contain no olefinic protons.

Hydrogenation of 2-Dimethylamino-1,3-butadiene.—The 2-dimethylamino-1,3-butadiene (4.0 g, 0.041 mole) was added to a Parr hydrogenation bottle containing 100 mg of platinum oxide. After flushing with nitrogen and then hydrogen the initial pressure was adjusted to 50 psig. The quantitative amount of hydrogen for two double bonds per molecule was taken up in one hour. After running overnight, the catalyst was removed by filtration to yield 2.8 g of yellow liquid: $\nu_{\max}^{\mathrm{CCl_4}}$ 2800, 2760, 1450, 1150, 1043 cm^{-1}; nmr 1.50 (multiplet, 1.0 H), 1.34 (multiplet, 14.0 H). Analysis by vapor phase chromatography on an eighteen-foot column (5% Tergitol NP-27 and 1% benzidine on Fluoropak 80) at 127° and a helium pressure of 55 psig gave a single peak with a retention time of 2.0 min.

Hydrogenation of 3-Dimethylamino-1-butyne.—3-Dimethylamino-1-butyne (4.0 g, 0.041 mole) was hydrogenated as described above to yield 2.9 g of colorless liquid. Infrared and nmr are identical with those described above. Analysis by vpc at those conditions described above gave a single peak with a retention of 2.0 min.

2-Diethylamino-1,3-butadiene.—A procedure similar to that utilized for studying the isomerization of 3-dimethylamino-1-butyne was employed with 3-diethylamino-1-butyne. A volatile fraction was vacuum distilled from the final reaction mixture to a −78° trap in good yield; the condensate was not satisfactorily characterized owing to its reactivity, but the infrared spectrum exhibited no allene or acetylene absorption, but did show diene absorption at 1830 cm^{-1}.

4-Methyl-3-morpholino-1-phenyl-1-pentyne.—To a 250-ml round-bottom flask was added 100 ml of benzene, 1.0 g of cuprous chloride, 22.5 g of phenyl acetylene, and 31 g of N-isobutenyl morpholine. The flask was fitted with a reflux condenser and equipped to maintain a nitrogen atmosphere. The mixture was heated on a steam bath and allowed to reflux for 20 hr. After the cuprous acetylide was removed by filtration, the brown filtrate was evaporated to dryness to leave 52 g (98%) of crude product as a red brown crystalline solid. The crude material was dissolved in hot *n*-hexane and filtered to remove a small amount of gummy red brown material. The clear yellow filtrate deposited crystals on cooling which were recovered by filtration to give 42.5 g (83 %) of product, mp 71–72°. An analytical sample, recrystallized slowly from *n*-hexane, was obtained as massive buff-colored prisms, mp 71.5–72.0°. The equivalent weight was found to be 235; $\nu_{\max}^{\mathrm{CCl_4}}$ 1450, 1330, 1120, 1070, 1030 cm^{-1}; nmr 7.37 (multiplet, 5.0 H); 3.69 (triplet, 4.0 H, J = 4.5–5.0 cps); 2.98 (doublet, 1.0 H, J = 10 cps); 2.60 and 2.52 (2 overlapping triplets; 4.2 H, J = 4.5–5.0 cps); 1.85 (multiplet, 1.0 H); 1.12 (doublet, 3.0 H, J = 5.5–6.0 cps); 1.01 (doublet 3.1 H).

Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70. Found: C, 79.48; H, 8.70.

4-Methyl-3-morpholino-1-phenyl-1-pentyne was initially obtained by the noncatalyzed addition of phenylacetylene to N-isobutenyl morpholine as a red brown solid, mp 71–73°. The infrared spectrum was superimposable with that from above.

***trans*-4-Methyl-1-phenyl-1-penten-3-one.**[23]—4-Methyl-3-morpholino-1-phenyl-1-pentyne (550 mg, 2.2 moles) was dissolved in 40 ml of dry dimethylformamide containing 100 mg of potassium tertiary butoxide. The solution was stirred at room temperature for 3 hr under a nitrogen atmosphere. The nmr of the crude reaction mixture showed resonances at 7.68 (multiplet, 5.1 H) and 5.98 (doublet, 1.0 H, J = 2.1 cps) in the region from δ 4 to 8. The nmr tube was heated on a steam bath for an hour with no change in the spectrum. The solvent was removed at 0.3-mm Hg pressure at 25°, and the oil remaining was quickly extracted between water and ether. The organic layer was washed with water, dried over sodium sulfate, and the solvent removed by rotary evaporation to leave 421 mg of yellow oil: $\nu_{\max}^{\mathrm{CCl_4}}$ 1680, 1630, 1198, 1132, 1115, 1050, 970 cm^{-1}; nmr 7.73 (doublet, 1.0 H, J = 16.2 cps), 7.2–7.5 (multiplet, 5.1 H), 2.86 (heptet, 1.0 H, J = 7.0 cps), 1.13 (doublet, 6.1 H, J = 7.0 cps). The 2,4-dinitrophenylhydrazine derivative melted at 148–150° (lit.[23] mp 153°).

Isomerization of 1-Hexyne and 3-Hexyne.—To a mixture of 8.21 g of dimethyl sulfoxide and 1.12 g of potassium tertiary butoxide under a nitrogen atmosphere at 25° there was added 8.21 g of 1-hexyne. The reaction was exothermic and the temperature rose to a maximum of 46°. After holding the system at 30° for 4 hr, the volatiles were stripped at 46° and 6.4 mm to a −78° cold trap giving 8.17 g of condensate which contained 95% 2-hexyne by vapor phase chromatography at 52° with a 4-m column of 30% silicone 550 and Carbowax 4000 (3:2) on Chromosorb W.

In another run the isomerization was repeated but with the system at 72° for 92 hr. The volatile product amounted to 8.00 g and was analyzed by vpc to be 2.3% 1-ethyl-1,3-butadiene, 52.0% *cis,trans*-2,4-hexadiene, 34.1% *trans,trans*-2,4-hexadiene, and 10.2% 2-hexyne.

An identical run at 72° starting with 3-hexyne gave the same product distribution as the run starting with 1-hexyne.

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[22] In all acetylene experiments the autoclave was filled with $^3/_8$-in.-o.d. stainless steel tubes to prevent acetylene detonations. Also flash arrestors were installed in the line leading from the acetylene cylinder to the autoclave.

[23] R. P. Mariella and R. R. Raube, *J. Am. Chem. Soc.*, **74**, 521 (1952)