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### Synthesis and Polymerization of Some New Bis-Triazolinediones: A Stability Study of 4-Substituted Triazolinediones

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## Synthesis and Polymerization of Some New Bis-Triazolinediones: A Stability Study of 4-Substituted Triazolinediones

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### ABSTRACT

Three new bis-triazolinediones, 3,3'-dimethyl-4,4'-bis-[3,5-dioxo-1,2,4-triazoline-4-yl]biphenyl, t-1,4-bis-[3,5-dioxo-1,2,4-triazoline-4-yl]methyl cyclohexane, and 4,4'-bis-[3,5-dioxo-1,2,4-triazoline-4-yl]phenyl ether, were synthesized from their corresponding bis-amines or bis-isocyanates. The compounds were identified by their quantitative ene reaction with 2,3-dimethyl-2-butene. The high degree of reactivity of the triazoline moiety makes solvent selection for reaction media rather difficult. This fact prompted a study of rates of reaction with a variety of polar and nonpolar solvents, including halogenated aliphatics, aromatics, tetrahydrofuran (THF), and N,N-dimethylformamide (DMF). The compounds exhibited reasonable stability in the halogenated solvents, as well as in the aliphatic and aromatic hydrocarbons, but they underwent reaction with THF and DMF. The structure of the reaction product of N-phenyl-1,2,4-triazoline-3,5-dione in DMF

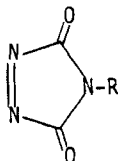
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solution was determined, and a mechanism for product formation was proposed. Two of the bis-triazolinediones were polymerized via a base-catalyzed condensation mechanism which eliminates  $N_2$  from the triazolinedione ring.

## INTRODUCTION

The high degree of reactivity of 4-substituted-1,2,4-triazoline-3,5-diones (4-R-TD) (4) as dienophiles and enophiles has been emphasized in the literature [1, 2]. However, until recently, little advantage has been taken of this high degree of reactivity in polymerization reactions.



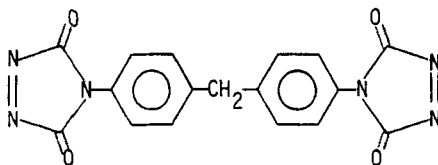
4a, R = nBu

4b, R =  $C_6H_5$

4c, R =  $CH_3$

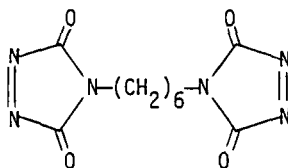
Pirkle and Stickler [3] homopolymerized 4-butyl-1,2,4-triazoline-3,5-dione (4a) in chlorinated solvents by photolyzing the solution with a visible light source, which resulted in a polymer with a degree of polymerization of 20. Depolymerization in solution occurred upon removal of irradiation, with regeneration of monomer in 73% yield. Butler, Guilbault, and Turner reported the copolymerization of 4-phenyl-1,2,4-triazoline-3,5-dione (4b) with vinyl ethers [4] and N-vinyl carbamates [5] via a 1,4-dipolar coupling mechanism.

The dimeric counterparts of 4-R-TDs, the bis-4-substituted-1,2,4-triazoline-3,5-diones (bis-triazolinediones), have also been only briefly studied. Saville [6] first synthesized a bis-triazolinedione, bis-p-[3,5-dioxo-1,2,4-triazoline-4-ylphenyl)methane (5), a highly reactive bifunctional enophile and dienophile. The ene reaction of this compound with various alkenes instantly gave polar ene adducts, and addition of this compound to a solution of natural rubber resulted in instant gellation. Wagener, Turner, and Butler [7] showed that 4b



undergoes reaction with vinyl esters to yield 1-formylmethyl-2-acyl-4-phenyl-1,2,4-triazoline-3,5-dione and proposed a 1,4-dipolar intramolecular rearrangement mechanism. Later, Wagener, Matyjaszewski, and Butler [8, 9] suggested the 1,4-dipolar rearrangement mechanism as a means of propagation in copolymerization of bis-triazolinediones with divinyl esters and bis-enol esters.

Cookson, Gilani, and Stevens [10] reported that 4b undergoes spontaneous reaction with styrene to give a double Diels-Alder adduct. Reinvestigation of this reaction by Wagener, Turner, and Butler [11] revealed that the Diels-Alder/ene adduct was also found in an approximate ratio of 2:1, favoring the ene reaction product. This observation led to the study of spontaneous copolymerization of styrene with bis-triazolinediones 5 and 6 to produce polymers containing both Diels-Alder/ene and double Diels-Alder repeating units.



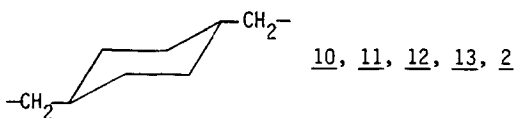
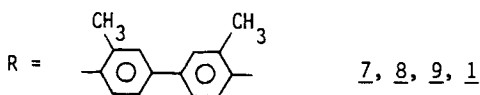
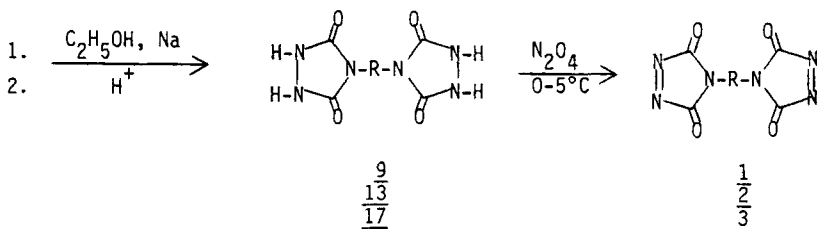
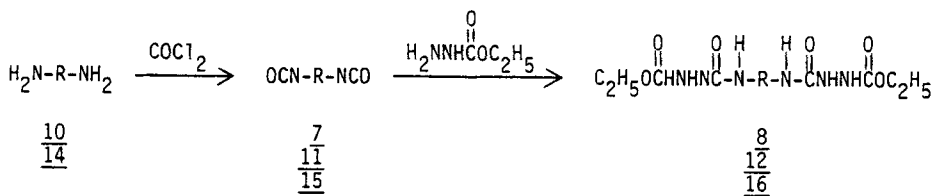
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In this paper we report the synthesis and identification of three new bis-triazolinediones for use as comonomers in further polymerization studies. We also report the stabilities of these novel compounds in a variety of solvents, as well as a novel reaction of the triazolinedione moiety with DMF.

## RESULTS AND DISCUSSION

Three bis-triazolinediones, 3,3'-dimethyl-4,4'-bis-[3,5-dioxo-1,2,4-triazoline-4-yl]biphenyl, 4-1,4-bis-[3,5-dioxo-1,2,4-triazoline-4-yl]-methyl cyclohexane, and 4,4'-bis-[3,5-dioxo-1,2,4-triazoline-4-yl]phenyl ether, 1, 2, and 3, respectively, were prepared by modified procedures developed by Saville [6], Turner [12], and Wagener [13] as shown in Eq. (1).

These three were chosen for several reasons: 1 was chosen because it contains the stiff aromatic ring, and its corresponding bis-isocyanate, 7, is commercially available; 2 was chosen because it contains a flexible aliphatic ring; 3 was chosen because it contains two aromatic rings linked by a heteroatom O, which is usually regarded as a "flexible" link in polymer structures.



(1)

The synthesis of 1 began with bis-isocyanate 7, followed by its reaction with ethyl carbazate to give a quantitative yield of the bis-semicarbazide 8. Cyclization of 8 by alcoholic base, followed by neutralization with acid, gave bis-urazole 9. Oxidation of 9 or its salt with nitrogen tetroxide in methylene chloride in the presence of sodium sulfate as a drying agent gave the desired bis-triazolinedione 1. However, 1 is not soluble in methylene chloride and, as will be shown later in this paper, the high degree of reactivity of the triazolinedione moiety with polar compounds severely limits the list of suitable solvents as reaction media for these compounds. These limitations led to some difficulty in the purification of 1. However, the crude product was thoroughly washed with water and quickly dried in vacuo.

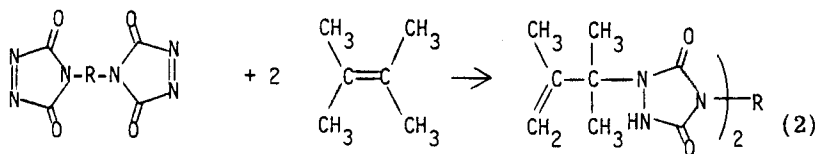
A differential scanning calorimetric (DSC) thermogram showed only one sharp peak at 208°C, indicating the sample to be reasonably pure. Triazolinediones generally are not soluble in nonpolar solvents and undergo reaction with such common solvents as ketones [10], THF [14], and DMF (this paper). NMR analyses could not be

done for these compounds. Thus, an indirect method for structural determination of these compounds was developed, which is described later in the paper.

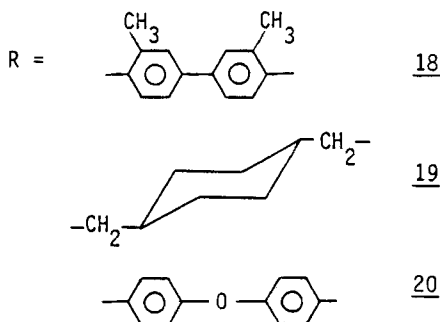
Bis-triazolinedione **2** was prepared by a similar procedure (Eq. 1), except that bis-isocyanate **11** was prepared by treating bis-amine **10** with phosgene. Again, **2** is not soluble in methylene chloride, and further purification by the usual techniques was not possible; therefore, its structure and purity were determined by the indirect method.

Bis-triazolinedione **3** was prepared in the same manner, starting with bis-amine **14** (Eq. 1). Although **3** is soluble in methylene chloride, once the solvent was evaporated, the sticky, reddish solid product decomposed spontaneously to a brown, smoking mass (Caution!). It was finally shown that **3** is very sensitive to oxygen and moisture, and its use in further reactions must be in solutions of nonreactive solvents and under protection from oxygen and moisture. A quantitative determination of **3** in solution was accomplished via visible absorption and, indirectly, by its quantitative ene reaction with 2,3-dimethyl-2-butene, to be described later. A study of the stabilities of 4-R-TDs revealed that both **4b** and **4c** are reasonably stable in methylene chloride, 1,2-dichloroethane (DCE), and benzene. Visible absorption studies showed no appreciable change in absorption of DCE solutions of **3**, even after 3 days.

4-R-TDs, as a class, have been described as the most reactive enophiles [2] and dienophiles [15] known. They undergo rapid and quantitative reaction with many alkenes, particularly highly substituted alkenes. Kinetic studies [16] have shown that the tetra-substituted alkene, 2,3-dimethyl-2-butene, undergoes reaction with the triazolinedione moiety faster than all other alkenes studied. Because of the lack of solubility of 1-3 in suitable solvents, or their extreme reactivity, their purity could only be indirectly determined. By taking advantage of their high reactivity as enophiles with 2,3-dimethyl-2-butene, the qualitative (structure) and quantitative (purity) identifications of 1-3 were accomplished as shown in Eq. (2).



Thus the red (or pink) suspensions (or solutions) of 1-3 in methylene chloride (or DCE) were allowed to react with 2,3-dimethyl-2-butene (in excess), which resulted almost instantly in yellow solutions. After removal of solvent and recrystallization, the purified ene products were fully identified by  $^1\text{H-NMR}$ , IR, and elemental analysis. Based on these results, the structures and purities of these bis-triazolinediones were completely and accurately determined.



The unusual reactivity of triazolinediones, not only as powerful enophiles [2] and dienophiles [15], but with polar solvents containing active hydrogens [10, 17], including aliphatic ethers [14], and with weakly nucleophilic solvents, thus limiting the availability of suitable solvents for use as reaction media, prompted us to study the stability of these compounds in selected solvents.

Herweh and Fantazier [19] reported that the parent compound of this series, 1,2,4-triazoline-3,5-dione, rapidly decomposed in certain solvents like DMF, DMSO, and diglyme. However, the decomposition products were not identified. No stability studies in common solvents have been reported for the 4-R-TDs. Obviously, the stabilities of these compounds in solvents must be carefully examined before reliable chemical studies can be done. This is particularly so when the rate of decomposition of the 4-R-TDs in a given solvent is significant compared with the rate of the desired reaction. In this paper we also report these solvent stability studies.

The solvents studied were methylene chloride, DCE, benzene, THF, and DMF. The rates of decomposition of the 4-R-TDs were determined quantitatively by following the decrease in the visible absorption at the characteristic  $\lambda_{\max}$  (resulting from  $n-\pi^*$  transition) of 4b and 4c in each solvent for a given period of time. Table 1 shows the maxima and extinction coefficients of 4b and 4c in these solvents. As expected, 4b always exhibits a longer wavelength  $\lambda_{\max}$  than 4c because of the greater delocalization of the  $\pi$ -electrons through the aromatic ring. Both 4b and 4c show hypochromic shifts in polar solvents because of the lowering of nonbonding orbitals by the solvents.

Both 4b and 4c, within experimental error, are quite stable in methylene chloride, DCE, and benzene. For these solvents, there is no significant change in visible absorbances over a period of 2 days. However, much greater decomposition rates were observed in THF and DMF. Figure 1 shows the decreases in concentration of 4b and 4c (as shown by the ratio of absorbances at time  $t$  to that at time  $t = 0$ ) in THF and DMF with time. It is clear that 1) 4-R-TDs decompose faster in DMF than in THF (the high polarity of DMF may account for this), and 2) 4b decomposes faster than 4c in both solvents. The higher reac-

TABLE 1. Visible Absorption of 4-R-TD in Methylene Chloride, DCE, Benzene, THF, and DMF

| R                              | Solvent                         |            |                  |            |                               |                   |                  |                   |                  |                   |                  |              |
|--------------------------------|---------------------------------|------------|------------------|------------|-------------------------------|-------------------|------------------|-------------------|------------------|-------------------|------------------|--------------|
|                                | CH <sub>2</sub> Cl <sub>2</sub> |            | DCE              |            | C <sub>6</sub> H <sub>6</sub> |                   |                  |                   | THF              |                   | DMF              |              |
|                                | $\lambda_{\max}$                | $\epsilon$ | $\lambda_{\max}$ | $\epsilon$ | $\lambda_{\max}$              | $\epsilon_{\max}$ | $\lambda_{\max}$ | $\epsilon_{\max}$ | $\lambda_{\max}$ | $\epsilon_{\max}$ | $\lambda_{\max}$ | $\epsilon^a$ |
| -C <sub>6</sub> H <sub>5</sub> | 546                             | 174        | 544              | 167        | 542                           | 230               | 528.5            | 162.3             | 523              | 166               |                  |              |
| -CH <sub>3</sub>               | 537.5                           | 188        | 534              | 190        | 537                           | 232               | 528              | 146               | 521              | 177               |                  |              |

<sup>a</sup> Estimated value. Because of the instability of triazolinedione in DMF, the absorbance at  $t = 0$  is obtained by extrapolation.



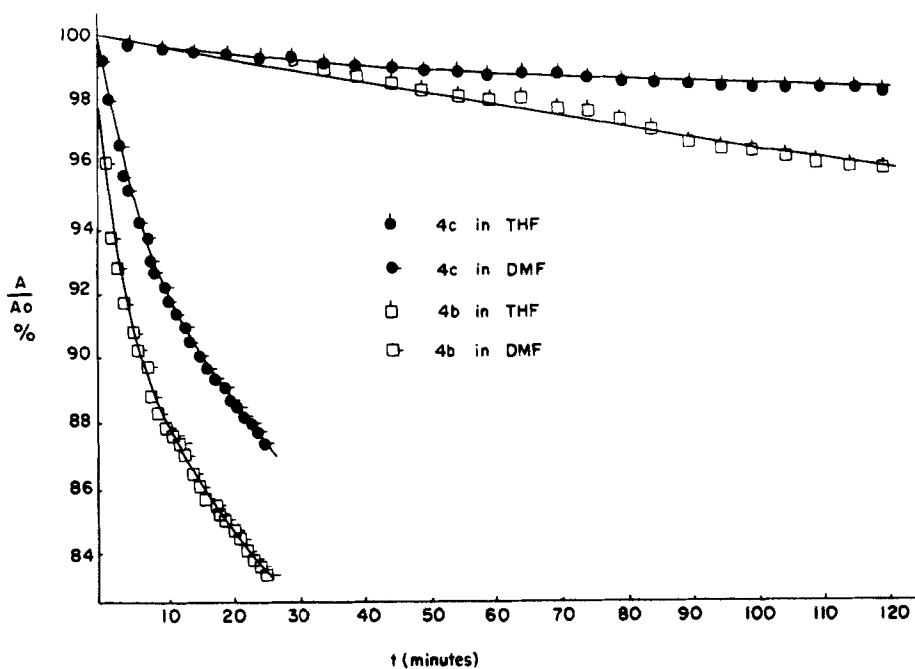


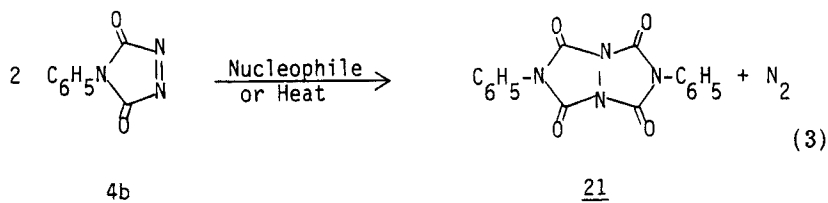
FIG. 1. Stabilities of 4b and 4c in THF and DMF as shown by  $A/A_0$  vs  $t$  curve.

tivity of 4b as the result of the contribution to the stabilization of the reaction intermediate by the aromatic ring may account for this.

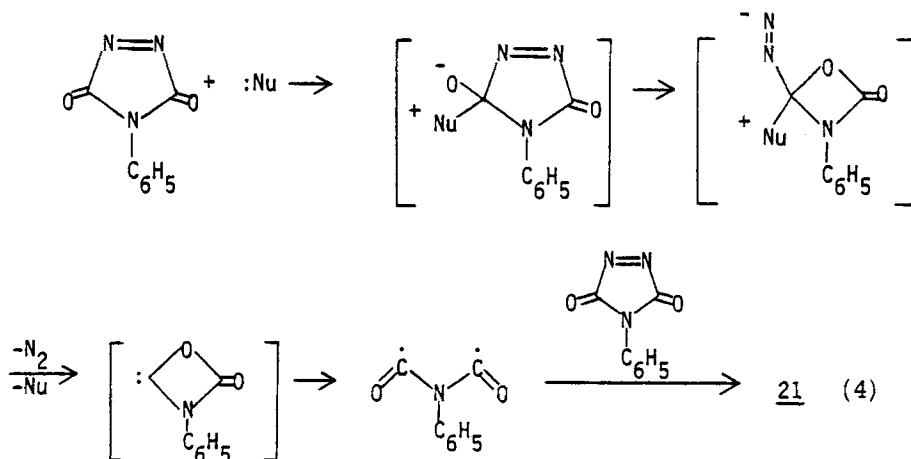
Even though the solvents were used in large excess (concentrations of 4-R-TDs were on the order of  $10^{-3}$  M), no apparent first- or second-order rate constant for the decomposition of the 4-R-TDs could be obtained, indicating the complexity of the mechanism of decomposition. Some useful data on the rates of decomposition are that 4b decomposes to the extent of 4.1%, as compared to 1.8% for 4c, in  $\overline{2}$  h in THF. In DMF, 4b decomposes to the extent of 16.7% and 4c to the extent of 12.8% in  $\overline{25}$  min.

For the decomposition of 4-R-TDs in THF, the data obtained were roughly in agreement with the results obtained by Wamhoff and Wald [14], one product being a 1:1 addition product of THF and the 4-R-TD, involving the  $\alpha$ -hydrogen of THF. However, in the decomposition of 4-R-TDs in DMF, the mechanism is obviously different. DMF, being a very polar species, may involve nucleophilic attack of DMF on the highly electron-deficient 4-R-TD, which may account for the decomposition. 4-Phenyl-TD (4b) has been shown to decompose thermally

[20, 21] to give 3,7-diphenyl-1,5-diazabicyclo [3.3.0] octa-2,4,6,8-tetraone (21), a compound characterized by IR and elemental analysis (Eq. 3).



In the presence of triethylamine [22], 4b gave an oligomeric material along with a small amount of 21. In the presence of stronger nucleophiles like sodium cyanide in DMF, 4b decomposed to 21 in 70-80% yield along with trace amounts of oligomeric material. More recently, Dao and Mackay [18] reported that in the presence of pyridine, 4b decomposed to give 21 quantitatively. From all these findings, it seems that nucleophiles, including DMF, can effect the decomposition of 4-R-TDs to give derivatives analogous to 21. In order to verify this proposal, a quantitative amount of 4b was allowed to react with DMF. After complete disappearance of the characteristic red color of 4b, the product was recovered by precipitating from hexanes and dried in vacuo at high temperature (110°C) for an extended time to guarantee complete removal of solvent. The IR spectrum of this product (Fig. 2a) is identical to that of 21 (Fig. 2b) which was obtained as a pyridine-catalyzed decomposition product of 4b. Clearly, the mechanism for decomposition of 4b in DMF and pyridine are similar. The mechanism, termed a decomposition-coupling reaction of 4-R-TD, as proposed by Turner [12], is shown in Eq. (4). The diradical intermediate was also proposed by Wamhoff and Wald in their later studies [14].



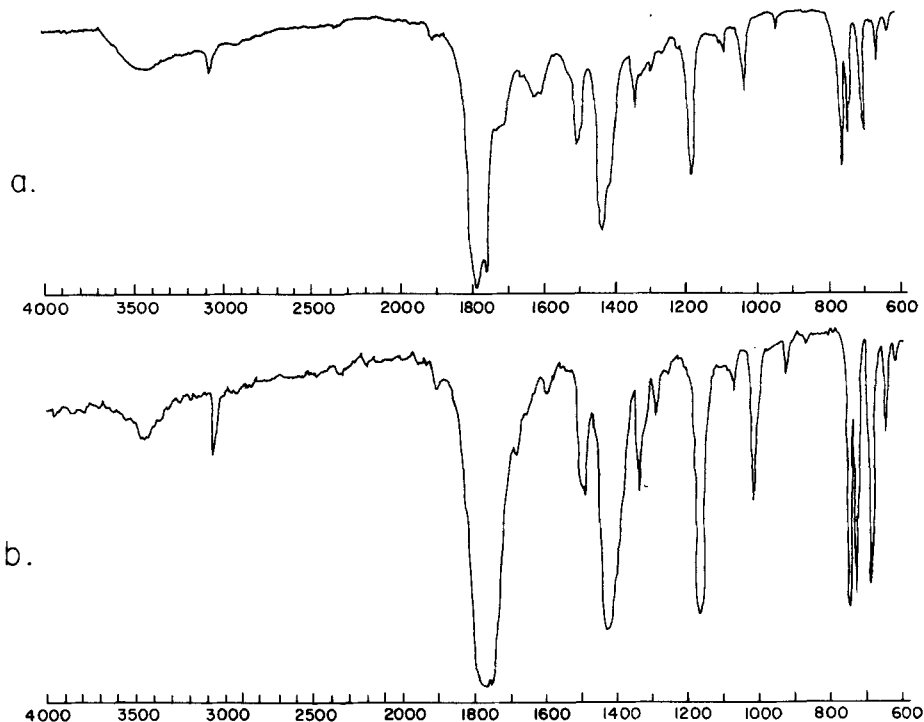
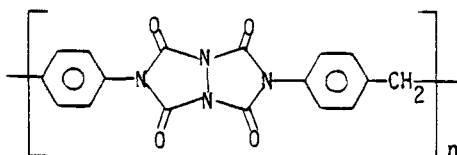


FIG. 2. (a) IR spectrum of the decomposition product of 4b in DMF. (b) IR spectrum of 21.

Nu = nucleophiles like DMF, pyridine, cyanides, etc.

N-Methyl-TD (4c) decomposed in DMF in the same fashion but at a much slower rate. However, no decomposition product was isolated due to the extremely high solubility of the decomposed product in DMF; this difficulty may be overcome by using DMF in only catalytic amounts. The proposed mechanism for decomposition of 4b and 4c in DMF is in agreement with the kinetic data for the decompositions shown in Fig. 1.

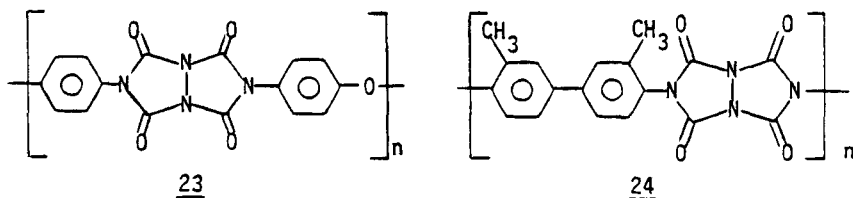
Turner [12] attempted polymerization of 5 using sodium cyanide in DMF but concluded that no polymer with structure 22 was formed.



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The homopolymerization of bis-triazolinediones is of theoretical interest from two viewpoints: 1) The polymers contain no aliphatic hydrogen except those present originally from the bis-triazolinedione molecule; thus, they would be expected to be thermally stable; and 2) the polymerization goes through an unusual condensation polymerization mechanism with loss of  $N_2$ .

Homopolymerization was carried out for bis-triazolinedione **3** in DCE in the presence of a trace amount of pyridine (6 drops). The characteristic red color of **3** disappeared completely in 30 min (in the presence of light) or after 1 h (in the dark). Polymers obtained in this way decomposed at  $291^\circ C$  (in the dark) and  $297^\circ C$  (in the presence of light). Structure **23** is proposed for this polymer, based upon the model compound reaction and the spectral (IR, NMR) properties of the polymer.



Bis-triazolinedione **1** was also polymerized similarly in the presence of light to give a yellow polymer, **24**, which decomposed at  $324^\circ C$  and which was characterized by IR and NMR to support the assigned structure, **24**.

## EXPERIMENTAL

### General

IR spectra were taken on a Perkin-Elmer 281 spectrophotometer,  $^1H$ -NMR spectra were taken on a Varian A-60A, and visible spectra were measured with a Beckman ACTA V spectrophotometer. Melting points were taken on a Thomas-Hoover melting apparatus and are reported uncorrected in degrees Celsius. Elemental analyses were done by Atlantic Microlab, Inc., Atlanta, Georgia. All reagents were obtained commercially and used as received unless otherwise specified. All reagent-grade solvents were purified by standard procedures [23] before use.

Synthesis of 3,3'-Dimethyl-4,4'-bis-[3,5-dioxo-1,2,4-triazoline-4-yl]-biphenyl (1)

Into a 500-mL three-necked flask equipped with reflux condenser, drying tube, dropping funnel, and mechanical stirrer was charged 3,3'-dimethyl-4,4'-diisocyanato-biphenyl (7) (26.4 g, 0.10 mol), purified by recrystallization from ethyl acetate before use, and 200 mL of a benzene solution of ethyl carbazate (20.8 g 0.21 mol) was added at such a rate that the reaction temperature was kept below 45°C. A white precipitate steadily formed. After complete addition of the ethyl carbazate, the system was refluxed for 4 h and then cooled. The crude product was filtered and dried, yielding 46.2 g (98%) of the bis-semicarbazide 8.

A portion of this was recrystallized from acetone/hexane; mp 222-224°C. IR absorbances were observed at (KBr): 3350 (s,b), 2980 (m), 1735 (s), 1655 (s), 1590 (n), 1530 (m,b), 1375 (m), 1300 (m), 1225 (s), 1050 (m), 860 (w), 790 (w), and 615 (m) cm<sup>-1</sup>. NMR signals were found at (DMSO-d<sub>6</sub>): δ 1.20 (t, J = 8 cps, 6), 2.27 (s,6), 4.10 (q, J = 8 cps, 4), 7.40 (d,4), 7.65 (d,b,2), 7.92 (s,2), 8.20 (s,2), and 8.80 (s,b,2).

Analysis: Calculated for C<sub>22</sub>H<sub>28</sub>N<sub>6</sub>O<sub>6</sub>: C, 55.95; H, 5.93; N, 17.79%. Found: C, 55.75; H, 6.19; N, 17.51%.

Absolute alcohol (450 mL) was charged into a 1000-mL three-necked round-bottomed flask equipped with reflux condenser and drying tube. Sodium (2.3 g, 0.1 mol), chopped into small pieces, was slowly added to the flask so that the temperature was kept at 50°C or lower. After complete addition of sodium, the bis-semicarbazide 8 (23.6 g, 0.050 mol) was added all at once. The color of the carbanion solution changed from red to orange to yellow. The system was refluxed for 34 h, followed by filtration and drying of the product, the disodium salt of bis-urazole 9. Yield: 20.94 g (99%). Ten drops of 6 N hydrochloric acid was added to neutralize 0.568 g of the product suspended in 80 mL water, after which the product was cooled, filtered, and dried to give 0.314 g (62%) of 9; mp 348-354°C<sup>d</sup>. IR absorbances were observed at (KBr): 3580-2500 (s,b), 1710 (m), 1660 (s), 1490 (m), 1420 (m), 1370 (m), 1200 (w), 770 (w), and 610 (w) cm<sup>-1</sup>. NMR signals were observed at (DMSO-d<sub>6</sub>): δ 2.25 (s,3), 4.00 (s,b,4), 7.33 (d,1), 7.65 (d,1), and 7.70 (s,1).

Analysis: Calculated for C<sub>18</sub>H<sub>16</sub>N<sub>6</sub>O<sub>4</sub>: C, 56.84; H, 4.21; N, 22.11%. Found: C, 56.85; H, 4.49; N, 22.23%.

The disodium salt of 9 (1.88 g, 4.43 × 10<sup>-3</sup> mol) was placed in a conical flask containing 8 g of anhydrous sodium sulfate and 100 mL of methylene chloride. The mixture was cooled to 0-5°C, and nitrogen tetroxide gas was passed into the suspension for 10 min, during which time the color changed to red. The excess N<sub>2</sub>O<sub>4</sub> gas was removed by bubbling with N<sub>2</sub>, and the red solid product 1 was isolated by filtration.

This product was placed in a flask and evacuated overnight to remove traces of  $N_2O_4$ . DSC measurement of the crude product showed the compound to decompose at  $206^\circ C$ ; the crude product was washed with 40 mL  $H_2O$  quickly and dried to give a pure product which decomposed at  $208^\circ C$ . No other peak was found in the DSC thermogram, indicating **1** to be quite pure. Preparation of **1** was also accomplished by oxidizing the recrystallized (from methanol) bis-urazole **9** in the absence of  $Na_2SO_4$ , and the product obtained showed a higher degree of purity. IR absorbances were observed at (KBr): 3020 (m,b), 1770 (s), 1705 (m,b), 1590 (n,b), 1490 (m), 1440 (s), 1175 (m), 1020 (w), 900 (w), 820 (w), 745 (m), and  $680 (m) cm^{-1}$ .

Reaction of 3,3'-Dimethyl-4,4'-bis-[3,5-dioxo-1,2,4-triazoline-4-yl]-biphenyl (**1**) and 2,3-Dimethyl-2-butene

Two samples of **1**, prepared from oxidation of recrystallized urazole **9** and weighing 0.150 g each, were placed in two round-bottomed flasks, each containing 10 mL methylene chloride, and 2,3-dimethyl-2-butene was added. The red color disappeared in less than 30 s, resulting in a yellow solution, after which the solvent was evaporated and the sample dried in vacuo to give 0.2102 g each of ene product. The purity of **1** is thus concluded to be 97%; mp  $227-228^\circ C$ . IR absorbances were observed at (KBr): 3500 (m,b), 3300-2800 (s,b), 1770 (s), 1750 (s), 1710 (s), 1695 (s), 1650 (m), 1605 (w), 1495 (s), 1435 (s), 1405 (m), 1370 (m), 1270 (m,b), 1190 (s), 1160 (s), 1120 (s), 1050 (m), 900 (m,b), 860 (m), 815 (s), 765 (m), 740 (m), 685 (m), and  $640 (m) cm^{-1}$ . NMR signals were observed at (acetone- $d_6$ ):  $\delta$  1.64 (s,6), 1.89 (s,6), 2.29 (s,3), 4.92 (s,b,1), 5.01 (s,b,1), 7.14-7.66 (m,3), and 8.31 (b,1).

Analysis: Calculated for  $C_{30}H_{36}N_6O_4$ : C, 66.18; H, 6.62; N, 15.44%. Found: C, 66.00; H, 6.68; N, 15.40%.

Synthesis of t-1,4-bis-[3,5-Dioxo-1,2,4-triazoline-4-yl]methyl cyclohexane (**12**) [6, 12, 24, 25]

trans-1,4-Bis(aminomethyl)cyclohexane (**10**) in acetone was converted to its dihydrochloride salt by bubbling in HCl generated from sulfuric acid and sodium chloride. The isolated salt (27.6 g, 0.126 mol) and cumene (200 mL) were placed in a three-necked flask equipped with gas inlet tube and reflux condenser with drying tube, which had been connected by a rubber tube to a trap containing a sodium bicarbonate solution. A mixture of phosgene and nitrogen in the ratio of 1:1 was bubbled into the system, with refluxing for 48 h,

after which all of the salt had gone into solution. The phosgene gas flow was stopped while continuing with  $N_2$  gas for another 24 h. The cumene was then removed by distillation, and the residue was distilled under reduced pressure to give 200 g (82%) of yellow product **11**, the bis-isocyanate; bp  $145^\circ C/4$  mm. IR absorbances were observed at: 3120 (w), 2940 (s), 2865 (m), 2280 (s), 1455 (m), 1365 (m), 1295 (w), 1220 (w), 950 (m), and 860 (s)  $cm^{-1}$ . NMR signals were observed at (acetone- $d_6$ ):  $\delta$  0.60-2.04 (m,10) and 3.25 (d,4).

Ethyl carbazate (22.9 g, 0.22 mol) solution in 200 mL benzene was added to a 1000-mL three-necked flask equipped with reflux condenser, mechanical stirrer, condenser, and dropping funnel containing **11** (19.5 g, 0.10 mol), after which the flask was cooled to  $5^\circ C$ . Compound **11** was slowly added over a period of 20 min, during which time a white precipitate formed. The system was refluxed for 1 h, and the precipitate was then filtered and washed with dry ether and dried in a vacuum oven at  $60^\circ C$  to give bis-semicarbazide **12** (40 g, 98.8%); mp  $243-244^\circ C$ . IR absorbances were observed at (KBr): 3300 (s,b), 2940 (s), 2870 (s), 1740 (s), 1500 (m,b), 1450 (s), 1365 (s), 1305 (m), 1220 (w), 950 (m), and 860 (m)  $cm^{-1}$ . NMR signals were observed at (DMSO- $d_6$ ):  $\delta$  0.60-1.80 (m,10), 1.17 (t,6,  $J = 6$  cps), 4.00 (q,4,  $J = 6$  cps), 6.26 (s,b,4), and 7.58 (s,b).

Analysis: Calculated for  $C_{10}H_{30}N_6O_6$ : C, 47.76; H, 7.46; N, 20.90%.

Found: C, 47.63; H, 7.50; N, 20.73%.

Absolute alcohol (110 mL) was added to a 250-mL three-necked round-bottomed flask equipped with reflux condenser and drying tube. Sodium (0.687 g, 0.0299 mol), chopped into small pieces, was slowly added to the solution so that the temperature was maintained at  $50^\circ C$  or below. Bis-semicarbazide **12** (5.460 g, 0.0136 mol) was added all at once, after which the system was refluxed for 24 h, cooled, and the precipitate filtered and neutralized with 34 mL 5% HOAc in  $H_2O$ . The product was filtered and dried to give 3.765 g (89.3%) of bis-urazole **13**. The compound was recrystallized from 95% alcohol; mp  $310^\circ C^d$ . IR absorbances were observed at (KBr): 3400 (m,b), 3300-2500 (s,b), 1710-1650 (s,b), 1610 (m), 1560 (w), 1500 (s), 1445 (s), 1430 (s), 1235 (w), 1230 (s), 1110 (m), 1050 (m), 1005 (m), 950 (w), 890 (m), 800 (s), 770 (s), 725 (w), 690 (m), 660 (m), and 640 (w)  $cm^{-1}$ . NMR signals were observed at (DMSO- $d_6$ ):  $\delta$  0.6-1.84 (m,10), 3.20 (d,4), and 8.90 (b,4).

Analysis: Calculated for  $C_{12}H_{18}N_6O_4$ : C, 46.45; H, 5.81; N, 27.16%.

Found: C, 46.38; H, 5.85; N, 27.06%.

Bis-urazole **13** (2.228 g, 7.187 mmol) was placed in a 500-mL conical flask containing 75 mL of methylene chloride. The mixture was cooled to below  $5^\circ C$ , and nitrogen tetroxide gas was bubbled into the solution for 5 min. Excess nitrogen tetroxide was removed after stirring for 1 h. The solid product was filtered and placed in a round-bottomed flask which was then connected to a vacuum pump overnight to remove the

last trace of  $N_2O_4$  to give bis-triazolinedione 2 (2.00 g). The DSC thermogram showed that 2 decomposed at 209°C, with no other peaks appearing in the thermogram. IR absorbances were observed at (KBr): 2970 (w), 2940 (s), 2880 (m), 1780 (s,b), 1520 (m), 1445 (s), 1390 (s), 1350 (s), 1335 (m), 1310 (w), 1290 (m), 1250 (s), 1220 (w), 1150 (s), 1010 (m,b), 980 (m), 940 (s), 920 (s), 810 (s), 740 (s), 700 (m), 680 (s), and 650 (s)  $cm^{-1}$ .

Reaction of trans-1,4-bis-[3,5-Dioxo-1,2,4-triazoline-4-yl]methyl cyclohexane (2) and 2,3-Dimethyl-2-butene

The quantitative ene reaction described for analysis of 1 was used to analyze for 2. The product was recrystallized from 95% alcohol; mp 215-216°C. IR absorbances were observed at (KBr): 3230 (s,b), 2980 (m), 2935 (m), 2915 (m), 2845 (m), 1760 (s), 1680 (s,b), 1645 (m), 1460 (s,b), 1445 (s), 1380 (s), 1365 (s), 1325 (m), 1280 (w), 1255 (m), 1200 (m,b), 1160 (s), 1120 (m), 1090 (w), 1065 (m), 985 (w), 945 (m), 880 (s), 790 (s), 770 (s), 745 (m), 725 (s), 690 (w), and 670 (w)  $cm^{-1}$ . NMR signals were observed at ( $CDCl_3$ ):  $\delta$  0.65-2.10

(m,10), 1.58 (s,12), 1.8. (s,6), 3.33 (d,4), 4.98 (s,b,4), and 8.80 (s,b,2).

Analysis: Calculated for  $C_{24}H_{38}N_6O_4$ : C, 60.76; H, 8.02; N, 17.72%.

Found: C, 60.72; H, 8.04; N, 17.68%.

Synthesis of 4,4'-bis-(3,5-Dioxo-1,2,4-triazoline-4-yl)phenyl Ether (3)

4-Aminophenyl ether (14) (49.5 g, 0.248 mol) was added to a beaker containing 300 mL 4 N HCl solution which was heated on a hot plate with stirring until complete dissolution, then cooled and chilled in an ice bath. The cold solution was filtered, washed with acetone, and dried in an oven at 110°C for 2 h to give 51.3 g (85%) 4-aminophenyl ether dihydrochloride. This salt (30.0 g, 0.11 mol) and 200 mL freshly distilled toluene were added to a 500-mL three-necked flask fitted with the same equipment used for the synthesis of 10. Phosgene and nitrogen, in the ratio of 1:1, were bubbled into the system for 18 h, after which excess phosgene was removed, and the solvent distilled to give 26.7 g (96.4%) of product 15. The IR spectrum of 15 in toluene showed strong absorption at 2280  $cm^{-1}$ , characteristic of the  $-N=C=O$  group. This compound was reported by Seifken [26] mp 66-68°C.

4-Isocyanatophenyl ether (15) in toluene solution was slowly added to a 500-mL three-necked flask containing ethylcarbazate (22.9 g, 0.22 mol) with mechanical stirring, keeping the temperature at 50°C or lower. A white precipitate formed, after which the system was refluxed for 2 h and cooled. The white precipitate was then filtered and washed



with ether to give bis-semicarbazide **16** (46.0 g, 94%); mp 235-236°C. IR absorbances were observed at (KBr): 3300 (s,b), 2940 (s,b), 2870 (s), 1740 (s), 1660 (s), 1620 (m), 1575 (s), 1555 (m), 1505 (m,b), 1305 (m), 1240 (s,b), 1160 (w,b), 1100 (w), 1065 (w), 1040 (m), 970 (w), 840 (m,b), and 530 (w,b) cm<sup>-1</sup>. NMR signals were observed at (DMSO-d<sub>6</sub>): δ 1.24 (t,6, J = 7 cps), 4.12 (q,4, J = 7 cps), 6.94 (d,4, J = 8.5 cps), 7.51 (d,4, J = 8.5 cps), 7.99 (s,2), 8.73 (s,2), and 8.82 (s,2).

Analysis: Calculated for C<sub>20</sub>H<sub>24</sub>N<sub>6</sub>O<sub>7</sub>: C, 52.17; H, 5.22; N, 18.26%. Found: C, 52.05; H, 5.28; N, 18.19%.

Bis-semicarbazide **16** (10.00 g, 0.0217 mol) was added to a round-bottomed flask containing 60 mL 1.5 N KOH. After refluxing for 2 h the solution was filtered, the filtrate acidified with concentrated HCl, cooled and chilled in an ice bath, and the crude product filtered and washed with distilled water and dried in an oven at 105°C to yield bis-urazole **17** (7.85 g, 98%). It was recrystallized from methyl alcohol; mp 314°C<sup>d</sup>. IR absorbances were observed at (KBr): 3320 (s,b), 3040 (s,b), 2940 (m,b), 2790 (m,b), 1765 (m), 1690 (s,b), 1620 (w), 1600 (m), 1560 (w), 1505 (s), 1450 (s), 1375 (w), 1315 (s), 1295 (m), 1260 (s), 1205 (w), 1170 (m), 1120 (m), 1095 (m), 1030 (w), 885 (m), 825 (s), 790 (s), and 635 (w) cm<sup>-1</sup>. NMR signals were observed at (DMSO-d<sub>6</sub>): δ 7.25 (d,4, J = 9 cps), 7.58 (d,4, J = 9 cps), and 10.5 (b,4).

Analysis: Calculated for C<sub>16</sub>H<sub>12</sub>N<sub>6</sub>O<sub>5</sub>: C, 52.17; H, 3.26; N, 22.83%. Found: C, 52.05; H, 3.29; N, 22.71%.

Bis-urazole **17** (1.00 g, 0.00273 mol) was added to a conical flask containing anhydrous sodium sulfate (2.00 g) and 100 mL methylene chloride, after which the mixture was cooled and stirred, and N<sub>2</sub>O<sub>4</sub> was bubbled in for 3 min. The system was then stirred for 30 min, filtered, and excess N<sub>2</sub>O<sub>4</sub> was expelled. The solvent was removed using a Rotavapor, but once the vacuum was released, the red sticky product decomposed to a brown mass (Caution!). Oxidation in benzene was carried out by the same procedure, also resulting in decomposition. The final modified procedure used was as follows: **17** (2.0 g, 0.00542 mol) was added to a conical flask containing 120 mL DCE and 10 g anhydrous sodium sulfate. The system was cooled to 0-5°C and stirred, and N<sub>2</sub>O<sub>4</sub> was bubbled in for 20 min, after which the system was filtered. Nitrogen was bubbled into the filtrate to remove excess N<sub>2</sub>O<sub>4</sub>, and the residual solution was concentrated, transferred to a 100-mL volumetric flask, and filled with DCE to the mark. The solution was then stored in the dark. The yield, after quantitative determination of product **3** by reacting with 2,3-dimethyl-2-butene, was 1.69 g (85.4%). The ene product was recrystallized from 95% alcohol/ mp 209-210°C<sup>d</sup>. IR absorbances were observed at (KBr): 3450 (m,b), 3300-2800 (s,b), 1770 (s), 1695 (s,b), 1645 (s), 1590 (m), 1495 (s), 1430 (s), 1380 (s), 1365 (m),

1295 (s), 1240 (s), 1150 (s), 1120 (s), 1095 (m), 1040 (w), 1010 (m)<sub>2</sub>, 915 (s), 895 (m), 860 (s), 830 (s), 770 (s), 735 (w), and 685 (w) cm<sup>-1</sup>. NMR signals were observed at (CDCL<sub>3</sub>):  $\delta$  1.60 (s,12), 1.82 (s,6), 4.97 (s,4), 7.05 (d,4, J = 9 cps), 7.47 (d,4, J = 9 cps), and 0.30 (s,b,2).

Analysis: Calculated for C<sub>28</sub>H<sub>32</sub>N<sub>6</sub>O<sub>5</sub>: C, 63.16; H, 6.02; N, 15.79%. Found: C, 63.15; H, 6.07; N, 15.78%.

### Synthesis of 4-R-TDs

Compounds **4b** and **4c** were synthesized according to procedures previously described [27, 28].

### Stability Measurements

The following solutions (25 mL solvent each) were prepared: For **4b**, 43.7 mg in methylene chloride, 21.0 mg in DCE, 19.7 mg in benzene, 19.6 mg in THF, and 22.1 mg in DMF. For **4c**, 28.2 mg in methylene chloride, 13.5 mg in DCE, 14.8 mg in benzene, 16.0 mg in THF, and 22.3 mg in DMF.

The visible absorptions of the above solutions were checked by using either a Beckman ACTA-V or a Cary 17D at their respective  $\lambda_{\max}$  values over a given period of time. The THF solutions were exposed to light only when absorbances were taken every 5 min for 2 h. For the solutions in DMF, measurements were taken for 0.5 h. For the solutions in the other solvents, absorbances were taken every 4 h for a total period of 2 days.

### Reaction of 4b with DMF

Compound **4b** (0.300 g) was added to DMF (5 mL). The red color disappeared in about 4 h, after which hexane (600 mL) was added to precipitate the product. After filtration and drying in vacuo at 110°C for 48 h, 0.182 g of **21** was obtained.

### Reaction of 4b with Pyridine

Compound **4b** (0.500 g) was dissolved in DCE (60 mL) in a conical flask, after which 6 drops of pyridine was added. The system was then stirred for 20 h. After removal of solvent and drying in vacuo, 0.442 g of **21** was obtained.

Pyridine-Catalyzed Homopolymerization of  
Bis-Triazolinediones 1 and 3

Pyridine (6 drops) was added to a flask containing 0.1511 g of 1 and 10 mL of DCE. The color changed from red to yellow in 10 hr. The product (24) was filtered, washed with DCE and methanol, and dried in vacuo at 50°C to give 0.691 g of product, mp 324°C<sup>d</sup>. IR absorbances were observed at (KBr): 3090 (m,b), 1735 (s,b), 1700 (s,b), 1595 (s,b), 1540 (s,b), 1495 (s,b), 1420 (s,b), 1280 (m,b), 1230 (s,b), 1160 (w,b), 1030 (m), 875 (m), 815 (m), 730 (m), and 620 (m) cm<sup>-1</sup>. NMR signals were observed at (DMSO-d<sub>6</sub>): δ 2.2-2.4 (6H) and δ 7.2-7.8 (6H).

Bis-triazolinedione 3 (0.1511 g) was homopolymerized in a similar manner by adding 6 drops of pyridine in the presence of light within 30 min to give polymer 23; mp 297°C<sup>d</sup>. IR and NMR data were in agreement with the assigned structure, 23.

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REFERENCES

- [1] R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, Tetrahedron Lett., **14**, 615 (1962).
- [2] W. H. Pirkle and J. C. Stickler, Chem. Commun., p. 760 (1967).
- [3] W. H. Pirkle and J. C. Stickler, J. Am. Chem. Soc., **92**, 7497 (1972).
- [4] G. B. Butler, L. J. Guilbault, and S. R. Turner, J. Polym. Sci., Part B, **9**, 115 (1971).
- [5] L. J. Guilbault, S. R. Turner, and G. B. Butler, J. Polym. Sci., Polym. Lett. Ed., **10**, 1 (1972).
- [6] B. Saville, Chem. Commun., p. 635 (1971).
- [7] K. B. Wagener, S. R. Turner, and G. B. Butler, J. Org. Chem., **37**, 1454 (1972).
- [8] K. B. Wagener, K. A. Matyjaszewski, and G. B. Butler, J. Polym. Sci., Polym. Lett. Ed., **17**, 129 (1979).
- [9] K. A. Matyjaszewski, K. B. Wagener, and G. B. Butler, Ibid., **17**, 65 (1979).
- [10] R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, J. Chem. Soc., p. 1905 (1967).

- [11] K. B. Wagener, S. R. Turner, and G. B. Butler, J. Polym. Sci., Polym. Lett. Ed., **10**, 805 (1972).
- [12] S. R. Turner, PhD Dissertation, University of Florida, 1971, p. 71.
- [13] K. B. Wagener, PhD Dissertation, University of Florida, 1973, p. 76.
- [14] H. Wamhoff and K. Wald, Chem. Ber., **110**, 1699 (1977).
- [15] W. J. Middleton, R. E. Heckert, and E. L. Little, J. Am. Chem. Soc., **80**, 2783 (1958).
- [16] S. Ohashi and G. B. Butler, J. Org. Chem., **45**, 3472 (1980).
- [17] A. G. Williams and G. B. Butler, Ibid., **45**, 1232 (1980).
- [18] L. H. Dao and D. Mackay, Chem. Commun., p. 326 (1976).
- [19] J. E. Herweh and R. M. Fantazier, Tetrahedron Lett., p. 2101 (1973).
- [20] R. Stolle, Ber., **45**, 273 (1912).
- [21] K. H. Koch and E. Fahr, Angew. Chem., Int. Ed. Engl., **9**, 634 (1970).
- [22] Reference 12, p. 58.
- [23] A. J. Gordon and R. A. Ford, Chemists Companion, Wiley, 1972, p. 429.
- [24] K. Adler and H. Niklas, Justus Liebigs Ann. Chem., **585**, 97 (1954).
- [25] L. F. Fieser and M. Fieser, Reagents for Organic Synthesis, Vol. 1, Wiley, 1967, p. 856.
- [26] W. Seifken, Justus Liebigs Ann. Chem., **562**, 75 (1949).
- [27] R. C. Cookson, S. S. Gupte, I. D. R. Stevens, and C. T. Watts, Org. Synth., **15**, 121 (1971).
- [28] J. C. Stickler and W. H. Pirkle, J. Org. Chem., **31**, 3444 (1966).

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