to be very hygroscopic and consistent elemental analyses were not obtained: infrared absorptions (KBr) 8.0–8.2, 9.19, 9.3, 9.5, 11.29, and 13.1 μ; n.m.r. spectrum (D_2O) doublet with $J = 10.9$ c.p.s. centered at 3.66 with an area equivalent to 3 protons ($-OCH_3$), single peak at 3.32 with an area equivalent to 9 protons $[-\overset{\oplus}{N}(CH_3)_3]$, peaks due to ($>N-CH-P<$) were overlapped by one of the ($-OCH_3$) and the ($>N-CH_3$) peaks, broad peak at 2.5, and pair of doublets at 1.32 $[-CH(CH_3)_2]$ p.p.m.

Anal. Calcd. for $C_8H_{20}NO_3P$: C, 45.9; H, 9.6; N, 6.7; P, 14.8; mol. wt., 209. Found: C, 44.1; H, 10.1; N, 7.1; P, 13.3; mol. wt. (ebullioscopic in ethyl alcohol), 202.

When the reaction was carried out in the presence of 0.1 g. of *p*-toluenesulfonic acid, essentially the same results were obtained.

Inner Salt of Butyl-[2-methyl-1-(methylphosphono)propyl]-ammonium Hydroxide (3).—Isobutyraldehyde (36 g., 0.5 mole) was added to a refluxing mixture of dimethyl hydrogen phosphite (55 g., 0.5 mole) and butylamine (36 g., 0.5 mole). The temperature of the mixture rose to 120°. Sodium sulfate was added to the mixture after it had cooled to room temperature. After standing for 72 hr. the mixture was filtered and the filtrate was distilled to a base temperature of 130° (2 mm.). The residue crystallized to a gummy solid which, on trituration with cold acetone, gave a 28-g. (25%) yield of the inner salt **3**: m.p. 181–185°; infrared absorptions (KBr) 8.2 (wide), 9.2–9.5, 13.2, and 14.15 μ; n.m.r. spectrum (D_2O) doublet at 3.69 with an area equivalent to 3 protons and $J = 10.9$ c.p.s. ($-OCH_3$), peaks centered at 3.23 $[>CH-\overset{\oplus}{N}(CH_2)<]$, broad peak at 2.34 (tertiary proton of the isopropyl group), broad peak at 1.58 ($\geqslant\overset{\oplus}{N}-CH_2-$), and two doublets with an overlapping triplet centered at 1.07 (methyl groups) p.p.m.

Anal. Calcd. for $C_9H_{22}NO_3P$: C, 48.4; H, 9.93; N, 6.3; P, 13.9; mol. wt., 223. Found: C, 48.4; H, 9.96; N, 6.4; P, 13.6; mol. wt. (ebullioscopic in ethyl alcohol), 231.

Dimethyl 1-(Butylamino)-2-methylpropylphosphonate (4).—The method described by Fields[1] was utilized in the preparation of this compound. It was obtained in 71% yield: b.p. 96–98° (*ca.* 0.25 mm.); n^{20}D 1.4418; n.m.r. spectrum (neat) pair of doublets with an area equivalent to 6 protons and with chemical shifts of 3.76 and 3.79 p.p.m. and $J = 10.0$ c.p.s. $[(^{-}OCH_3)_2]$, peaks centered at 2.70 ($-CH_2-\overset{|}{N}-CH<$), broad peak centered at 2.03 (tertiary proton of the isopropyl group), broad peak at 1.40 ($-CH_2CH_2CH_2-N<$), and three peaks, probably two doublets with an overlapping triplet at 1.00 (methyl groups) p.p.m.

Anal. Calcd. for $C_{10}H_{24}NO_3P$: C, 50.6; H, 10.2; N, 5.9; P, 13.1. Found: C, 50.6; H, 10.3; N, 5.7; P, 13.1.

The residue from the distillation of **4** gave a 2-g. yield of solid which was identical with **3**.

Inner Salt of Butylmethyl-[2-methyl-1-(methylphosphono)-propyl]ammonium Hydroxide (5).—Dimethyl 1-(butylamino)-2-methylpropylphosphonate (20 g., 0.08 mole) was heated to 190° over a period of 0.5 hr. A viscous oil resulted which did not give a yield of solid on treatment with various solvents. This oil appeared by n.m.r. spectroscopy to be impure **5**: n.m.r. spectrum (D_2O) doublet at 3.65 with $J = 11.0$ c.p.s. and an area equivalent to 3 protons ($-OCH_3$), single sharp peak at 3.19 $[\geqslant\overset{\oplus}{N}-CH_3$ which overlapped peaks for the $-CH_2-\overset{\oplus}{N}(CH-)<]$ with total area equivalent to 6 protons, broad band from 1.2 to 2.2 (tertiary proton of the isopropyl group and methylene protons of the butyl group), and three peaks centered at 1.08 (methyl groups) p.p.m.

Reaction of Benzoyl Azide with Aldimines and Ketimines

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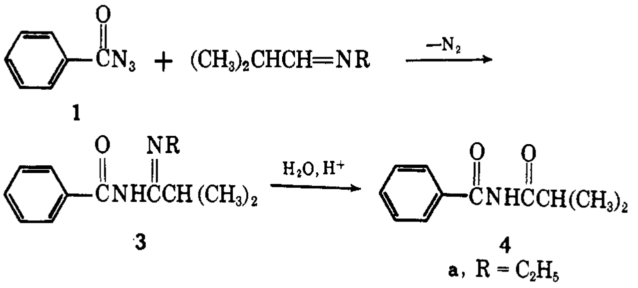
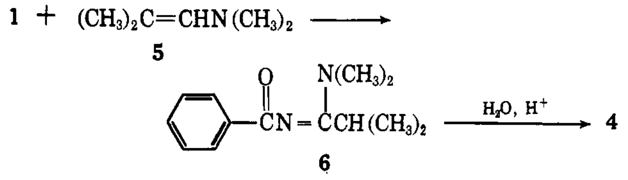
Papers dealing with reactions of azides and other 1,3-dipolar compounds with enamines have appeared recently.[1-5] Similar reactions were carried out in these laboratories and the results were found to be in agreement with those reported. The reaction of azidobenzene with alicyclic ketone anils to give triazoles was reported by Alder and Stein.[6]

We made a brief study of the reactions of benzoyl azide (**1**) with selected aldimines and ketimines. When **1** was allowed to react with N-alkylisobutylideneamines **2a** and **2b**, spontaneous loss of nitrogen occurred and the benzamide derivatives **3a** and **3b** resulted. Acidic hydrolysis of **3a** and **3b** gave N-isobutyrylbenzamide (**4**).



N-Isobutyrylbenzamide (**4**) was also prepared by allowing **1** to react with N,N-dimethyl-2-methylpropenylamine (**5**) and hydrolyzing the product.



The structural assignments of **3b** and **6** were based on their n.m.r. spectra and on their hydrolysis to **4**. Structure **3b** rather than its tautomer was chosen because of the absence of splitting of the N-methyl peak in its n.m.r. spectrum and the low-field position of the NH resonance (11.61 p.p.m.). The assignment of **3b** is also supported by n.m.r. spectra of similar compounds and by analogy with spectra of amides and imides, in which the imides give the lower NH peak position.

With N-cyclohexylideneisopropylamine (**7**), **1** gave a product **8** which resulted from contraction of the cyclohexane ring. A similar ring contraction was observed in the reaction of a sulfonyl azide with an alicyclic enamine.[3] Hydrolysis of **8** gave N-(cyclopentylcarbonyl)benzamide (**9**) which was also obtained from the reaction of **1** and 4-(1-cyclohexen-1-yl)morpholine (**10**). In the structural assignment of **8**, its tautomer was ruled out on the basis of the NH peak position in its n.m.r. spectrum.

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(1) M. E. Kuehne, S. J. Weaver, and P. Franz, *J. Org. Chem.*, **29**, 1582 (1964).

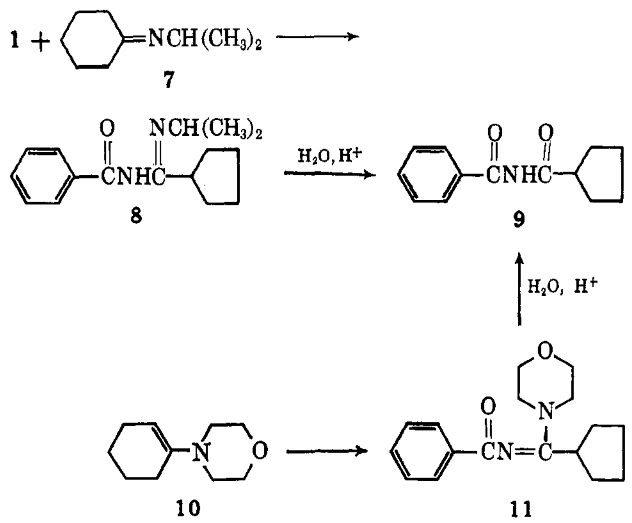
(2) M. E. Munk and Y. K. Kim, *J. Am. Chem. Soc.*, **86**, 2213 (1964).

(3) R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Chem. Ber.*, **96**, 802 (1963).

(4) R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Gazz. chim. ital.*, **91**, 849, 933 (1961); **92**, 1040 (1962).

(5) While this paper was in preparation, G. Bianchetti, P. D. Croce, and D. Pocar [*Tetrahedron Letters*, **No. 25**, 2043 (1965)] published similar work on the reactions of various Schiff bases with *p*-toluenesulfonyl azide and 1-azido-4-nitrobenzene.

(6) K. Alder and G. Stein, *Ann. Chem.*, **501**, 1 (1933).



Experimental Section[7]

General Procedure.—Benzoyl azide (1) was added to the imine or enamine in either acetonitrile or benzene. The same results were obtained when either solvent was used; however, the reaction proceeded at a faster rate in the more polar solvent. The reaction was exothermic and the temperature of the mixture was maintained at 25 ± 5° by means of intermittent cooling. Nitrogen was evolved and after standing for 16 to 20 hr., the solvent was removed under reduced pressure. After examining the crude product, it was subjected to hydrolysis by allowing it to stand in excess 10% hydrochloric acid solution for 12 to 16 hr. The precipitated imide was removed by filtration.

N-Isobutyrylbenzamide (4). A.—The reaction of 1 (28 g., 0.19 mole) and 2a (20 g., 0.20 mole) in acetonitrile gave a 25-g. yield of crude 3a: infrared absorptions 3.0, 4.95, and 6.2–6.4 (s) μ. Compound 3b, prepared in the same manner as 3a, had a similar spectrum. Hydrolysis of 3b (2.95 g., 0.014 mole) gave an 1.78-g. (69%) yield of 4, which had an infrared spectrum identical with that of the material prepared subsequently by the reaction of 1 and 5. The n.m.r. spectrum (CCl_4) of crude 3b showed a doublet at 1.22 (isopropyl group), a single peak at 2.92 (N-methyl) which overlaps the peaks due to the tertiary proton of the isopropyl group, peaks at 7.47 and 8.40 (aromatic protons), and a broad peak at 11.61 (>N-H) p.p.m.

B.—The reaction of 1 (14 g., 0.095 mole) and 5 (10 g., 0.10 mole) in benzene (50 ml.) gave a 22-g. yield of crude 6 as an oil: infrared absorptions (neat) 2.95 (w) and 6.2–6.4 (s) μ; n.m.r. spectrum (CCl_4) doublet centered at 1.24 and septet at 3.06 (isopropyl group), peak at 3.12 (dimethylamino group), and peaks at 7.66 and 8.39 (aromatic protons) p.p.m. Hydrolysis of 6 (22 g., 0.10 mole) gave a 16-g. (88%) yield of 4: m.p. 153–154° (lit.[8] m.p. 154–155.5°); infrared absorption (KBr) 5.83 μ; n.m.r. spectrum (CH_2Cl_2) doublet at 1.28 and septet at 3.73 (isopropyl group), peaks at 7.88 and 9.28 (aromatic protons), and broad peak at 9.12 (>N-H) p.p.m.

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.1; H, 6.9. Found: C, 69.2; H, 7.2.

N-(Cyclopentylcarbonyl)benzamide (9). A.—The reaction of 1 (14 g., 0.095 mole) and 7 (14 g., 0.1 mole) in acetonitrile gave an 11-g. (45%) yield of crude 8, m.p. 70–72°. A sample recrystallized from a hexane–pentane mixture melted at 73.5–75°: infrared absorption (KBr) 6.3 (s) μ; n.m.r. spectrum doublet at 1.21 and broad peak at 3.83 (isopropyl group), two broad peaks at 1.85 (methylene protons of the cyclopentane ring) and 2.91 (tertiary proton of the cyclopentane ring), peaks at 7.43 and 8.36 (aromatic protons), and a broad peak at 11.85 (>N-H) p.p.m.

Anal. Calcd. for $C_{16}H_{22}N_2O$: C, 74.4; H, 8.6; mol. wt., 258. Found: C, 73.8; H, 8.3; mol. wt. (ebullioscopic in benzene), 257.

Hydrolysis of 8 (3 g., 0.012 mole) gave a 48% yield of 9 which had an infrared spectrum identical with that of the imide prepared subsequently from 1 and 10.[9]

B.—The reaction of 1 (28 g., 0.2 mole) and 10 (33 g., 0.2 mole) in benzene (50 ml.) gave a 59.5-g. yield of crude 11 as an oil: n.m.r. spectrum (CH_2Cl_2) broad peaks at 1.82 and 3.17 (protons of the cyclopentane ring), peak at 3.79 (protons of the morpholine ring), and peaks at 7.78 and 8.47 (aromatic protons) p.p.m. Hydrolysis of 59.5 g. of crude 11 gave a 35.5-g. (82%) yield of 9: m.p. (after one recrystallization from hexane) 140–141°; infrared absorptions (KBr) 5.83 and 6.0 μ; n.m.r. spectrum (CH_2Cl_2) broad peaks at 1.84 and 3.93 (protons of the cyclopentane ring), peaks at 7.95 and 8.34 (aromatic protons), and broad peak at 9.32 (>N-H) p.p.m.

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.8; H, 7.0. Found: C, 71.9; H, 7.1.

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[7] Melting and boiling points are corrected. The melting points were determined on a Fischer-Johns melting point block. N.m.r. spectra were measured at 60 Mc. on a Varian A-60 spectrometer with tetramethylsilane as an internal standard. The infrared spectra were determined on Baird AB-2 and MK-1A spectrophotometers.

[8] C. J. Eby and C. R. Hauser, *J. Am. Chem. Soc.*, **79**, 723 (1957).

[9] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *ibid.*, **85**, 207 (1963).

Ketenes. VI. The Stereospecific Cycloaddition of Dimethylketene to *cis*- and *trans*-Butenyl Ethyl Ethers[1,2]

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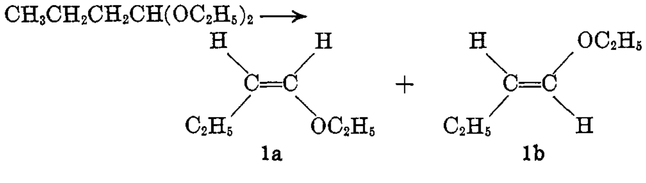
In an earlier paper in this series[3] we described the 1,2 cycloaddition of unsaturated ethers to dimethylketene to give 3-alkoxycyclobutanones and mentioned the probability that this cycloaddition is stereospecific. This paper is a more thorough treatment of that subject. 1-Butenyl ethyl ether, as prepared from butyraldehyde diethyl acetal, is a mixture of *cis* (**1a**) and *trans* (**1b**) isomers in the ratio of 2:1 as determined by g.l.p.c.[4] Careful fractionation through a 72-in. wire spiral column gave a fraction high (88%) in **1a** and a fraction high (97%) in **1b**.



1a 1b

When dimethylketene reacted with a mixture of 48% **1a** and 52% **1b** in benzene, the yellow color which is characteristic of dimethylketene persisted for 40 hr. This indicated that the cycloaddition was quite slow for at least one of the isomers. Analysis by g.l.p.c. of the low-boiling portion of the reaction mixture showed that it contained a substantial amount of unchanged **1b** and no **1a**. Analysis by g.l.p.c. of the high-boiling portion showed that it contained 76% *cis*-3-ethoxy-4-ethyl-2,2-dimethylcyclobutanone (**2a**), 10%

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[1] Paper V: J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965).

[2] While this paper was in preparation, R. Huisgen, L. Feiler, and G. Binsch [*Angew. Chem.*, **76**, 893 (1964)] published similar work on the cycloaddition of diphenylketene to *cis*- and *trans*-propenyl propyl ethers.

[3] R. H. Hasek, P. G. Gott, and J. C. Martin, *J. Org. Chem.*, **29**, 1239 (1964).

[4] All g.l.p.c. separations were made on a 0.25 in. × 6 ft. column packed with 20% Carbowax 20M on Chromosorb P. Compositions of mixtures are reported in area per cent.