bimolecular addition of the type we have proposed, although the possibility of such a process was considered.[20,21] These differing results may be rationalized in part by the greater electrophilicity of CF_3SO_2OX and CF_3CO_2Cl.

Recently, an interesting discussion on the stereochemistry of electrophilic addition, based on an orbital symmetry approach, has appeared.[22] The addition of X–Y to an olefin is regarded as a $[2_\pi + 2_\sigma]$ cycloaddition, and a concerted cis addition is increasingly favored as the nucleophilicity of the olefin increases or the electrophilicity of X–Y increases. For the pseudo [4 + 2] additions of CF_3SO_2OX and CF_3CO_2Cl which we have proposed, the very pronounced electrophilicity of the hypohalites should favor the concerted syn addition.

(20) de la Mare, P. B. D.; O'Connor, C. J.; Wilson, M. A. *J. Chem. Soc., Perkin Trans. 2* **1975,** 1150. de la Mare, P. B. D.; Wilson, M. A.; Rosser, J. M. *Ibid.* **1973,** 1480. Wilson, M. A.; Woodgate, P. D. *Ibid.* **1976,** 141.

(21) de la Mare, P. B. D.; O'Connor, C. J.; Rosser, M. S.; Wilson, M. A. *Chem. Commun.* **1970,** 731.

(22) Epiotis, N. D. *J. Am. Chem. Soc.* **1973,** *95,* 1191.

Reactions of Acetoacetic Ester Blocked Cyclohexyl Isocyanate

Zeno W. Wicks, Jr.,* and Kuang-Jong Wu

Polymers and Coatings Department, North Dakota State University, Fargo, North Dakota 58105

Acetoacetic ester has been widely reported to be a blocking agent for isocyanates. However, we find that only a trace of isocyanate is formed by thermolysis of acetoacetic ester blocked cyclohexyl isocyanate, **1**, at 150 °C and atmospheric pressure. The major portion is unchanged even after 8 h, with some conversion to acetylmalonic ester, **2**, and acetyl-*N,N'*-dicyclohexylmalonamide, **3**. Alcoholysis does not yield the "normal" urethane as blocked isocyanates do but rather esters of **1** with some diesters of **2** and smaller amounts of **3**. Significant amounts of *N*-cyclohexylacetamide, *N*-cyclohexylmalonamate ester, and some *N,N'*-dicyclohexylmalonamide are also obtained. Aminolysis leads to N-substituted acetamides and *N*-cyclohexylmalonamate but no substituted ureas, the "normal" products for aminolysis of blocked isocyanates. In the presence of acid catalysts, alcoholysis leads to *N*-cyclohexylmalonamates with acetate esters as the other product.

In our continuing work on blocked isocyanates,[1–3] we have investigated the reactions of acetoacetic ester blocked cyclohexyl isocyanate. Petersen reported that acetoacetic ester blocked hexamethylene diisocyanate had a low "splitting temperature" of about 140 °C based on the cross-linking of partially acetylated cellulose on heating for 0.5 h.[4] Several papers and patents also report the use of acetoacetic ester blocked isocyanates.[1] Since the cited review paper, other patents have been issued,[5] and a commercial product reported to be an acetoacetic ester blocked polyfunctional isocyanate has become available.[6] Implicit in all of these reports is the assumption that the blocked isocyanates cleave to give the isocyanate which

then reacts with hydroxy groups to give polyurethanes. However, no evidence for the structure of the reaction products has been published.

In view of the "abnormal" products obtained with malonic ester blocked isocyanates,[2,3,7] we decided to investigate the reactions of an acetoacetic ester blocked isocyanate. Since two of the isocyanates in wide commercial use are bis(4-isocyanatocyclohexyl)methane and 1-(isocyanato)-3-(isocyanatomethyl)-3,5,5-trimethylcyclohexane, we selected cyclohexyl isocyanate as a monofunctional model isocyanate.

Results and Discussion

Acetoacetic ester blocked cyclohexyl isocyanates (acetyl-*N*-cyclohexylmalonamates) **1** were found to be essentially 100% enolized in $CDCl_3$ with an extreme downfield NMR shift of the enol H (δ 18.6). The products of thermolysis at 150 °C and atmospheric pressure and alcoholysis with 1-hexanol at 120–150 °C are shown in Scheme I.

In the thermolysis reaction, only a trace of isocyanate was formed, and no urethane was detected from the al-

(1) Wicks, Z. W., Jr. *Prog. Org. Chem.* **1973,** *3,* 73.

(2) Wicks, Z. W., Jr.; Kostyk, B. W. *J. Coat. Technol.* **1977,** *49* (634), 77.

(3) Kostyk, B. W.; Wicks, Z. W., Jr. *J. Polym. Sci.* **1979,** *17,* 2423.

(4) Petersen, S. *Justus Liebigs Ann. Chem.* **1949,** *562,* 205.

(5) Dailbur, H. German Offen. 2612638, 1976; *Chem. Abstr.* **1977,** *86,* 141797; German Offen. 2612783, 1977; *Chem. Abstr.* **1978,** *88,* 8589; German Offen. 2612784, 1977; *Chem. Abstr.* **1977,** *87,* 169322; German Offen. 2612785, 1977; *Chem. Abstr.* **1977,** *87,* 168321; German Offen. 2612786, 1977; *Chem. Abstr.* **1977,** *87,* 169315. Heldt, H.; Schmidt, R. G. F. German Offen. 2632081, 1977; *Chem. Abstr.* **1978,** *88,* 52035. Ostrovskii, V. I.; Khromova, N. S.; Pavlov, S. A. *Nauchn. Tr.-Mosk. Tekhnol. Inst. Legk. Promsti.* **1976,** *40,* 145; *Chem. Abstr.* **1977,** *86,* 91365.
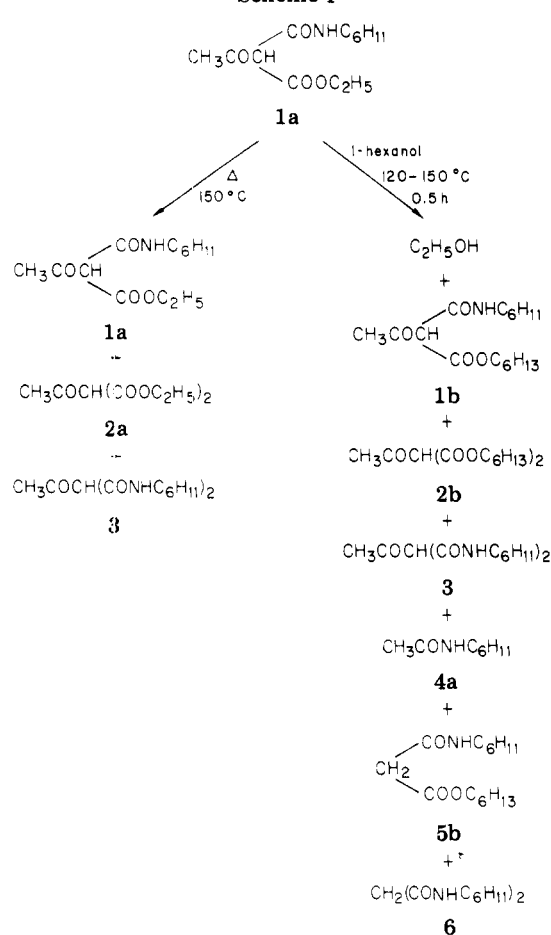
(6) Additol VXL 81, American Hoechst Corp., Industrial Chemicals Division, Somerville, NJ 08876.

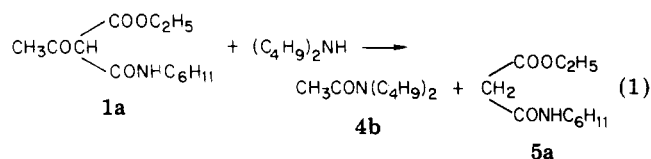(7) Agawa, T.; Minami, T.; Minami, S. *Kogyo Kagaku Zasshi* **1965,** *68,* 2370.

(8) Furuya, Y.; Goto, S.; Itoko, K.; Uraski, I.; Morita, A. *Tetrahedron* **1968,** *24,* 2367.

(9) Levine, A. W.; Fech, J., Jr. *J. Org. Chem.* **1972,** *37,* 1500.

Scheme I

$$CH_3COCH \begin{array}{c} \diagup CONHC_6H_{11} \\ \diagdown COOC_2H_5 \end{array}$$

1a

Δ, 150 °C

1-hexanol, 120–150 °C, 0.5 h

$$CH_3COCH \begin{array}{c} \diagup CONHC_6H_{11} \\ \diagdown COOC_2H_5 \end{array}$$

1a

--

$$CH_3COCH(COOC_2H_5)_2$$

2a

--

$$CH_3COCH(CONHC_6H_{11})_2$$

3

$$C_2H_5OH$$

+

$$CH_3COCH \begin{array}{c} \diagup CONHC_6H_{11} \\ \diagdown COOC_6H_{13} \end{array}$$

1b

+

$$CH_3COCH(COOC_6H_{13})_2$$

2b

+

$$CH_3COCH(CONHC_6H_{11})_2$$

3

+

$$CH_3CONHC_6H_{11}$$

4a

+

$$CH_2 \begin{array}{c} \diagup CONHC_6H_{11} \\ \diagdown COOC_6H_{13} \end{array}$$

5b

+

$$CH_2(CONHC_6H_{11})_2$$

6

$$CH_3C \!=\! C \begin{array}{c} OH \\ \diagup COOC_2H_5 \\ \diagdown CONHC_6H_{11} \end{array}$$

$$O\!=\!C\!=\!C \begin{array}{c} \diagup COCH_3 \\ \diagdown COOC_2H_5 \end{array} + C_6H_{11}NH_2$$

7

$$O\!=\!C\!=\!C \begin{array}{c} \diagup COCH_3 \\ \diagdown CONHC_6H_{11} \end{array} + C_2H_5OH$$

8

coholysis reaction. Furthermore, cyclohexyl isocyanate adducts of acetoacetic esters did not form ureas when reacted with amines but rather gave substituted acetamides and N-cyclohexylmalonamates. For example, 1a reacted quantitatively with 1 equiv of dibutylamine when a solution in toluene with excess amine was heated 5 h at 80 °C to give 4b and 5a (eq 1). Analogously 1a reacted

$$CH_3COCH \begin{array}{c} \diagup COOC_2H_5 \\ \diagdown CONHC_6H_{11} \end{array} + (C_4H_9)_2NH \longrightarrow CH_3CON(C_4H_9)_2 + CH_2 \begin{array}{c} \diagup COOC_2H_5 \\ \diagdown CONHC_6H_{11} \end{array} \quad (1)$$

1a   **4b**   **5a**

with cyclohexylamine to yield 4a and 5a. Formation of substituted acetamides has been reported to result from aminolysis of isocyanate adducts of 2,4-pentanedione[10] and acetylmalonic ester.[11]

In contrast, blocked isocyanates normally give isocyanates by thermolysis, urethanes by alcoholysis, and ureas by aminolysis. The cross-linking of hydroxy functional polymers by acetoacetic ester blocked diisocyanates which has been widely reported apparently results from formation of ester cross-links and not urethane cross-links as has been assumed. Acetoacetic ester blocked diisocyanates would be ineffective as cross-linkers for amine functional polymers.

A possible reaction pathway is via cleavage of the enol form to ketenes 7 and 8. The reactions would be reversible, but also ketene 7 could react with C_2H_5OH to give 2a, and ketene 8 could react with cyclohexylamine to give
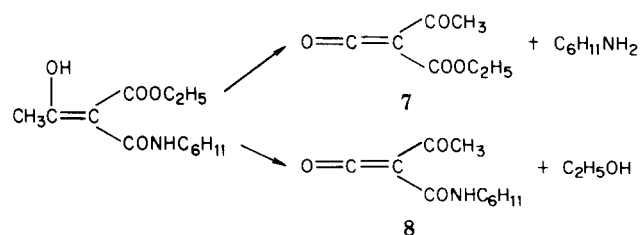
3. Similar cleavages have been proposed to account for the thermolysis products of malonic ester blocked isocyanates[2,3,7] and acetoacetanilide.[12] In the alcoholysis reaction, a more complex mix of products results from secondary reactions of the cyclohexylamine to yield N-cyclohexylacetamide, 4a, and malonic acid derivatives 5b and 6. While cleavage to ketenes seems to be a likely intramolecular reaction course, intermolecular reactions that would lead to the reaction products are also possible. Further work should be done to determine whether ketenes are actually formed as reaction intermediates.

At least in part, the formation of 1b as the major product of the alcoholysis reaction could result from transesterification. It is well-known that acetoacetic esters undergo transesterification reactions very easily,[13] and the further substitution by the carbamoyl group might further accelerate transesterification. Since transesterifications are acid catalyzed, 1a was reacted with ethanol in the presence of H_2SO_4. The products were ethyl acetate and 5a. Recently Nelson et al. have shown that the N-phenyl counterpart of 1 also reacts with ethanol in the presence of H_2SO_4 to give ethyl N-phenylmalonamate.[14] Surprisingly, it was found that diamide 3 readily reacts with ethanol even in the absence of catalyst to give ethyl acetate and 6. Nelson et al.[14] report that acetodiphenylmalonamide reacts with ethanol in the presence of H_2SO_4 to give analogous products but do not report on the reaction without catalyst.

Experimental Section

NMR spectra were obtained by using a Varian EM-390 90-MHz NMR spectrometer. A Perkin-Elmer Model 137 IR spectrophotometer was used. Elemental analyses were run by Chemalytics, Inc.

Ethyl Acetoacetate Blocked Cyclohexyl Isocyanate (1a). (Ethyl Acetyl-N-cyclohexylmalonamate). Ethyl acetoacetate (25.5 mL, 0.2 mol) was added dropwise over 15 min to a well-stirred mixture of sodium ribbons (4.6 g, 0.2 mol) in 300 mL of anhydrous ether. An additional 300 mL of anhydrous ether was added, and the reaction mixture was refluxed for 4 h. Freshly distilled cyclohexyl isocyanate (25.5 mL, 0.2 mol) was added dropwise to the viscous heterogeneous mixture. After being refluxed for 50 h, the system was diluted with 150 mL of benzene and neutralized by adding an aqueous phosphate buffer solution while stirring vigorously. The benzene extracts were washed with 5% $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated to dryness under reduced pressure. The crude product (31 g, 60%) was recrystallized three times from hexane: mp 47.2–48 °C; IR 3250, 1720, 1670, 1650, 1550, 1330, 1300, 1275, 1120, 1090 cm^{-1}; NMR ($CDCl_3$) δ 18.6 (s, 1 H), 9.5–9.0 (1 H), 4.4–4.1 (q, 2 H, J = 7 Hz), 3.95–3.65 (s, 1 H), 2.48 (s, 3 H), 2.1–1.05 (m, 13 H). Anal. Calcd for $C_{13}H_{21}NO_4$: C, 61.16; H, 8.28; N, 5.48. Found: C, 61.05; H, 8.40; N, 5.47.

Methyl Acetoacetate Blocked Cyclohexyl Isocyanate (Methyl Acetyl-N-cyclohexylmalonamate). By use of the same procedure as for 1a, the methyl ester was synthesized in

(10) Eckberg, R. P.; Nelson, J. H.; Kenney, J. W.; Howells, P. N.; Henry, R. A. *Inorg. Chem.* **1977**, *16*, 3128.

(11) Böhme, H.; Braun, R. *Justus Liebigs Ann. Chem.* **1971**, *744*, 15.

(12) Mukaiyama, T.; Tokizawa, M.; Nohura, H.; Takei, H. *J. Org. Chem.* **1961**, *26*, 4381.

(13) Bader, A. R.; Cummings, L. D.; Vogel, H. A. *J. Am. Chem. Soc.* **1951**, *73*, 4195.

(14) Nelson, J. H.; Landen, G. L.; Stevens, B. N. *Synth. React. Inorg. Met.-Org. Chem.* **1979**, *9*, 435.

64% yield by starting with methyl acetoacetate. The melting point after recrystallization from hexane was 61.5–62.2 °C. Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94; N, 5.81. Found: C, 59.76; H, 8.12; N, 6.01. The structure was confirmed by IR and NMR. The suspension of the sodium salt of methyl acetoacetate was low enough in viscosity that the second 300-mL portion of ethyl ether was not necessary for good agitation. However, when the reaction was run with the smaller amount of ethyl ether, a significant fraction of cyclohexyl isocyanate trimer was formed. It was identified by melting point [142–143 °C (lit.[15] mp 140 °C)] and IR, NMR (CDCl₃) [δ 4.8–3.67 (tt, 3 H), 2.1–1.0 (m, 30 H)], and mass spectrometry. The molecular ion signal in the mass spectrograph at m/e 375 was very weak. The major peaks were at m/e 294, 212, and 130, showing loss of C_6H_9 and then successive C_6H_{10}'s.

Thermolysis of 1a. A 51-g (0.2 mol) sample of 1a was heated at atmospheric pressure at 150 °C for 5 h, and then the reaction mixture was vacuum distilled. A first fraction was taken up to 132 °C at 0.08 kPa and a second fraction at 132–133 °C at 0.08 kPa. A trace of material was collected in a liquid N₂ trap. It was shown to be a mixture of cyclohexyl isocyanate and ethanol by taking an IR spectrum immediately. The second fraction was unchanged 1a. The first fraction was redistilled, and a 1.3-g fraction was collected at 74–75 °C at 0.08–0.09 kPa (lit.[16] 65–70 °C at 0.07 kPa). It was identified as diethyl acetylmalonate 2a by refractive index [n_D^{23} 1.4472 (lit.[16] n_D^{25} 1.4435)], IR, and NMR. On the basis of the NMR in CDCl₃, it was approximately 70% enolized (lit.[17] 60% without solvent). Dilution of the residue of the original vacuum distillation with acetone led to the precipitation of 2.7 g of crystals. (The soluble fraction was primarily 1a.) Recrystallization from methyl ethyl ketone gave white crystals (mp 189–190 °C) of acetyl-N,N'-dicyclohexylmalonamide (3): IR 3225, 1650, 1550 cm⁻¹; NMR (CDCl₃) δ 15.9 (s, 0.4 H), 8.1–7.73 (d, 0.6 H), 7.8–7.4 (d, 1 H), 6.2–5.9 (d, 0.4 H), 4.33 (s, 0.6 H), 4.03–3.5 (s, 2 H), 2.3 (s, 1.8 H), 2.2 (s, 1.2 H), 2.1–0.9 (m, 20 H). Anal. Calcd for $C_{17}H_{28}N_2O_3$: C, 66.20; H, 9.15; N, 9.08. Found: C, 66.10; H, 8.91; N, 8.80. On the basis of yields of isolated products and estimates of the ratios in mixtures by NMR, the mole ratio of 1a/2a/3 was about 20:1:1. In another run, it was found that the ratio of 1a/2a/3 was essentially constant when samples were taken after 2, 4, and 6 h at 150 °C and after a further 2.5 h at 165 °C.

Aminolysis of Acetoacetic Ester Blocked Isocyanates. A solution of 1a (5.1 g, 0.02 mol) and di-n-butylamine (12.9 g, 0.1 mol) in 50 mL of dry toluene was heated at 80 °C. Aliquots were removed hourly and titrated with aqueous HCl. After 5 h an equimolar amount of amine had disappeared, and no further loss of amine was found. After the toluene was distilled off, 2.5 g (74%) of N,N-dibutylacetamide (4b) distilled at 83–84 °C at 0.17 kPa (lit.[18] 116.5 °C at 1.1 kPa). The structure was confirmed by IR, NMR, and refractive index [n_D^{24} 1.4459 (lit.[18] n_D^{25} 1.4451)]. The residue was recrystallized from petroleum ether to give 3.4 g (80%) of ethyl N-cyclohexylmalonamate (5a): mp 73–73.5 °C; IR 3225, 1725, 1630, 1540, 1295, 1235, 1145, 1090 cm⁻¹; NMR (CDCl₃) δ 7.3–6.8 (s, 1 H), 4.56–4.1 (q, 2 H, $J = 8$ Hz), 4.1–3.55 (s, 1 H), 3.3 (s, 2 H), 2.1–0.8 (m, 13 H). Anal. Calcd for $C_{11}H_{19}NO_3$: C, 61.94; H, 8.98; N, 6.57. Found: C, 61.80; H, 9.12; N, 6.76.

In a similar fashion, the methyl ester of 1 was reacted with di-n-butylamine to give 4b and the methyl ester of 5. After

recrystallization from petroleum ether, the latter melted at 79.5–80.2 °C: IR 3255, 1735, 1635, 1545, 1300, 1275, 1150, 1095 cm⁻¹; NMR (CDCl₃) δ 7.3–6.7 (s, 1 H), 3.8 (s, 1 H), 3.75 (s, 3 H), 3.3 (s, 2 H), 2.1–1.0 (m, 10 H). Anal. Calcd for $C_{10}H_{17}NO_3$: C, 60.30; H, 8.54; N, 7.04. Found: C, 60.59; H, 8.40; N, 7.29.

Cyclohexylamine reacted with 1a to form 5a and N-cyclohexylacetamide (4a), mp 104–105 °C (lit.[19] mp 103–105 °C). The structure was confirmed by IR and NMR.

Alcoholysis of 1a with 1-Hexanol. A solution of 13.77 g (0.05 mol) of 1a in 40.64 g (0.4 mol) of 1-hexanol in a flask with a distillation head and condenser was heated in an oil bath. Bubbles started forming at 120 °C, the solution boiled vigorously at 135 °C, and by the time 150 °C had been reached distillation ceased. During the 20-min time of heating, 1.72 g (75%) of ethanol was collected. The reaction mixture was cooled and allowed to stand 2 days. A small amount (0.2 g) of N,N'-dicyclohexylmalonamide (6) crystallized from the solution; mp 173–174 °C (lit.[20] mp 175 °C). The structure was confirmed by NMR. After 6 was filtered off, excess hexanol was removed by vacuum distillation at low temperature. No hexyl acetate or other products were detected by gas chromatography. The residue was vacuum distilled. The first fraction (1.5 g, 21% yield) was N-cyclohexylacetamide (4a) as confirmed by melting point and NMR. The second fraction (146–155 °C at 0.03 kPa) was shown by NMR to be a mixture of n-hexyl acetyl-N-cyclohexylmalonamate (1b), di-n-hexyl acetylmalonate (2b), and n-hexyl N-cyclohexylmalonamide (5b) in a ratio of approximately 4:1:1. By repeated vacuum distillation 1b was isolated (by NMR, it still contained traces of 2b and 5b but gave a satisfactory elemental analysis). Anal. Calcd for $C_{17}H_{29}NO_4$: C, 65.57; H, 9.39; N, 4.50. Found: C, 65.40; H, 9.09; N, 4.68. The distillation residue was diluted with hexane, and 0.3 g of acetyl-N,N'-dicyclohexyl malonamide (3) was obtained. The structure was confirmed by NMR and melting point (189–191 °C). The hexane-soluble portion was found by NMR to be principally 1b with some N,N'-dicyclohexylmalonamide (6).

Acid-Catalyzed Alcoholysis of 1a. A solution of 10.2 g (0.04 mol) of 1a, 2.3 mL (0.04 mol) of anhydrous ethanol, 100 mL of anhydrous benzene, and 20 drops of concentrated H_2SO_4 was refluxed for 4 h. The product was washed with phosphate buffer, 5% NaHCO₃ solution, and water and dried (MgSO₄). The solvent was removed by vacuum distillation and shown by GC to contain ethyl acetate. The residue (7.2 g, 85% yield) was shown to be ethyl N-cyclohexylmalonamate (5a) by melting point (73–74 °C), IR, and NMR.

Alcoholysis of 3. A solution of 0.45 g of 3 in 3.77 g of anhydrous ethanol was refluxed for 0.5 h. When the mixture cooled, 0.24 g (61% yield) of N,N'-dicyclohexylmalonamide (6) crystallized out. The structure was confirmed by melting point (174–176 °C), IR, and NMR.

(15) Gulbins, E.; Morlock. R.; Hamann, K. *Justus Leibigs Ann. Chem.* **1966**, *698*, 180.

(16) Barnes, H. K.; Kundiger, D.; McElvain, S. W. *J. Am. Chem. Soc.* **1940**, *62*, 1281.

(17) Bohman, O.; Allemark, S. *Acta Chem. Scand.* **1968**, *22*, 2716.

(18) Robson, J. R.; Reinhard, *J. Am. Chem. Soc.* **1956**, *77*, 498.

(19) Reid, S. T.; Tucker, J. N. *J. Chem. Soc. D* **1970**, 1286.

(20) Glasoe, P. K.; Audrieth, L. F. *J. Org. Chem.* **1939**, *4*, 54.