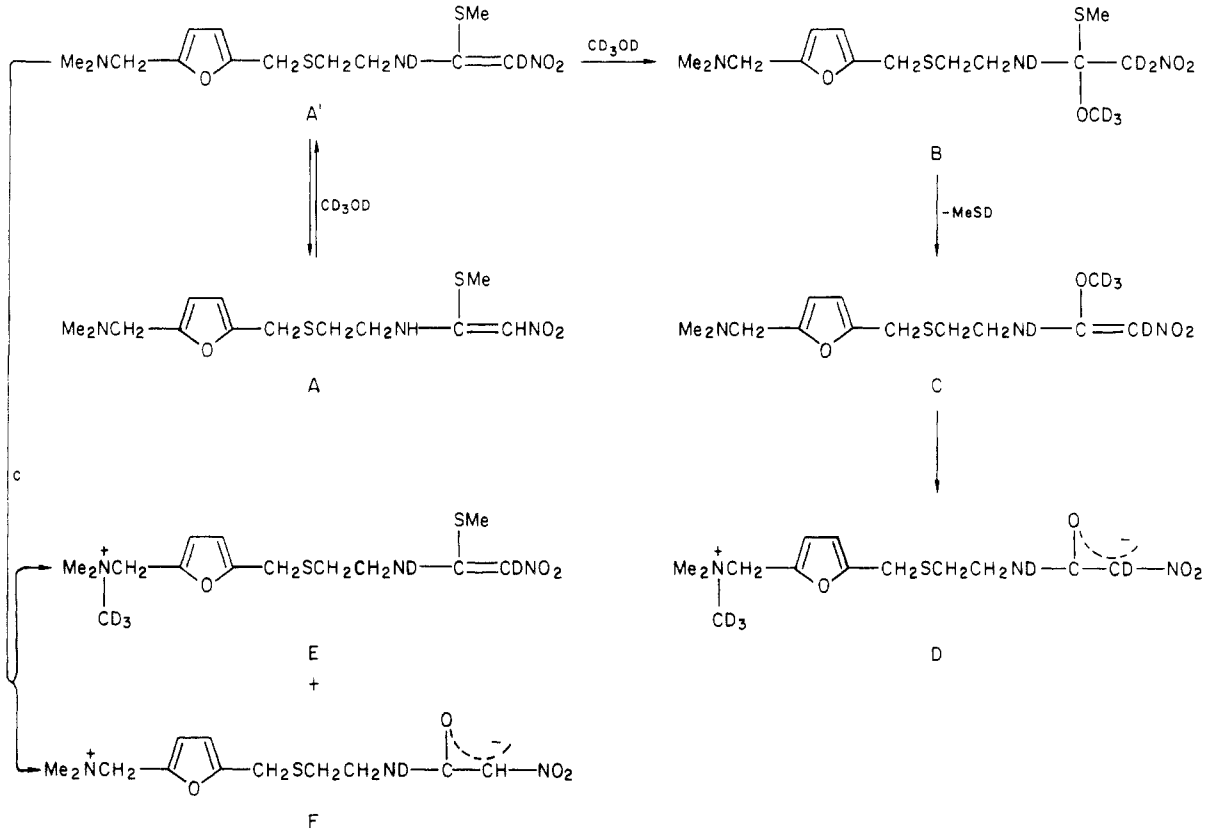
Scheme II



tion and/or migration steps.

Complete H–D exchange of the vinylic proton in both III and V in CD_3OD solution (see A–A′ in Scheme II) is clearly evident from the NMR spectrum. This type of exchange in aqueous media, over a range of pH values, for ranitidine and related model compounds, has been thoroughly investigated and was found to be of pseudo-first-order pH-dependent kinetics. It should be noted, however, that even at a pH of ca. 6, the rate of exchange was extremely small (virtually negligible after 24 h).[11] In our case the exchange is quite fast, and within less than 4 h complete H/D exchange is observed, suggesting that a rapid equilibrium between A and A′ exists. Moreover, the H→D exchange process in CD_3OD may contribute to the *E*/*Z* configurational instability of the nitro ethene functional group in both III and V. This is in agreement with the reported data for the inversion barriers around a double bond for some nitro ethylenes.[11]

An experiment conducted in two methanolic dilutions, where the concentration of III was in one case 10 times greater than in the other, indicated that the rate of formation of V was considerably faster in the concentrated solution. It may thus be concluded, that the O→N migration is an intermolecular and not an intramolecular process.

Experimental Section

1-Oxo-1-[(2-(((((5-trimethylammonio)methyl)-2-furanyl)methyl)thio)ethyl)amino]-2-nitroethene (*V*). A solution of III (5.0 g, 15 mmol), crystallized from toluene and recrystallized from acetone/water, mp 70–71 °C, in absolute methanol (50 mL) was set aside at room temperature for 7 weeks. The solvent was removed under reduced pressure, and the red brown solid residue was treated with a mixture of acetone/methanol (20:1). The yellow suspension was stirred at room temperature for 0.5 h, filtered, washed with acetone, and dried to give V (2.8 g, 8.8 mmol, 59% yield) as a cream colored solid: mp 168–169 °C; ^{13}C NMR ($CDCl_3$) 165.8 (CO^-), 155.8 (CCH_2S), 142.7 ($^+NCH_2C$), 118.4 (*C*HCH), 110.0 (CH*C*H), 109.4 ($CDNO_2$, t, $^1J_{CD}$ = 29 Hz), 62.3 ($^+NCH_2$), 53.1 (Me_3N^+), 38.5 (CH_2NH), 31.6 (SCH_2), 28.0 ppm (CCH_2S), [these assignments are confirmed by single-frequency off-resonance decoupled spectra, which provide signal multiplicity and ^{13}C–^1H correlation]; IR (KBr) 3430, 1600, 1530, 1460, 1215, 1025, 965, 880 cm^{-1}; MS (EI), *m*/*e* (relative intensity) 272 ($M^+ - Me_3 + H^+$) (5), 240 ($M^+ - Me_3NO$) (8), 169 (240 – CH_2=$CHNO_2$) (42), 137 (55), 125 (169 – $CH_2CH_2NH_2$) (49), 110 (74), 94 (2,5-$(CH_2)_2C_4H_2O$) (19).

Anal. Calcd for $C_{13}H_{21}N_3O_4S$: C, 49.49; H, 6.56; N, 13.38; S, 10.11. Found: C, 49.50; H, 6.71; N, 13.32; S, 10.17.

Registry No. III, 72115-14-1; V, 100045-25-8; MeOH, 67-56-1; H_2, 1333-74-0.

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3-Imino-1,4,2-dioxazolidines by [1 + 2 + 2] Cycloaddition of an Isocyanide, 2-Methyl-2-nitrosopropane, and a Carbonyl Compound

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In a current study on the cycloaddition of 2-methyl-2-nitrosopropane (1) to *N*-aryl-*tert*-butylketeneimines such as **4** we observed that, under certain conditions, small amounts of the 3-imino-1,4,2-dioxazolidines **3e–g** were produced (Scheme I, eq 2).[1] These compounds—members of a novel class of 1,4,2-dioxazolidines— do not arise from the respective 3-imino-1,2-oxazetidines (i.e., the regular

(1) Yields range from below 5% (**3f,g**) to 15% (**3e**); the products did not form under N_2 or at higher temperatures (as exemplified for **3e**).

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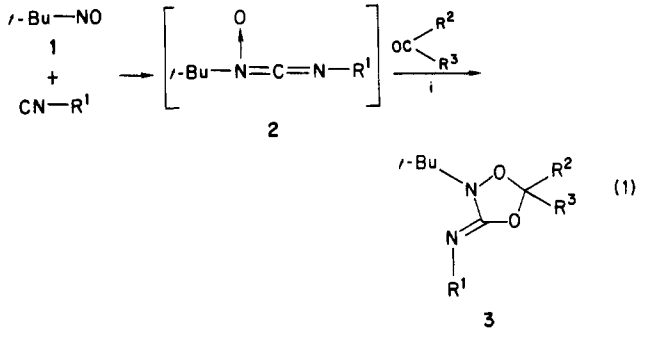
Table I. Yields and Physical Properties Including Spectral Data of Compounds 3

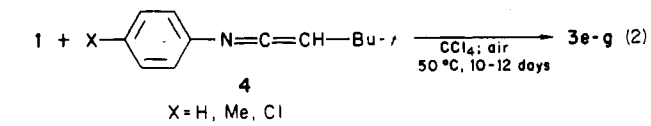
compd	yield, %	mp [bp (mmHg)], °C	n^{20}_D	IR, cm^{-1} (C=N)	^{1}H NMR[a] [5-H]	^{13}C NMR[a] [C-5, C-3]	MS,[b] *m/e* (M$^+$ [relative intensity])	Anal.[c]
3a	73	[88 (1.3)]	1.4696	1715	5.41 (q)	98.5 (d), 149.3	240 [14]	$C_{13}H_{24}N_2O_2$
3b	64	[66 (0.01)]	1.5272	1710	5.50 (q)	99.4 (d), 150.5	234 [63]	$C_{13}H_{18}N_2O_2$
3c	55	[38 (0.05)]	1.4338	1715	4.94	106.2 (d), 147.6	256 [28]	$C_{14}H_{28}N_2O_2$
3d	69	[77 (0.02)]	1.4610	1715	4.95	105.9 (d), 149.5	282 [28]	$C_{16}H_{30}N_2O_2$
3e	59	73[d]		1710	5.04	106.9 (d), 150.7	276 [65]	$C_{16}H_{24}N_2O_2$
3f	60	40[e]		1710	5.04	106.9 (d), 150.5	290 [69]	$C_{17}H_{26}N_2O_2$
3g	56	61–62[e]		1710	5.06	107.1 (d), 151.1	312/310 [43/67]	$C_{16}H_{23}ClN_2O_2$
3h	26	63–64[e]		1705	5.12	107.8 (d), 152.0[f]	321 [11]	$C_{16}H_{23}N_3O_4$
3i	75	84[d]		1710	6.17	100.7 (d), 148.8	302 [18]	$C_{18}H_{26}N_2O_2$
3k	39	[54 (3)]	1.4295	1710		105.9, 147.9	228 [32]	$C_{12}H_{24}N_2O_2$
3l	48	[57 (0.1)]	1.4638	1710		105.9, 149.5	254 [38]	$C_{14}H_{26}N_2O_2$

[a] Signals are singlets unless otherwise indicated. [b] Ion-source temperature, °C: **3a–d,f,k,l**, 30; **3e,g**, 40; **3h**, 50; **3i**, 70. [c] Satisfactory analytical data were obtained for all compounds listed in the table. C, H, N analyses; ±0.3%. [d] From light petroleum. [e] From aqueous methanol. [f] Assignment ambiguous.

Scheme I[a]



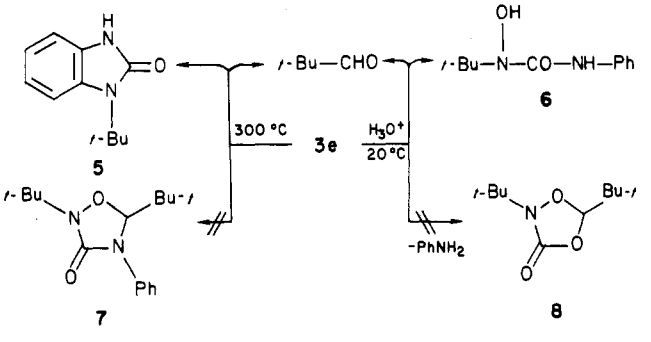
	R¹	R²	R³		R¹	R²	R³
3a	*c*-C_6H_{11}	Me	H	**3g**	4-ClC_6H_4	*t*-Bu	H
b	Ph	Me	H	**h**	4-$NO_2C_6H_4$	*t*-Bu	H
c	*t*-Bu	*t*-Bu	H	**i**	*c*-C_6H_{11}	Ph	H
d	*c*-C_6H_{11}	*t*-Bu	H	**k**	*t*-Bu	Me	Me
e	Ph	*t*-Bu	H	**l**	*c*-C_6H_{11}	Me	Me
f	4-MeC_6H_4	*t*-Bu	H	**m**	*c*-C_6H_{11}	Ph	Me

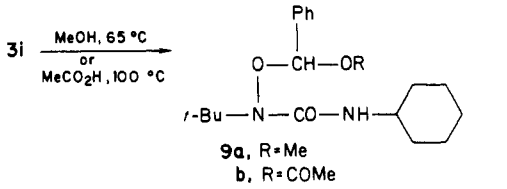


[a] (i) **3a–i**, 100 °C/24 h; **3k**, 70 °C/7 days; **3l,m**, 100 °C/48 h.

[2 + 2] cycloadducts from **1** and **4**[2]) or from the aryl-*tert*-butylcarbodiimides (generated by thermolysis of the oxazetidines[2]); so **3e–g** might be the result of a four-step process as follows: (i) epoxidation of **4** to afford an iminooxirane,[3] (ii) fragmentation of this ring into pivalaldehyde and an aryl isocyanide,[3,4] (iii) combination of the latter component with **1** to give **2** (R^1 = aryl),[5] and (iv) trapping of **2**—a transient 1,3-dipole[5]—by the aldehyde liberated in step ii. This view led us to treat mixtures of **1** and various isocyanides with both aldehydes and ketones (eq 1). The experiments not only gave the above cyclo-

Scheme II





adducts **3e–g** in satisfactory yield (Table I), but also showed this approach to be a fairly general one (compared to the routes to other types of 1,4,2-dioxazolidines[6]). Limitations of the scope of the present method, however, became apparent on employment of an aryl ketone such as acetophenone; thus, **3m** was obtained in poor yield only,[7] and derivatives **3** (R^1 = 4-MeC_6H_4 or *t*-Bu; R^2 = Ph; R^3 = Me) to be made from *p*-tolyl and *tert*-butyl isocyanide,[8] respectively, could not be isolated at all.

Structural proof of **3** (which essentially means exclusion of the Dimroth rearrangement product, i.e., a 1,2,4-oxadiazolidin-3-one like **7**) is provided by (i) ^{13}C NMR (C-5 of **3** absorbs in a region typical of C-2 of dioxolanes[9] rather than of C-2 of oxazolidines;[10] cf. also ref 6c), (ii) high-

(2) Structure and thermolytic behavior of these oxazetidines (obtained by heating mixtures of **1** and **4** in refluxing toluene) are analogous to those prepared by: Barker, M. W.; Gill, J. T. *J. Heterocycl. Chem.* **1970**, *7*, 1203 [Moderhack, D.; Stolz, K., unpublished results].

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(7) Unstable oil that could not be purified.

(8) In the latter case, substantial quantities of di-*tert*-butyldiaziridinone have been obtained instead (cf. ref 5); this compound was also formed as byproduct of **3k**.

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resolution mass spectrometry of **3e** (a peak appearing at m/e 174.1149 can be assigned to *tert*-butylphenylcarbodiimide[11]), and (iii) X-ray analyses of **3e** and **3i**.[12]

Attempts to rearrange compounds **3** or to hydrolyze their imino function met with failure: thermolysis of **3e** resulted in loss of pivalaldehyde with concomitant formation of the known benzimidazolone **5**,[13] while acid hydrolysis furnished the *N*-hydroxyurea **6**,[14] neither **7** nor **8** being detected (Scheme II). Solvolytic reactions of **3i**, such as methanolysis and acetolysis, gave rise to the open-chain compounds **9a,b**, which on heating to 250 °C recyclized to the starting ring, not to the isomeric oxadiazolidinone akin to **7**.[15]

Experimental Section

Melting points are uncorrected. IR spectra were measured on a Pye-Unicam SP 1100 spectrometer (in cases not indicated, liquids were recorded neat, solids in KBr). ^{1}H NMR spectra were taken on a Varian EM-390 instrument, ^{13}C NMR spectra were run on Varian XL-100 and Bruker AM-300 or WM-400 spectrometers (in cases not indicated, $CDCl_3$ was used as solvent; chemical shifts are in δ relative to internal Me_4Si). Mass spectra were determined on a Varian MAT CH-7 instrument (70 eV).

Substituted 2-*tert*-Butyl-3-imino-1,4,2-dioxazolidines 3. General Procedure. A mixture of **1**,[16] the isocyanide,[17] and the aldehyde (30 mmol each) in anhydrous benzene (10 mL) was transferred to an autoclave and heated to 100 °C for 24 h; acetone was employed in tenfold excess without additional benzene. Reaction conditions were 70 °C for 7 days for **3k** and 100 °C for 48 h for **3l**. After evaporation of the solvent and other volatiles in vacuo, the product was isolated by crystallization or distillation [in the case of **3k**, a short spinning-band column was used in order to separate di-*tert*-butyldiaziridinone (IR in accord with that in the literature[18])]. Most runs gave trace amounts of the symmetrical *N,N'*-disubstituted urea derived from the isocyanide employed [identified by comparison (mp, IR) with authentic samples]. Data of compounds **3** are summarized in Table I [**3m** omitted (cf. ref 7); preparation analogous to that of **3a–i** except for prolonged heating (48 h)].

(i) Thermolysis and (ii) Hydrolysis of the 1,4,2-Dioxazolidine 3e. (i) Compound **3e** (0.55 g, 2 mmol) was heated neat to 300 °C for 15 min such as to allow volatiles to distill into 50 mL of a solution of 2,4-dinitrophenylhydrazine (2,4-DNPH) (0.50 g, 2.51 mmol) in 99:1 methanol–12 N HCl. After 1 h at 20 °C and 4 h at 5 °C the 2,4-dinitrophenylhydrazone of pivalaldehyde was collected by filtration, 0.43-g (81%) yield, identified by comparison (mp, IR) with an authentic sample. The residue from heating **3e** was dissolved in benzene; on addition of light petroleum 1-*tert*-butyl-2,3-dihydro-2-benzimidazolone (**5**) separated as plates: 0.26-g (68%) yield; mp 144–145 °C (lit.[13] mp 145–146 °C); IR (KBr) 3300–2700 (br, NH), 1690 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.83 (s, 9 H, *t*-Bu), 6.9–7.5 (m, 4 H, Ar), 10.47 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 29.5 (q, Me), 58.0 (s, CMe_3), 109.4, 111.9, 120.3, and 120.8 (d, CH of Ar), 129.0 and 130.5 (s, quaternary C of Ar), 156.2 (s, C-2); MS (70 eV, 90 °C), m/e (relative intensity) 190 (M^+, 74), 134 (100).

(ii) The above 2,4-DNPH reagent (5 mL, 0.25 mmol) was added to a solution of **3e** (0.055 g, 0.2 mmol) in methanol (5 mL). After 1 h at room temperature cooling to 5 °C caused separation of the 2,4-dinitrophenylhydrazone of pivalaldehyde: 0.041-g (77%) yield. In another run a solution of **3e** (0.50 g, 1.81 mmol) in tetrahydrofuran (5 mL) was mixed with water (0.2 mL) and concentrated sulfuric acid (0.1 g). After 2 h at room temperature ether (5 mL) and water (5 mL) were added. The organic layer was separated and dried over anhydrous magnesium sulfate. Solvent removal in vacuo at room temperature gave crystalline *N*-*tert*-butyl-*N*-hydroxy-*N'*-phenylurea (**6**), 0.32-g (85%) yield, identified by comparison (mp, IR) with an authentic sample.[14]

***N*-*tert*-Butyl-*N'*-cyclohexyl-*N*-[(α-methoxybenzyl)oxy]urea (9a).** The 1,4,2-dioxazolidine **3i** (2.0 g, 6.61 mmol) was refluxed in methanol (20 mL) for 30 min. After solvent removal in vacuo, addition of ether, and cooling to −10 °C the product separated as coarse needles: 1.46-g (66%) yield; mp 78 °C; IR (KBr) 3430 (NH), 1680 and 1515 (amide I and II) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.2 (m, 10 H, CH_2 of *c*-C_6H_{11}), 1.40 (s, 9 H, *t*-Bu), 3.4–3.7 (m, 1 H, CH of *c*-C_6H_{11}), 3.56 (s, 3 H, Me), 5.43 (s, 1 H, CHPh), 6.49 (d, J = 7 Hz, 1 H, NH), 7.1–7.5 (m, 5 H, Ph). Anal. Calcd for $C_{19}H_{30}N_2O_3$: C, 68.23; H, 9.04; N, 8.38. Found: C, 68.30; H, 9.14; N, 8.39.

***N*-[(α-Acetoxybenzyl)oxy]-*N*-*tert*-butyl-*N'*-cyclohexylurea (9b).** A solution of **3i** (0.5 g, 1.65 mmol) in anhydrous acetic acid (5 mL) was heated to 100 °C for 30 min. The solvent was evaporated in vacuo and the residue treated with ether–light petroleum. After several days at −10 °C the product crystallized as needles: 0.31-g (52%) yield; mp 74–75 °C; IR (KBr) 3405 (NH), 1745 (ester), 1670 and 1520 (amide I and II) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.1 (m, 10 H, CH_2 of *c*-C_6H_{11}), 1.38 (s, 9 H, *t*-Bu), 2.08 (s, 3 H, Me), 3.5–3.8 (m, 1 H, CH of *c*-C_6H_{11}), 6.08 (d, J = 8 Hz, 1 H, NH), 6.84 (s, 1 H, CHPh), 7.1–7.5 (m, 5 H, Ph). Anal. Calcd for $C_{20}H_{30}N_2O_4$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.31; H, 8.35; N, 7.76.

Thermolysis of 9a,b. General Procedure. The urea **9a** or **9b** (3 mmol) was heated neat to 250 °C for 30 min. Cooling to room temperature gave a dark residue whose IR spectrum (film) was essentially identical with that of **3i**. Traces of **9a** and **9b** respectively were detected by TLC.

Acknowledgment. We thank Dr. L. Grotjahn of Gesellschaft für Biotechnologische Forschung mbH, D-3300 Braunschweig-Stöckheim, West Germany, for performing the high-resolution mass spectral analysis of compound **3e**. Thanks are equally due to Fonds der Chemischen Industrie for financial support.

Registry No. **3a**, 99948-57-9; **3b**, 99948-58-0; **3c**, 99948-59-1; **3d**, 99948-60-4; **3e**, 99948-61-5; **3f**, 99948-62-6; **3g**, 99948-63-7; **3h**, 99948-64-8; **3i**, 99948-65-9; **3k**, 99948-66-0; **3l**, 99948-67-1; **3m**, 99948-68-2; **5**, 31562-06-8; **6**, 29586-31-0; **9a**, 99948-69-3; **9b**, 99948-70-6; CH_3CHO, 75-07-0; 4-$CH_3C_6H_4NC$, 7175-47-5; $(CH_3)_3CCHO$, 630-19-3; PhCHO, 100-52-7; CH_3COCH_3, 67-64-1; $PhCOCH_3$, 98-86-2; *t*-BuNO, 917-95-3; *c*-C_6H_4NC, 931-53-3; PhNC, 931-54-4; *t*-BuNC, 7188-38-7; 4-ClC_6H_4NC, 1885-81-0; 4-$NO_2C_6H_4NC$, 1984-23-2; *t*-BuCHO, 630-19-3; 2,4-$(CH_3)_2C_6H_3NHN{=}CHBu$-t, 13608-36-1.

(11) Determined on an AEI MS 902 S instrument; exact mass calcd for $C_{11}H_{14}N_2$ 174.1157.
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Homogeneous, Palladium-Catalyzed, Selective Hydrogenolysis of Organohalides

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The hydrogenolysis of organohalides with molecular hydrogen over an heterogeneous transition-metal catalyst (e.g., Pd/C) is a well-known and widely applied reaction, performed at low hydrogen pressure and ambient temperature.[1] However, this nonselective dehalogenation

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