to the norbornenyl ring double bond in the same system;[5] further, while "activated" sulfur adds exclusively to the norbornenyl ring double bond in **1**, CSI adds only to the exocyclic double bond. In this latter reaction, whatever the balance between steric factors (involving the approaching electrophile) and the intrinsic reactivity (of each double bond in **1**), the surprising result discourages even tentative mechanistic speculation without further and more comprehensive experimental data.

Experimental Section

Reaction of 5-Ethylidenebicyclo[2.2.1]hept-2-ene (1)[10] with CSI.—A solution of 5.0 g (0.04 mol) of **1** in 20 ml of absolute ether was cooled to −30° by means of a Dry Ice–ethanol bath. To this was added dropwise a solution of 5.9 g (0.04 mol) of CSI in 15 ml of absolute ether. The mixture was stirred at −30° for 30 min, then warmed to room temperature, and stirred again for an additional 30 min. Approximately half of the solvent was removed by passing a stream of nitrogen through the solution and gentle heating. Cooling at −20° for 6 hr afforded the colorless crude **1-chlorosulfonyl-3-methyl-2-azetidinone-4-spiro-5′-bicyclo[2.2.1]hept-2′-ene (3)**. Recrystallization from pentane yielded 9.4 g (86%) of **3** as fine needles: mp 69–70°; ir (CCl_4) 5.48 (C=O), 7.06 and 8.43 μ (SO_2); nmr ($CDCl_3$) δ 1.14 (d, 3, J = 7.5 Hz, CH_3) 1.80 (m, 2, C-7′ protons), 2.25 (m, 2, C-6′ protons), 3.02–3.33 (m, 3, C-3, -1′, -4′ protons), 6.08 (split doublet, 1, C-2′ proton), 6.40 (split doublet, 1, C-3′ proton).

Anal. Calcd for $C_{10}H_{12}NSO_3Cl$: C, 45.89; H, 4.62; N, 5.35. Found: C, 45.59; H, 4.86; N, 5.26.

Treatment of 1 equiv of **1** with 2 equiv of CSI gave only the monoadduct **3**.

Reduction of 3 with Benzenethiol–Pyridine.—A solution of 0.64 g (0.008 mol) of pyridine in 7 ml of acetone was added slowly to a solution of 1.77 g (0.007 mol) of **3** and 1.49 g (0.014 mol) of benzenethiol in 18 ml of acetone cooled to −30° in a Dry Ice–ethanol bath. After 4 hr, 18 ml of water was added dropwise. Phenyl disulfide precipitated and the mixture was filtered while still cold. The solution was extracted with three 50-ml portions of ether, dried (Na_2SO_4), filtered, and evaporated. The residual oil was extracted with 50 ml of boiling pentane and the extract was cooled to −20° for 24 hr to yield 0.40 g (36%) of **3-methyl-2-azetidinone-4-spiro-5′-bicyclo[2.2.1]hept-2′-ene (4)**: mp 97–98°; ir (CCl_4) 2.94 (free NH), 3.12 (bonded NH), 5.66 μ (C=O, doublet); nmr ($CDCl_3$) δ 1.06 (d, 3, J = 7.5 Hz, CH_3), 1.66 (split singlet, 4, C-6′, -7′ protons), 2.87 (broad complex, 3, C-3, -1′, -4′ protons), 6.03 (split doublet, 1, C-2′ proton), 6.22 (split doublet, 1, C-3′ proton), 7.60 (broad singlet, 1, NH).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.84; H, 8.02; N, 8.44.

The analytical sample was prepared by sublimation at 88–89° (0.25 mm).

Catalytic Hydrogenation of 4.—A solution of 0.76 g (0.005 mol) of **4** in 40 ml of absolute ethanol was hydrogenated (5% Pd–C) at an initial hydrogen pressure of 38 psi in a Parr shaker for 1 hr. The catalyst was filtered and the ethanol was evaporated *in vacuo*. The solid residue was recrystallized twice from pentane to give 0.49 g (65%) of **3-methyl-2-azetidinone-4-spiro-2′-bicyclo-[2.2.1]heptane (5)**: mp 76–77°; ir (CCl_4) 2.95 (NH, free), 3.15 (bonded NH), 5.66 μ (C=O, doublet); nmr ($CDCl_3$) δ 1.18 (d, 3, J = 7.5 Hz, CH_3), 1.45 (broad complex, 8, C-3′, -5′, -6′, -7′ protons), 2.15 (broad singlet, 1, C-4′ proton), 2.32 (broad singlet, 1, C-1′ proton) 3.00 (q, 1, J = 7.5 Hz, C-3 proton) 7.38 (broad singlet, 1, NH).

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.47. Found: C, 72.61; H, 9.14; N, 8.45.

Hydrolysis of 4 with Hydrochloric Acid.—A 0.30-g (0.002 mol) sample of **4** was dissolved in just enough concentrated HCl to cover the solid material and allowed to stand at room temperature for 2 hr. The thick, transparent paste was dried under vacuum with P_2O_5 giving a white solid. Recrystallization from methanol–ether gave 0.37 g (97%) yield of the amino acid hydrochloride (**6**): mp 245–247° dec; ir (KBr) 3.39 (NH), 5.87 μ (C=O); nmr (D_2O) δ 1.37 (d, 3, J = 7.5 Hz, CH_3) 1.82 (broad singlet, 4, C-6, -7 protons), 2.57 [q, 1, J = 7.5 Hz, $-CH(CH_3)COOH$], 3.12 (broad singlet, 2, C-1, -4 protons), 6.20 (m, 1, C-2 proton), 6.42 (m, 1, C-3 proton).

Anal. Calcd. for $C_{10}H_{16}NO_3Cl$: C, 55.17; H, 7.41; N, 6.43. Found: C, 54.87; H, 7.25; N, 6.72.

(10) Graciously supplied in research quantities by Union Carbide Corp., Chemicals and Plastics, South Charleston, W. Va. 25303.

Registry No.—**1**, 16219-75-3; **3**, 24265-81-4; **4**, 24265-82-5; **5**, 24265-83-6; **6**, 24265-84-7; chlorosulfonyl isocyanate, 1189-71-5.

5-Tetrazolyl Ylides

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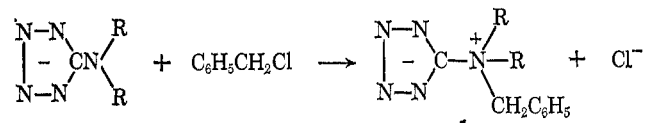
The monoalkylation of a 5-substituted tetrazole, as its anion, normally leads to a mixture of 1- and 2-alkyl-5-substituted tetrazoles; the ratio of isomers is influenced by the nature of the 5 substituent.[1] Even when this substituent is amino or substituted amino, ring alkylation, rather than alkylation on the *exo* nitrogen atom, has been reported to occur preferentially.[2] It has now been found that the monobenzylation of sodium 5-dimethylaminotetrazole in aqueous ethanol gives not only the expected, previously undescribed, 1- and 2-benzyl isomers, poorly soluble in water and readily soluble in benzene, but a third isomer (29% yield), poorly soluble in benzene and soluble in water. The solubility behavior and the high melting point (205° *vs.* 78 and 95°, respectively) suggested the novel ylide **1** (R = CH_3), which would result from benzylation on the *exo* nitrogen. Support



1

for this assignment comes from the ^1H nmr spectrum; the signal for methyl protons is shifted to lower field while that for the benzyl methylene protons is shifted to higher field than those observed with either the 1 or 2 isomer (Table I). The chemical-shift values found for the ylides are in the range normally observed for similar quaternary ammonium salts. For example, benzyltrimethylammonium iodide (in Polysol) gives values of τ 6.77 and 5.18 for the methyl and benzyl methylene proton shifts.

The nmr spectrum of the diethyl ylide (**1**, R = C_2H_5) shows the same complex phenyl multiplet observed for the dimethyl compound and the chemical shift of the benzyl methylene protons is nearly the same. Convincing proof of tetrahedral substitution on the exo nitrogen is provided by the 2-Hz splitting of the ethyl

(1) F. R. Benson in "Heterocyclic Compounds," Vol. 8, R. C. Elderfield, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, p 53.

(2) R. A. Henry and W. G. Finnegan, *J. Amer. Chem. Soc.*, **76**, 923 (1954).

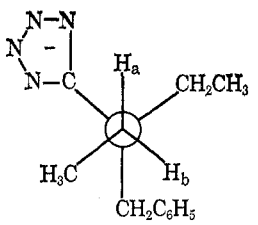
TABLE I

NMR CHEMICAL-SHIFT VALUES FOR BENZYLATION PRODUCTS OF 5-DIALKYLAMINOTETRAZOLES

Product[a]	R	Phenyl	Benzyl CH_2	R CH_2	CH_3	Solvent
1-Benzyl	CH_3	2.63	4.37		7.05	DMSO-d_6
		2.66	4.50		7.02	$CDCl_3$
2-Benzyl	CH_3	2.60	4.28		7.06	DMSO-d_6
		2.63	4.43		6.95	$CDCl_3$
exo-N-Benzyl	CH_3	2.72[b]	4.94		6.42	DMSO-d_6
1-(3-Chlorobenzyl)	CH_3	2.6[b]	4.39		7.02	DMSO-d_6
		2.75[b]	4.54		7.10	$CDCl_3$
2-(3-Chlorobenzyl)	CH_3	2.6[b]	4.30		7.05	DMSO-d_6
		2.75[b]	4.47		7.05	$CDCl_3$
exo-N-(3-Chlorobenzyl)	CH_3	2.7[b]	4.93		6.42	DMSO-d_6
1-Benzyl	CH_2CH_3	2.68	4.59	6.77	9.00	$CDCl_3$
2-Benzyl	CH_2CH_3	2.68	4.47	6.53	8.88	$CDCl_3$
exo-N-Benzyl	CH_2CH_3	2.85[b]	4.95	6.09, 6.13[c]	8.70	Polysol[d]

[a] Respective registry numbers follow: 24301-98-2, 24301-99-3, 24302-00-9, 24302-01-0, 24302-02-1, 24302-03-2, 24302-04-3, 24302-05-4, 24302-06-5. [b] Complex multiplet about τ 0.4-0.6 wide. [c] Two overlapping quartets due to intrinsic asymmetry. [d] A proprietary solvent with properties similar to DMSO-d_6 obtained from Stohler Isotope Chemicals, Azusa, Calif.

methylene signal into overlapping quartets. This can only arise from the intrinsic asymmetry of substitution on the nitrogen which leads to chemical nonequivalence of the geminal protons as shown in the projection diagram.



A suspension of **1** (R = CH_3) in a small volume of absolute ethanol at room temperature undergoes no change during several weeks. The addition of an equimolar amount of methyl iodide, however, causes a moderately rapid solution of the ylide; both isomerization to 2-benzyl-5-dimethylaminotetrazole (confirmed by melting point and ir spectrum) and debenzylation to 5-dimethylaminotetrazole occur. Sodium iodide (molar equivalent) also effects a slow isomerization in ethanol (16% in 3 weeks). Isomerization results when the ylides are heated in solution. For example, **1** (R = C_2H_5) is about 50% converted into 2-benzyl-5-diethylaminotetrazole (trace of 1 isomer) after 10 hr in D_2O at 96°, based upon changes in the ^1H nmr spectra with time. When **1** (R = CH_3) is heated at 96° in dimethyl sulfoxide-d_6, 50% of the ylide disappears in 24 hr; however, only about half of this loss corresponds to isomerization, the other half of the ylide having gone to 5-dimethylaminotetrazole (CH_3, τ 7.02) and benzaldehyde (CH, τ −0.10). The latter compound arises from an oxidation of a benzyl group by the solvent since dimethyl sulfide (CD_2H, τ 7.82) also appears. By way of contrast, the 3-chlorobenzyl analog of **1** (R = CH_3) is almost quantitatively converted into the 2 isomer after 2 hr at 96° in dimethyl sulfoxide with no detectable concurrent formation of aldehye and 5-dimethylaminotetrazole.

This isomerization of the ylide resembles the Stevens rearrangement which involves migration of a benzyl group from nitrogen to carbon in quaternary ammonium salt.

Experimental Section

Benzylation of Sodium 5-Dimethylaminotetrazole.—A solution consisting of 33.9 g (0.3 mol) of 5-dimethylaminotetrazole, 120 ml of water, 240 ml of 95% ethanol, 12 g (0.3 mol) of sodium hydroxide, and 38.0 g (0.3 mol) of benzyl chloride was refluxed overnight. After the pH had been readjusted to the phenolphthalein end point, the solution was evaporated to dryness and the solids extracted with one 200-, one 100-, and two 50-ml portions of boiling benzene. Evaporation of the combined benzene extracts left 29.9 g (49%) of mixed 1- and 2-benzyl-5-dimethylaminotetrazoles. Part of the mixture was chromatographed on silica gel–Celite (2:1) using chloroform–benzene (1:1 v/v) to elute first the 2 isomer, then chloroform to remove the 1 isomer;[3] the ratio of the former to the latter was 8:1.

The **2-benzyl-5-dimethylaminotetrazole** was recrystallized from either cyclohexane or benzene: mp 94–95°; uv (95% ethanol) 218 nm (ϵ 4400), 272 (2500).

Anal. Calcd for $C_{10}H_{13}N_5$: C, 59.09; H, 6.45; N, 34.46. Found: C, 59.01; H, 6.44; N, 34.33.

The **1-benzyl-5-dimethylaminotetrazole** was obtained as colorless needles from cyclohexane: mp 77–78°; uv (95% ethanol) 217 nm (ϵ 4350), 239 (3500).

Anal. Calcd for $C_{10}H_{13}N_5$: C, 59.09; H, 6.45; N, 34.46. Found: C, 59.18; H, 6.48; N, 34.40.

The residue remaining after the initial benzene extractions was digested with 400 ml of boiling 2-propanol and filtered. After the crystalline product had been removed from the chilled filtrate, the mother liquors were used again to extract the cake. The yield of crude ylide **1** (R = CH_3) recovered after this operation had been repeated four times was 18.1 g (28.8%): mp 185–195° (recrystallization of a portion from 2-propanol raised the melting point of the fine, felted needles to 204–205°); uv (95% ethanol) 217 nm (ϵ 4500), 258 (330), 263 (460), 270 (410).

Anal. Calcd for $C_{10}H_{13}N_5$: C, 59.09; H, 6.45; N, 34.46. Found: C, 59.16; H, 6.54; N, 34.36.

The 1- and 2-benzyl-5-dialkylaminotetrazoles, as well as the parent 5-dialkylaminotetrazoles, all show a strong absorption in their ir spectra in the range of 1590–1640 cm^{-1}. This absorption is absent with the ylides.

Benzylation of Sodium 5-Diethylaminotetrazole.—A procedure similar to the above was employed except that the dried mixture of products was extracted with cyclohexane rather than benzene. The yield of mixed 1- and 2-benzyl-5-diethylaminotetrazole was 65%; the ratio of isomers was 1:5 based on ^1H nmr. The ylide **1** (R = C_2H_5) was extracted from the cyclohexane-insoluble residue with boiling benzene–2-propanol (85:15) and crystallized slowly when the filtrate was chilled at 5° for several days. Recrystallization from acetone gave large, transparent colorless prisms of a monohydrate, mp 125–130°, with slumping from 110°. The yield was about 13%.

(3) The first material off the column is assigned the 2-isomer structure since such isomers are more soluble and less polar than the corresponding 1 isomers [M. H. Kaufman, F. M. Ernsberger, and W. S. McEwan, *J. Amer. Chem. Soc.*, **78**, 4197 (1956)].

Anal. Calcd for $C_{12}H_{17}N_5 \cdot H_2O$: N, 28.09; H_2O, 7.33. Found: N, 28.16; H_2O, 7.9.

2-Benzyl-5-benzylmethylaminotetrazole.—Benzylation of sodium 5-benzylmethylaminotetrazolate in an analogous manner gave a 55% yield of mixed 1- and 2-benzyl-5-benzylmethylaminotetrazole (1:5 based on ^1H nmr analysis), mp 56–57°. The 2 isomer, mp 58–59°, was recovered when the crude product was recrystallized from *n*-hexane.

Anal. Calcd for $C_{16}H_{17}N_5$: C, 68.79; H, 6.14; N, 25.07. Found: C, 68.49; H, 6.09; N, 25.40.

No ylide was found.

5-(3-Chlorobenzyldimethylammonium)tetrazolate.—This ylide, prepared in 33% yield, decomposed at 227–228° after recrystallization from 95% ethanol.

Anal. Calcd for $C_{10}H_{12}N_5Cl$: N, 29.47; Cl, 14.91. Found: N, 29.33; Cl, 15.01.

The ratio of 1- and 2-(3-chlorobenzyl)-5-dimethylaminotetrazoles, also recovered (56% yield) in this alkylation, was 1:10.

Registry No.—2-Benzyl-5-benzylmethylaminotetrazole, 24302-07-6.

The Chemistry of Cumulated Double-Bond Compound. VIII. The Reaction of Phosphonium Ylide with Carbodiimide

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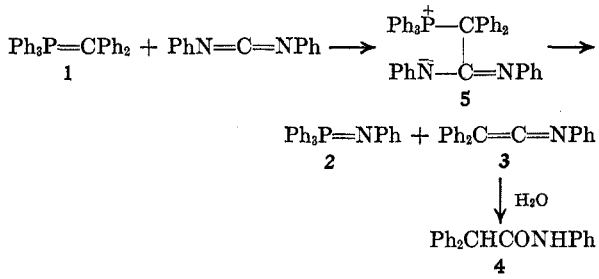
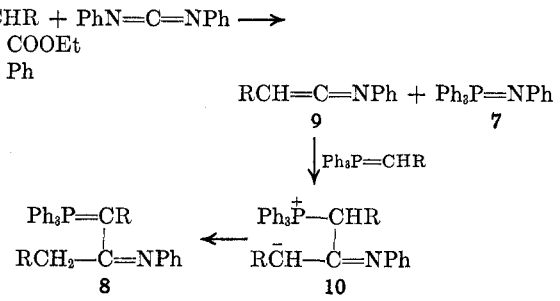
Reactions of phosphonium ylides with ketenes or isocyanates have been reported in a few papers. Luscher had reported that the reaction of diphenylmethylenetriphenylphosphorane with diphenylketene yielded tetraphenylallene and triphenylphosphine oxide.[1] On the other hand, Staudinger and Meyer reported that the reaction of the same ylide with phenyl isocyanate yielded ketenimine.[2] Trippet and Walker observed that the products varied with the structure of ylides.[3]

In this paper, we studied the reactions of phosphonium ylides with carbodiimides.

The reaction of diphenylmethylenetriphenylphosphorane (**1**) with diphenylcarbodiimide yielded N-phenyliminotriphenylphosphorane (**2**) and triphenylketenimine (**3**) in good yield. The ketenimine **3** exhibited the principal infrared peak at 2000 cm^{-1} (C=C=N) and was hydrolyzed easily to diphenylacetanilide (**4**). The reaction process seemed to involve the intermediate **5** according to Wittig-type reaction. Bestmann and Seng[4] reported a similar reaction between phenylmethylenetriphenylphosphorane and benzalaniline to afford stilbene and N-phenyliminotriphenylphosphorane.

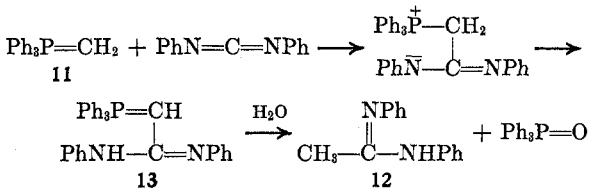


In the reaction of the ylides **6**, containing a hydrogen atom on the ylide carbon, diphenylcarbodiimide reacted with two molecules of the ylide **6**, and N-phenyliminotriphenylphosphorane (**7**) and the ylides **8** were obtained.



In the nmr spectrum of the ylide **8a**, the chemical shifts of the two ethyl protons were separated at δ 0.58 (t, CH_3)–3.85 (q, CH_2) and δ 1.02 (t, CH_3)–4.12 (q, CH_2); the methylene group adjacent to the imino group was seen as a singlet at δ 4.11. The infrared spectrum of the ylide **8a** in a Nujol mull indicated the peak at 1570 cm^{-1} (imino group). Similar absorption was observed at 1530 cm^{-1} for the ylide **8b**. In these reactions, the ketenimines **9**, formed in the initial step, react immediately with additional ylide **6** to give **8** *via* the betaine **10** by a prototropic shift.

Methylenetriphenylphosphorane (**11**) reacted with an equimolar quantity of diphenylcarbodiimide in dimethyl sulfoxide; N,N′-diphenylacetamidine (**12**) and triphenylphosphine oxide were obtained by treatment with water. The ylide **13** was not isolated; only the acetamidine **12**, presumably formed by hydrolysis of the ylide **13**, was obtained as a major product.



No reaction was observed between dicylohexylcarbodiimide and the ylides **2** and **6**. This may be due to the lower reactivity of the carbodiimide.

Experimental Section

Preparation of the Carbodiimides.—A mixture of 15.7 g of phenyl isocyanate and 1.73 g of triphenylphosphine was refluxed for 10 hr and distilled to give 8.9 g (70%) of diphenylcarbodiimide, bp 122–127° (1 mm). The physical constants and the infrared spectrum were identical with the reported data.[5]

Dicyclohexylcarbodiimide was purchased and distilled, bp 135–138° (1 mm).

(1) G. Luscher, *Diss. Eidg. Techn. Hochschule, Zurich* (1922); A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, p 132.
(2) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919).
(3) S. Trippet and D. M. Walker, *J. Chem. Soc.*, 3874 (1959).
(4) H. J. Bestmann and F. Seng, *Angew. Chem.*, **75**, 475 (1963); *Tetrahedron*, **21**, 1373 (1965).
(5) F. Kurzer and K. Douraghizadeh, *Chem. Rev.*, **67**, 107 (1962).