proton. It therefore would be associated with the A part of the observed spectrum.
(8) E. Wenkert, A. Afonso, P. Beak, R. W. J. Carney, J. W. Jeffs, and J. D. McChesney, *J. Org. Chem.*, **30**, 713 (1965).
(9) Interpretation of the solvent effect on the chemical shifts of the two CCH_3 groups of podocarpinol *O*-methyl ether **3d** is questionable (Table I).
(10) C. R. Bennet and R. C. Cambie, *Tetrahedron*, **23**, 927 (1967).
(11) E. F. Knights and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 5280 (1968).
(12) S. W. Pelletier and D. L. Herald, *Chem. Commun.*, 11 (1971).
(13) No depression of the melting point was observed when the latter aldehyde was mixed with authentic *O*-methylpodocarpinal. The crude alkylation product contains about 50% of the enol ether of **12**.
(14) The occurrence of such a doublet in the deuterated aldehyde confirms the previously described spin decoupling experiments, there being no coupling between the aldehyde proton and the 4α-methyl group.
(15) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Am. Chem. Soc.*, **93**, 1637 (1971).
(16) D. H. Wertz and N. L. Allinger, *Tetrahedron*, **30**, 1579 (1974).
(17) N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, **95**, 3893 (1973).
(18) The computation of the energy of a given conformation of the acetate **3c** takes about 3 min with the IBM 370/168 computer. Thirty seven points (every 10°) were calculated.
(19) D. J. Cram and F. A. Abd Elhafez, *J. Am. Chem. Soc.*, **74**, 5828 (1952).
(20) J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 112 (1959).
(21) G. J. Karabatsos, *J. Am. Chem. Soc.*, **89**, 1367 (1967).
(22) M. Cherest, H. Felkin, and N. Prudent, *Tetrahedron Lett.*, 2201 (1968).
(23) M. Cherest and H. Felkin, *Tetrahedron Lett.*, 2205 (1968).
(24) N. T. Anh and O. Eisenstein, *Tetrahedron Lett.*, 155 (1976).
(25) As expected in the most stable conformation the carbonyl group and the C(3)–C(4) bond are eclipsed.
(26) They all contribute to increasing the bulk of the oxygen of the carbonyl dipole.
(27) M. Fétizon, G. Moreau, and N. Moreau, *Bull. Soc. Chim. Fr.*, 1614 (1969).
(28) By the use of Karabatsos's transition state for the prediction of the reaction course we once believed[27] that the lithium aluminium hydride reduction of **20** would give 19*S* secondary alcohol. Hence we thought that the major compound, now known to be 19*R*, represented an exception to Horeau's rule, now shown to be an erroneous assumption.
(29) A. Horeau and H. B. Kagan, *Tetrahedron*, **20**, 2431 (1964).
(30) "Organic Syntheses", Collect. Vol. 2, Wiley, New York, N.Y., 1963, p 607.
(31) G. Aranda and M. Fetizon, *Synthesis*, 330 (1975).

Notes

Kinetics and Mechanism of Ynamine–Isocyanate Additions[1]

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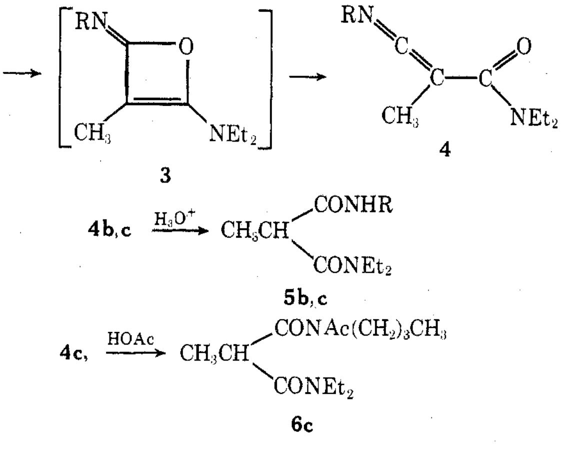
Alkyl isocyanates **1a–c** and the ortho-blocked aryl isocyanate **1d** react with 1-diethylaminopropyne to give ketenimines.[3] The products are easily identified by their characteristic infrared absorption bands just above 2000 cm^{-1}. Reactions with aqueous acid and acetic acid parallel those previously reported for ketenimines.[4]

In contrast to these 2 + 2 additions to the C–O π bond, aryl isocyanates typically give solvent-dependent product mixtures from competing 2 + 2 and 4 + 2 additions involving the C–N π bond,[5a] and other conjugated isocyanates undergo 4 + 2 additions.[5] The C–O π bond involvement is not unique, however. One example involving phenyl isocyanate and a cyanoynamine has been reported,[6] and a reexamination of the reaction of phenyl isocyanate with **2** indicates that in CCl_4 a ketenimine (IR 2010 cm^{-1}; NMR δ 1.92 (s)) forms and disappears in the reaction mixture. We have not been able to determine the fate of the ketenimine.

$$R{-}N{=}C{=}O + CH_3{-}C{\equiv}C{-}NEt_2$$

1a, R = Me **2**
b, R = Et
c, R = n-Bu
d, R = 2,6-Me_2Ph



These reactions are very solvent dependent. In acetonitrile, phenyl isocyanate and **2** react rapidly to produce the 4 + 2 adduct. No intermediates are detectable by IR or NMR. Ketenimine **4d** also forms rapidly and in high yield in acetonitrile but slowly and in poor yield in CCl_4. Solvent effects are expected to be significant for reactions which proceed through zwitterionic intermediates such as **7**,[7] and ynamine reactions are characteristically solvent sensitive.[8] For that reason it was surprising to find that the alkyl isocyanate reactions did not show either product or significant rate dependence on solvents. The rate of the reaction of **2** with methyl isocyanate was followed by NMR and found to be first order in each reactant with rate constants as shown in Table I. The factor of 8 difference between rate constants in benzene and acetonitrile at 34 °C can be compared to factors of 10^3–10^4 for tetracyanoethylene/enol ether additions for which a zwitterionic intermediate has been established.[7] From the temperature dependence of the rate constant in benzene, values of 13 ± 2 kcal/mol and −31.5 ± 5 eu can be derived for the activation

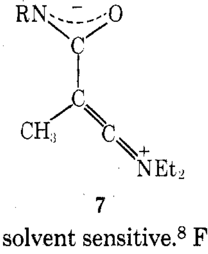


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Table I. Solvent and Temperature Dependence of Rate Constants for Formation of 4a

Solvent	*T*, °C	$k \times 10^4$, $M^{-1}\,s^{-1}$
C_6H_6	16	0.45 ± 0.05
C_6H_6	34	1.8 ± 0.1
C_6H_6	56	8.8 ± 0.5
$C_6H_5NO_2$	34	9.5 ± 1.0
C_6H_5CN	34	8.0 ± 0.5
CD_3CN	34	15.3 ± 1.6

enthalpy and entropy, respectively. The negative activation entropy indicates that the rate-determining step involves formation of either **3** or **7**.

Uncertainties in the interpretation of solvent effects make it impossible to rule out **7** as an intermediate in the alkyl isocyanate reactions. At least two cases exist in which the formation of a polar intermediate from less polar reactants will not be reflected in solvent effects. A reaction which proceeds through an electronically early transition state which does not reflect the character of the intermediate will be solvent insensitive.[9] A more likely consideration for the alkyl isocyanate reactions is the possibility of offsetting solvent effects in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$,[10] a point which is difficult to probe because of the stringent requirements on the precision of the rate constants.[11] The probability that the measured rate constants contain contributions from partitioning of **7** between starting materials and **3** has been discussed by Huisgen.[12]

Experimental Section

Spectra were obtained from the following instruments: IR, Beckman IR20; NMR, Hitachi Perkin-Elmer R-20; MS, DuPont Instruments 21-491. Melting points and boiling points are uncorrected.

***N,N*-Diethyl-2-methyl-3-(alkylimino)-2-propenamides 4a–c.** A solution of 0.03 mol of isocyanate and 0.03 mol of diethylamino-1-propyne in 50 mL of dry carbon tetrachloride or benzene was allowed to stand 3–5 days under nitrogen at room temperature. After concentration under reduced pressure, the residue was distilled.

From methyl isocyanate **4a** was obtained in 78% yield: bp 73–6 °C (0.3 mm) [lit.[3b] bp 70 °C (0.2 mm)]; IR (CCl_4) 2010, 1615 cm^{-1}; NMR (CCl_4) δ 1.10 (t, 6 H), 1.73 (s, 3 H), 3.21 and 3.31 (overlapping s and q, 7 H).

From ethyl isocyanate **4b** was obtained in 67% yield: bp 67–9 °C (0.3 mm); IR (CCl_4) 2010, 1615 cm^{-1}; NMR (CCl_4) δ 1.09 and 1.27 (overlapping triplets, 9 H), 1.73 (s, 3 H), 3.30 and 3.47 (overlapping quartets, 6 H); mass spectrum, *m/e* 81 (B), 109, 167, 182. Anal. Calcd for $C_{10}H_{18}N_2O$: C, 65.90; H, 9.95; N, 15.37. Found: C, 65.67; H, 9.90; N, 15.39.

From *n*-butyl isocyanate **4c** was obtained in 51% yield: bp 89–91 °C (0.3 mm); IR (CCl_4) 2010, 1615 cm^{-1}; NMR (CCl_4) δ 1.10 (t, 3 H), 0.9–1.7 (m, 10 H), 1.72 (s, 3 H), 3.29 and 3.42 (overlapping q and t, 6 H). Anal. Calcd for $C_{12}H_{22}N_2O$: N, 13.32. Found: N, 13.25.

***N,N*-Diethyl-2-methyl-3-(2,6-dimethylphenylimino)-2-propenamide (4d).** To a solution of 2.94 g (0.02 mol) of 2,6-dimethylphenyl isocyanate in 10 mL of acetonitrile under nitrogen and in a room-temperature water bath was added a solution of 2.72 g (0.02 mol) of diethylamino-1-propyne in 10 mL of acetonitrile dropwise with stirring over 20 min. The resulting solution was concentrated under reduced pressure at 50 °C. The residue showed only product NMR absorptions. Distillation gave a small forerun of unchanged isocyanate and 1.8 g (35%) of the ketenimine: bp 144–9 °C (0.4 mm); IR (CCl_4) 2015, 1610 cm^{-1}; NMR (CCl_4) δ 1.08 (t, 6 H), 1.90 (s, 3 H), 2.34 (s, 6 H, 3.36 (q, 4 H), 6.93 (s, 3 H). A large pot residue appeared to be polymeric material. Anal. Calcd for $C_{16}H_{22}N_2O$: C, 74.38; H, 8.58; N, 10.84. Found: C, 74.17; H, 8.65; N, 11.02.

***N*-Alkyl-*N′,N′*-diethyl-2-methylpropanediamides 5b and 5c.** The addition of 1.0 g of the ketenimine to 15 mL of cold, 6 M hydrochloric acid resulted in a clear solution which was extracted several times with chloroform. The extracts were dried over anhydrous sodium sulfate and concentrated, and the residue was distilled.

The amide **5b** was obtained in 50% yield: bp 85–90 °C (0.3 mm); IR (CCl_4) 3340, 1675, 1635, 1530 cm^{-1}; NMR (CCl_4) δ 1.07 (t), 1.16 (t), 1.31 (d) all overlapping (12 H), 3.0–3.5 (m, 6 H), 6.9 (broad s, 1 H).

The amide **5c** was obtained in 75% yield as a waxy solid: bp 90–95 °C (0.3 mm); mp 43–5 °C; IR (CCl_4) 3340, 1675, 1632, 1530 cm^{-1}; NMR (CCl_4) δ 0.8–1.6 (m, 16 H), 2.9–3.6 (m, 7 H), 7.2 (broad s, 1 H). Anal. Calcd for $C_{12}H_{24}N_2O_2$: C, 63.12; H, 10.59; N, 12.27. Found: C, 63.32; H, 10.80; N, 12.48.

***N*-(1-Butyl)-*N*-acetyl-*N′,N′*-diethyl-2-methylpropanediamide (6c).** To a solution of 1.6 g (9.5 mmole) of ketenimine **4c** in 10 mL of CCl_4 under nitrogen was added a solution of 0.57 g (9.5 mmol) of anhydrous acetic acid in 5 mL of CCl_4. An exothermic reaction occurred which was complete within an hour. The solution was concentrated and the residue was distilled giving 1.0 g of **4c**: bp 58–60 °C (0.3 mm); IR (CCl_4) 1660 cm^{-1}, unresolved band; NMR (CCl_4) δ 1.03 (t, 6 H), 1.50 (d, 3 H), 1.87 (s, 3H), 2.85 and 2.92 (overlapping s and q, 7 H), 4.13 (q, 1 H). Anal. Calcd for $C_{11}H_{26}N_2O_3$: C, 57.87; H, 8.83; N, 12.27. Found: C, 57.75; H, 8.80; N, 12.38.

Kinetics. Diethylamino-1-propyne was obtained from Columbia Organic Chemicals and redistilled under nitrogen. Methyl isocyanate was redistilled immediately before use. Solvents were reagent grade, redried, and distilled. For 34 °C runs (ambient probe temperature for the thermostated permanent magnet) 0.5 to 1 M solutions of the two reactants were mixed at 34 °C and an aliquot in a NMR sample tube was kept in the probe throughout the entire run. For high- or low-temperature runs, the reaction was carried out in a constant temperature bath (± 0.2 °C) and aliquots were withdrawn periodically. The probe was maintained at the same temperature (± 1 °C) as determined by ethylene glycol or methanol calibration spectra. Integrals were recorded as the average of four sweeps at 60 or 120 Hz sweep widths and 1 Hz/s sweep times. The rf level was kept well below saturation, generally 500 μV. The integrals were reproducible within ±4% and the instrument stability was such as to necessitate no rebalancing of the integration circuit throughout the course of a run. The peaks monitored were those of the C-methyl singlets of the ynamine, ketenimine, and isocyanate. Trial runs indicated that the ketenimine did not react with either the ynamine or the isocyanate under the reaction conditions.

The rate constants reported in Table I are averages of three independent runs. Second-order plots for the reactions in benzene were linear through 75% completion. In other solvents, curvature was noticeable after 50% completion.

Registry No.—**1a**, 624-83-9; **1b**, 109-90-0; **1c**, 111-36-4; **1d**, 28556-81-2; **2**, 4231-35-0; **4a**, 36277-29-9; **4b**, 63815-28-1; **4c**, 63797-98-8; **4d**, 63797-99-9; **5b**, 63798-00-5; **5c**, 63798-01-6; **6c**, 63798-02-7.

References and Notes

(1) Supported by grants from the Research Corporation and the Simmons College Fund for Research.

(2) Deceased.

(3) (a) J. U. Piper, M. B. Allard, and V. Lee, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D.C., September 1971, ORGN 103; (b) J. Ficini and J. Pouliquen, *Tetrahedron Lett.*, 1139 (1972).

(4) C. L. Stevens and M. E. Munk, *J. Am. Chem. Soc.*, **80**, 4065 (1958).

(5) (a) M. E. Kuehne and P. J. Sheeran, *J. Org. Chem.*, **33**, 4407 (1968); M. E. Kuehne and H. Linde, *ibid.*, **37**, 1846 (1972); (b) H. J. Gais and K. Hafner, *Tetrahedron Lett.*, 5101 (1970); (c) G. J. Mikol, Abstracts, 166th National Meeting of the American Chemical Society, Chicago, Ill., August 1973, ORGN 102.

(6) M. E. Kuehne and H. Linde, *J. Org. Chem.*, **37**, 1846 (1972).

(7) R. Huisgen, *Acc. Chem. Res.*, **10**, 117 (1977).

(8) J. Ficini, *Tetrahedron*, **32**, 1449 (1976).

(9) D. C. Wigfield and B. Lem, *Tetrahedron*, **31**, 9 (1975).

(10) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, p 324.

(11) R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).

(12) R. Huisgen and G. Steiner, *Tetrahedron Lett.*, 3769 (1973).

Organometallic Chemistry. 16.[1a] Carbon-13 Nuclear Magnetic Resonance Spectroscopic Structural Investigation of Protonated Cyclooctatetraeneiron Tricarbonyl in Superacid Solution

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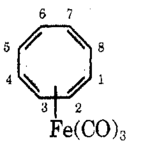
Cyclooctatetraeneiron tricarbonyl **1**[2] has been extensively studied as one of the earliest examples of the fluxional behavior of organometallic compounds.[3] Both proton[4] and carbon-13[5] NMR spectroscopic studies have unequivocally



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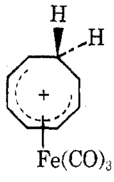

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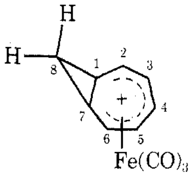

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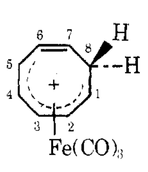

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