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The Isocyanurates. II. The Syntheses of Several Unsaturated Aliphatic Isocyanurates

By Fumio TANIMOTO, Takatomi TANAKA, Hisao KITANO and Kenichi FUKUI

Department of Fuel Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

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Triallyl, trimethallyl and tripropargyl isocyanurates were synthesized in good yields by the reaction of the corresponding halides with potassium cyanate in dimethylformamide or dimethyl sulfoxide. Allyl and ethyl isocyanates were easily trimerized in the presence of alkaline salts in dimethylformamide. Tris(1, 3-pentadienyl) isocyanurate was synthesized by the trimerization of 1, 3-pentadienyl isocyanate in a saturated solution of sodium benzoate in dimethylformamide. 1, 3-Butadienylene-1, 4-diisocyanate was also polymerized in the same solvent; it formed black solid mass, suggesting a polyisocyanurate structure of a low molecular weight.

In the literature considerable attention has been directed to the preparation[1] of and the properties[2] of unsaturated isocyanurates. A method of preparing triallyl isocaynurate from allyl chloride and alkali cyanates had early been patented by Kaiser,[3] but the method consisted of drastic reaction conditions and the yield of the isocyanurate was very poor. Himel and DePree[4] obtained isocyanurates by the reaction of organic halides with alkali cyanates catalyzed by

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[1] a) T. C. Frazier, *J. Org. Chem.*, **25**, 1944 (1960); b) A. A. Sayligh, *J. Chem. Soc.*, **1961**, 3148; c) E. C. Juenge and W. C. Francis, *J. Org. Chem.*, **26**, 3334 (1961); d) R. W. Cummins, ibid., **28**, 85 (1963); e) *Chem. Week*, Aug. **18**, 63 (1962); f) T. C. Frazier, U. S. Pat. 3065231 (1963); g) J. J. Tazuma and R. Miller, U. S. Pat. 3075979 (1963); h) E. D. Little and B. T. Poon, U. S. Pat. 3088948 (1963); i) F. E. G. Tate and J. H. Wild, Brit. Pat. 856372 (1960); j) W. C. Francis, Brit. Pat. 912964 (1962); k) H. France, Japanese Pat. 1963—6397; l) E. Nachbauer and W. Gottardi, *Monatsh.* (3), **94**, 584 (1963).

[2] R. W. Roth, *J. Polymer Sci.*, **55**, 41 (1961); *Chem. Week*, Apr. **25**, 127 (1964); K. Thinius, *Plaste und Kautschuk*, **6**, 275, 375, 439 (1959).

[3] D. W. Kaiser, U. S. Pat. 2536849 (1951).

[4] C. M. Himel and L. M. Richards, U. S. Pat. 2866802 (1958); D. O. DePree, U. S. Pat. 2866803 (1958).

TABLE I. TRIMERIZATION OF ALLYL ISOCYANATE

Allyl isocyanate g.	Solvent	g.	Catalyst	g.	Temp. °C	Time hr.	Yield %
10	PY.	(50)[1]	nil		15—20	700	0
10	TEA.	(50)[2]	nil		15—20	700	0
10	DMF[3]	50	nil		15—20	700	0
10	DMF	50	KOCN	1	15—20	500	75
10	DMF	50	K_2CO_3	1	15—20	500	70
10	DMF	50	CH_3COONa	1	100—110	4	94
10	DMF	50	C_6H_5COONa	1	100—110	4	97
10	DMF	20	PY.	9.5[4]	100—110	6	trace
10	DMSO[5]	20	KOCN	1	100—190[6]	0.5	75

1) 50 ml. of pyridine was used.
2) 50 ml. of triethylamine was used.
3) Dimethylformamide
4) Equivalent mol. of pyridine to the isocyanate.
5) Dimethyl sulfoxide
6) The temperature was raised by the reaction heat.

TABLE II. TRIMERIZATION OF ETHYL ISOCYANATE

Ethyl isocyanate g.	Solvent	g.	Catalyst	g.	Temp. °C	Time hr.	Yield %
10	DMF	50	nil		10—20	2400	0
10	DMF	50	KOCN	1	10—15	500	80
10	DMF	50	K_2CO_3	1	10—15	500	57
10	DMF	50	PY.	(1)[1]	10—15	1000	trace
10	TOL.[2]	50	KOCN	1	100—110	4	trace
10	PY.	50	KOCN	1	100—110	4	7

1) 1 ml. of pyridine was used.
2) Toluene

tertiary amines.

The reaction of organic halides with alkal cyanates was systematically investigated in our laboratory[5]; it was found that the reaction could successfully be carried out in several aprotic solvents. In our previous paper[6] the physico-chemical properties of triallyl isocyanurate and its related compounds were partially discussed.

For the present paper, the preparation of several unsaturated isocyanurates was executed in detail. Triallyl, trimethallyl and tripropargyl isocyanurate were synthesized by the reaction of their corresponding halides with potassium cyanate in dimethylformamide or dimethyl sulfoxide. Tris-(1, 3-pentadienyl) isocyanurate and a polymer of 1, 3-butadienylene-1, 4-diisocyanate were prepared by the trimerization of their corresponding isocyanate in dimethylformamide.

In the reaction of the alkenyl halides with potassium cyanate, the nucleophilic substitution of the halide for the isocyanate was generally fast, while the trimerization of the isocyanate to the isocyanurate might be delayed, because of the reaction conditions. Various alkaline salts, such as potassium cyanate, potassium carbonate, sodium acetate, and sodium benzoate, were found to facilitate the trimerization in the aprotic solvent under anhydrous conditions, in spite of thier low solubility in the solvent (for example, the solubility of potassium cyanate in dimethylformamide was about 0.6 wt.% at 100°C). Potassium cyanate and potassium carbonate accelerated the trimerization of allyl isocyanate in dimethylformamide,[7] even at room temperature, as is shown in Table I; the effect of the same catalysts on ethyl isocyanate trimerization was also studied (cf. Table II). The isocyanurate formation from the isocyanate was deeply favored by the presence of the aprotic solvent and the alkaline salt, but the best-known solvents for isocyanates, toluene and pyridine, were not effective for the trimerization of the

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5) K. Fukui and H. Kitano, Japanese Pat. 270734 (1960); 276856 (1960); 277389 (1961); 281924 (1961); 282405 (1961); Italian Pat. 60082 (1958); Brit. Pat. 858810 (1961); German Pat. 1124957 (1962); U. S. Pat. 3037979 (1962); Canadian Pat. 624454 (1964).

6) K. Fukui, H. Kato, T. Yonezawa, F. Tanimoto and H. Kitano, This Bulletin, **34**, 851 (1961).

7) W. J. Balon, Abst. Papers, 130th Meeting, Am. Chem. Soc., Atlantic City, N. J., Sept. 1956, p. 15; U. S. Pat. 2683144 (1954); I. C. Kogon, *J. Am. Chem. Soc.*, **73**, 4911 (1957); U. S. Pat. 2838511 (1958); Bolon demonstrated that the trimerization of aromatic diisocyanates was effectively catalyzed by sodium benzoate in dimethylformamide; Kogon also reported, with respect to the trimerization of aromatic isocyanates in ethyl alcohol, that the reaction was affected by the use of *N*-methylmorpholine as the catalyst. Aromatic or vinyl isocyanates are known to have a greater tendency to trimerize than allyl isocyanate.[1c]

isocyanate in the presence of the alkaline salt.

When a mixture of allyl, methallyl or propargyl halide and potassium cyanate was kept at 100—145°C in dimethylformamide or dimethyl sulfoxide, the reaction took place in a few minutes and was completed in 2—4 hr., giving the corresponding trialkenyl or trialkynyl isocyanurate in a good yield.

Some unsaturated aliphatic isocyanurates with carbon-carbon multiple bonds directly adjacent to the nitrogen atoms of the triazine ring were difficult to prepare by means of the reaction of corresponding halides with alkali cyanates. For this reason 1, 3-pentadienyl isocyanate and 1, 3-butadienylene-1, 4-diisoycanate were prepared by the Curtius rearrangement of the corresponding acid azide.[8,9]

1, 3-Pentadienyl isocyanate was treated with sodium benzoate in dimethylformamide to give tris(1,3-pentadienyl) isocyanurate. 1,3-Butadienylene-1, 4-diisocyanate was also treated with sodium benzoate in dimethylformamide. The product was a black solid mass which could be dissolved in dimethylformamide to form a black or a deep-colored solution. The analysis of the product suggested the formation of the low-molecular-weight isocyanurate polymer by the trimerization of the diisocyanate.

Experimental[10]

Triallyl Isocyanurate.—In a 1-l. flask 300 g. (4.1 mol.) of dimethylformamide and 200 g. (2.5 mol.) of potassium cyanate were placed. The mixture was then heated to 135°C while being stirred; 190 g. (1.5 mol.) of allyl bromide was then added through the dropping funnel over a period of 2 hr. After the bromide had been added, the reaction mixtute was kept between 135—140°C for an additonal hour. The mixture was then cooled to room temperature, mixed with about 200 ml. of anhydrous acetone, and left to stand overnight. The mixture was filtered, and the precipitate of inorganic salts was washed with acetone. The combined solution of the filterate and acetone was concentrated under reduced pressure. After the solvents had been removed, crude triallyl isocyanurate boiling at 130—145°C/4 mmHg was obtained in a 90% yield (based on the allyl bromide). This crude triallyl isocyanurate was then mixed with about 100 ml. of ligroin and left to stand overnight at 0—10°C. A small amount of white needles (1, 3-diallylurea) was filtered off, and the ligroin was evaporated from the filtrate. The residue was mixed with 50 ml. of petroleum ether, and the mixture was placed in an ice box for a day. Colorless hexagonal plates of pure triallyl isocyanurate were thus obtained in an 80% yield. M. p. 25.0—26.0°C; b. p. 144—146°C/4 mmHg; n_D^{25} 1.5110.

Found: N, 16.82. Calcd. for $C_{12}H_{15}O_3N_3$: N, 16.86%.

Trimethallyl Isocyanurate.—A mixture of 50 g. (0.6 mol.) of potassium cyanate and 110 g. (1.5 mol.) of dimethylformamide was heated to 140°C. Then 45 g. (0.5 mol.) of methallyl chloride was added in about a 1 hr. period. After the chloride had been added, the reaction was continued for 3 hr. at about 140°C. The reaction mexture was then cooled, diluted with 150 ml. of dry benzene, and poured into brine, and the benzene layer was separated. After the solvent had been removed, 47 g. of crude trimethallyl isocyanurate was obtained as a crystalline cake in a 97% yield. The recrystallization of the cake from methanol gave pure trimethallyl isocyanurate, m. p. 85—86°C.

Found: N, 14.38. Calcd. for $C_{15}H_{21}O_3N_3$: N, 14.42%.

Tripropargyl Isocyanurate.—Into a mixture of 27 g. (0.3 mol.) of potassium cyanate and 76 g. (1 mol.) of dimethyl sulfoxide, 24 g. of propargyl bromide (0.2 mol.) was stirred at room temperature. The exothermic reaction took place, and the mixture turned dark. The flask was then immersed in a water bath for 1 hr. to cool the mixture, and then it was warmed to 100°C. After the temperature had been maintained at about 100°C for an additional 3 hr. the mixture was treated as in the case of trimethallyl isocyanurate. The yield of crude tripropargyl isocyanurate was 34% (5.5 g.); the pure isocyanurate had a melting point of 160.5—161.0°C. The yield was increased to as high as 83% when dimethylformamide was used as the solvent.

Found: N, 17.10. Calcd. for $C_{12}H_9O_3N_3$: N, 17.28%.

The Trimerization of Isocyanates to Isocyanurates.—*Trimerization under High Pressure.*—In a 100 ml. autoclave, 10 g. (0.12 mol.) of allyl isocyanate and 50 ml. of anhydrous pyridine were charged and heated at 180—190°C for 10 hr. while being stirred. After it had cooled, the reaction mixture was distilled under reduced pressure in order to collect the fraction boiling at 139—144°C/3 mmHg. The distillate was triallyl isocyanurate, and the yield was about 15%. This material was characterized by infrared analysis, which showed the carbonyl peak at 5.9 μ and the isocyanurate peak at 13.04 μ.

Trimerization under Atmospheric Pressure.—The trimerization of allyl or ethyl isocyanate was carried out in a round-bottomed flask under suitable conditions, as is shown in Tables I and II. After the reaction had been completed, the reaction mixture was filtered. The unchanged isocyanate and the solvent were removed from the filtrate by evaporation under reduced pressure. The residual product was dissolved in benzene and washed with brine. The distillation of the solution under reduced pressure gave a product which was identified as the isocyanurate by infrared analysis.

Sorboyl Azide.—To a suspension of 19.5 g. (0.30 mol.) of activated sodium azide in 120 ml. of pure 1, 4-dioxane, there was added, drop by drop, 30 g. (0.28 mol.) of sorboyl chloride[11] (b. p. 55.5°C/6.5

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[8] E. W. Barret and C. W. Portar, *J. Am. Chem. Soc.*, **63**, 3434 (1941).

[9] H. M. Singleton and W. R. Edwards, Jr., ibid., **60**, 540 (1938).

[10] The boiling points and the melting points are uncorrected.

[11] R. Adams and L. H. Ulich, *J. Am. Chem. Soc.*, **42**, 599 (1920); K. Taufel, Cl. Franzke and P. Dietze, *Fette, Seifen, Anstrichmittel*, **62**, 592 (1960).

mmHg, n_D^{19} 1.5771) at 10—14°C over a period of 1 hr. After the addition of the chloride had been completed, the mixture was stirred for 24 hr. at 10—14°C, with the subsequent addition of a further 6 g. (0.09 mol.) of sodium azide, and then it was stirred for an additional 24 hr. at that temperature. The reaction mixture was filtered to remove inorganic salt, and sorboyl azide was used without being separated from the dioxane solution.

1, 3-Pentadienyl Isocyanate.—The dioxane solution of sorboyl azide was warmed to 52°C under a slightly reduced pressure. The Curtius rearrangement took place gradually, and the temperature of the reaction mixture was slowly raised to 76°C so as to complete the rearrangement in the period of 4 hr. When the mixture was cooled, there precipitated a yellowish solid material, which was filtered off; the filtrate was distilled to give 1, 3-pentadienyl isocyanate boiling at 27—30°C/8—9 mmHg. The redistillation of the product afforded the pure isocyanate (b. p. 27—28°C/8 mmHg, in a 20% yield based on sorboyl chloride), which was highly reactive and so was converted into stable 1-benzyl-3-(1, 3-pentadienyl) urea, m. p. 157°C, by treatment with benzyl amine and then analyzed.

Found: C, 71.82; H, 7.20; N, 13.30. Calcd. for $C_{13}H_{16}ON_2$: C, 72.19; H, 7.39; N, 12.95%.

Tris(1, 3-pentadienyl) Isocyanurate.—A mixture of 5 g. (0.045 mol.) of 1, 3-pentadienyl isocyanate and 50 ml. of dimethylformamide was added carefully to 100 ml. of a saturated solution of sodium benzoate in dimethylformamide which had been chilled in an ice bath. An exothermic reaction took place immediately, and the solution turned pale yellow. The reaction mixture was then allowed to stand at 60—70°C for 5 hr. After the solvent had been evaporated under reduced nitrogen pressure, the residual mass was washed with water, alcohol, and ether, and then recrystallized from dimethylformamide to give pure tris(1, 3-pentadienyl) isocyanurate (m. p. 235—236°C, in a 90% yield). The isocyanurate was confirmed by infrared analysis.

Found: C, 65.77; H, 6.35; N, 13.14%. Calcd. for $C_{18}H_{21}O_3N_3$: C, 66.04; H, 6.47; N, 12.83%.

Muconyl Diazide.—Muconyl diazide was prepared from the reaction of sodium azide with muconyl dichloride[12] (m. p. 96°C) in a manner similar to that described for sorboyl azide. The dioxane solution of muconyl diazide without purification was used for the preparation of the isocyanate.[13]

1, 3-Butadienylene-1, 4-diisocyanate.—The Curtius rearrangement of muconyl diazide to the diisocyanate was carried out first at 40°C and then at 58°C and a 3 hr. period under slightly reduced pressure. Although the solution was considerably darkened during the reaction, no precipitation of a solid substance was observed. After two-thirds of the solvent had been removed, however, a yellow solid material was precipitated; this material was removed by filtration. The dioxane solution of the diisocyanate was submitted to isocyanate-group determination.[14] It was thus confirmed that 50 ml. of the solution contained 2 g. of the isocyanate. A small portion of the solution was treated with about two equivalent mol. of benzyl amine to afford 1,4-bis(3-benzylureido)-butadiene-1,3, which was then recrystallized from benzene to give colorless crystals melting at 278—279°C.

Found: C, 69.54; H, 6.53; N, 15.60. Calcd. for $C_{20}H_{22}O_2N_4$: C, 68.55; H, 6.33; N, 15.99%.

The Polymerization of 1, 3-Butadienylene-1, 4-diisocyanate.—To 100 ml. of a saturated solution of sodium benzoate in dimethylformamide, 50 ml. of a dioxane solution containing about 2 g. of the diisocyanate was added. The mixture soon darkened, and it turned almost black in a minute. After the solvents had been removed from the reaction mixture under reduced pressure, a small amount of ether was added to the residue and the black solid mass was triturated in the ether. The black powder was collected by filtration, dried over phosphorus pentoxide, and pulverized in a mortar. The powder was dissolved in dimethylformamide to afford a dark solution. The solution could not be decolorized with Norit Extra or other decolorizing agents. The black solution was then painted on a glass plate, and the solvent was evaporated under reduced pressure to give a dark brown film, which was insoluble in methanol, ethanol, gasoline and benzene. If the black polymer had isocyanuric rings connected with each other by conjugated double bonds, the polymer might have electrically-interesting characteristics.[15]

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[12] D. S. Bailey, *J. Am. Chem. Soc.*, **71**, 2370 (1949); **78**, 5905 (1956).

[13] After the solvent had been removed, the pale yellow residue was recrystallized from methanol and ether to afford white leaflets of pure muconyl diazide, which decomposed explosively when heated to 80°C.

[14] T. Yamabe, A. Nagasawa, H. Kitano and K. Fukui, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **66**, 821 (1963).

[15] The amounts of the polymeric products obtained were too small for them to be subjected to electrical tests.