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Reaction of Polyarylated Carbinols. V. Mechanism of the Reaction of Sodium Amide with 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol

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The kinetics of the reaction of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (**1**) with <1 molar equiv of sodium amide in isoamyl ether (IAE) at 173° has been investigated. These reactions are observed to be first order in the disappearance of dienol **1** to produce the unconjugated ketone 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (**2**) and the conjugated ketone 2,3,4,5,5-pentaphenyl-2-cyclopenten-1-one (**3**). The rate constant (k) obtained for the conversion of **1** to **2** with 10% sodium amide was found to be 5.27×10^{-5} sec^{-1} and 1.24×10^{-4} sec^{-1} for the conversion of **2** to **3**, while with 20% sodium amide the rate constants (k) obtained were 5.58×10^{-3} sec^{-1} and 5.31×10^{-4} sec^{-1}, respectively. The results obtained indicate that dienol **1** is not a quenching agent in the reaction, that the conversion of **2** to **3** is base catalyzed, and that **2** is a mandatory intermediate for the formation of **3**. These results lead to a simple proposed mechanism.

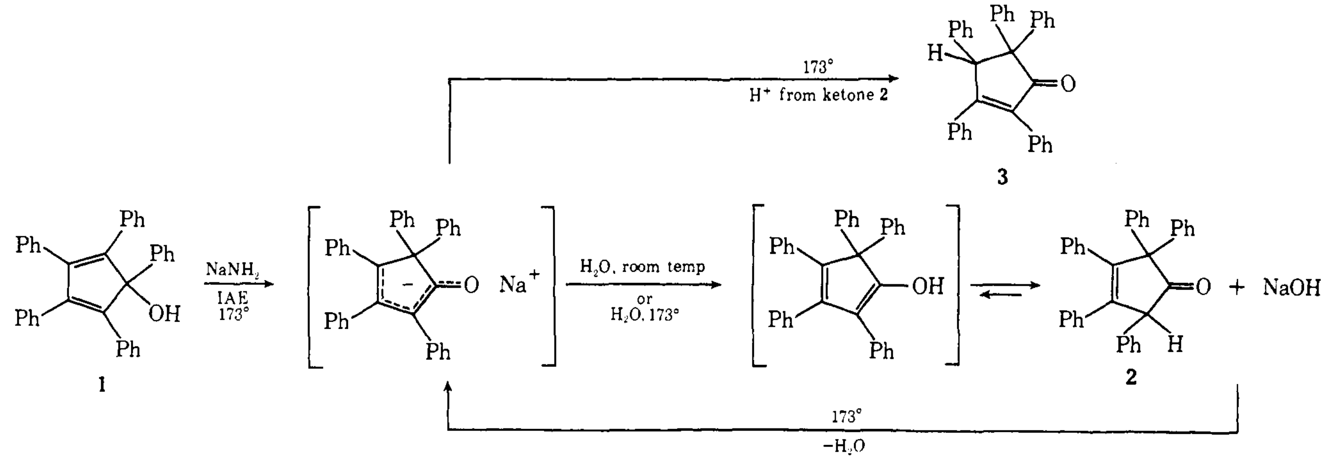
We have previously reported[1,2] that 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-one (**1**) undergoes a thermally induced suprafacial [1,5]-sigmatropic phenyl shift to produce 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (**2**). We have also previously reported[3] that treatment of dienol **1**, ketone **2**, or 2,3,4,5,5-pentaphenyl-2-cyclopenten-1-one (**3**) at 173° in isoamyl ether (IAE) with 1 molar equiv of sodium amide, followed by cooling of the anion solution to room temperature and quenching with water, produced exclusively ketone **2**. However, if the anion solution prepared in the same manner from either dienol **1**, ketone **2**, or ketone **3** is quenched at 173° with water, ketone **3** was produced exclusively. These results led to the previously reported[3] mechanism shown in Scheme I.

With this mechanism established for the reaction of dienol **1**, unconjugated ketone **2**, or conjugated ketone **3** with equimolar amounts of sodium amide, it became of interest to investigate the mechanism of the reaction of dienol **1** with less than 1 molar equiv of sodium amide. This reaction appeared interesting, because unlike the previously studied reaction of dienol **1**, ketone **2**, or ketone **3** with 1 molar equiv of sodium amide, where the only quenching agent was the water externally added, in this reaction of the dienol **1** with <1 molar equiv of sodium amide, extensive high-temperature internal quenching by more than one source, the unreacted dienol **1** or the thermally formed ketone **2**, is possible. It thus became of interest to establish to what extent this internal quenching by dienol **1** or thermally formed ketone **2** was important to the production of products from this reaction. Moreover, a study of the reaction of dienol **1** with other bases[4] had already established that ketone **2** was a required intermediate in the conversion of dienol **1** to ketone **3** and it became of importance to establish mechanistically if ketone **2** was also a required intermediate for the production of ketone **3** in the reaction of dienol **1** with <1 molar equiv of sodium amide.

Results

The evaluation of the kinetic data was complicated by the lack of reliable values for the initial concentration of either the dienol **1** or the added sodium amide base. This was true because as can be seen from Scheme I, the conjugate base of ketone **2** and ketone **3** is a catalyst in this reaction which upon quenching affords ketone **2**. However, ketone **2**

Scheme I



is also formed directly from dienol **1** via an uncatalyzed thermal [1,5]-sigmatropic phenyl rearrangement. Therefore, the amount of ketone **2** formed from the enolate upon quenching must be subtracted from the observed total of ketone **2**. Another complication was caused by the fact that the kinetically important amount of dienol **1** began at less than 100% because an amount of dienol **1** equal to the concentration of the sodium amide was converted immediately to the enolate ion at time zero.

With these limitations in mind we proceeded to evaluate the kinetic data. Since the concentration–time curves for the reaction resembled a consecutive first-order reaction sequence (eq 1), plots of the logarithm of the starting dienol **1** vs. time were made to establish the first-order character of the disappearance of the dienol **1**. These plots for the 10 and 20% sodium amide reactions were both linear. A linear least-squares computer program was used to evaluate the rate constant, k_1, and the initial concentration of the dienol **1**. Evaluation of these data for the nominal 10% sodium amide reaction by use of the linear least-squares program afforded a $k_1 = 5.27 \times 10^{-5}$ sec^{-1} and an initial concentration of dienol **1** of 100 ± 2%, while in the nominal 20% sodium amide reaction, this evaluation afforded a $k_1 = 5.58 \times 10^{-3}$ sec^{-1} and an initial concentration of dienol **1** of 81.3 ± 2%. With this information in hand, a nonlinear least-squares computer program was used to calculate the best value of k_2 based upon the exact solutions of the kinetic expression for calculating ketone **2** and ketone **3**

$$\text{dienol } \mathbf{1} \xrightarrow{k_1} \begin{matrix}\text{unconjugated}\\ \text{ketone } \mathbf{2}\end{matrix} \xrightarrow{k_2} \begin{matrix}\text{conjugated}\\ \text{ketone } \mathbf{3}\end{matrix} \qquad (1)$$

$$\text{ketone } \mathbf{2} = \frac{k_1\,[\text{dienol } \mathbf{1}]_0}{k_2 - k_1}\left(e^{-k_1t} - e^{-k_2t}\right)$$

$$\text{ketone } \mathbf{3} = [\text{dienol } \mathbf{1}]_0 \left[1 - \frac{(k_2e^{-k_1t} - k_1e^{-k_2t})}{k_2 - k_1}\right]$$

where [dienol **1**]$_0$, the best value for the initial concentration of dienol **1**, and the rate constant, k_1, were both determined from the linear least-squares computer program discussed above. The values required as input for this nonlinear least-squares program were k_1 and the true concentration of ketone **3** at the time specified. These values of ketone **3** were obtained by dividing the observed concentration of ketone **3**, at the specified times, by the percentage of dienol **1** actually present at the start of the reaction (time zero); for 10% sodium amide, 95%, and for 20% sodium amide, 81.3%.

Using this nonlinear least-squares program and the input described above and allowing for numerous iterations until convergence and minimization was obtained afforded the best value of the rate constant, k_2, the corresponding calculated concentrations of unconjugated ketone **2** and conjugated ketone **3**/[dienol **1**]$_0$, and the initial concentration of dienol **1** of approximately 95 and 81.3% based upon the best calculated values of the k_2's for the 10 and 20% sodium amide reactions, respectively. Table I shows the data and the calculated concentrations, and also that the agreement of the observed and calculated values of unconjugated ketone **2** and conjugated ketone **3**/[dienol **1**]$_0$ are well within the uncertainty expected. The rate constants obtained for the two molar ratios of sodium amide used are $k_1 = 5.27 \times 10^{-5}$ sec^{-1} and $k_2 = 1.24 \times 10^{-4}$ sec^{-1} for the nominal 10% molar ratio sodium amide reaction, and $k_1 = 5.58 \times 10^{-3}$ sec^{-1} and $k_2 = 5.31 \times 10^{-4}$ sec^{-1} for the nominal 20% molar ratio sodium amide reaction.

Discussion

The addition of sodium amide to the dienol **1** is assumed to form the conjugate base of the alcohol immediately. The anion formed rearranges rapidly at the temperature of the reaction, 173°.

The reactions which can take place at this point are (1) thermal conversion[1,2] of the dienol **1** to unconjugated ketone **2**, (2) quenching of the rearranged anion produced from the dienol **1** to yield either unconjugated ketone **2** or conjugated ketone **3**, and (3) quenching of the rearranged anion produced by unconjugated ketone **2** to produce conjugated ketone **3**.

Since quenching of the rearranged anion by either dienol **1** or unconjugated ketone **2** produces rearranged anion as a product, this process is catalytic and the amount of catalyst (rearranged anion) should remain constant.

The k_1 value for the thermal rate[2] (0% sodium amide) is 4.6×10^{-5} sec^{-1} and for the nominal 10 and 20% sodium amide reactions the k_1 values are 5.27×10^{-5} and 5.58×10^{-3} sec^{-1}, respectively. The upward trend of these values may be attributed to the differences in boiling point elevation produced by the differing concentrations of salt. Temperature increases in the boiling point of the IAE solvent of 1 and 2° have been observed in the solution containing the sodium amide over the temperature observed when the reaction is run with 0% sodium amide, and these increases in the boiling point of the solutions easily account for the slight upward trend of the rate constant k_1. Viewed together these results indicate that the rate of disappearance of the dienol **1** shows no significant dependence upon the concentration of the base. This observation rules out the possibility that the rearranged dienol **1** is quenched initially by the starting dienol **1** to yield either unconjugated ketone **2** or conjugated ketone **3**. Therefore, the first step in this reaction must be the thermal rearrangement of the starting dienol **1** to unconjugated ketone **2**.

The values of k_2 are 1.24×10^{-4} sec^{-1} (10% sodium amide reaction) and 5.31×10^{-4} sec^{-1} (20% sodium amide reaction). These pseudo-first-order rate constants become second-order rate constants when divided by the base concentration. The average concentration of catalyst in the 10% sodium amide reaction is 2.2×10^{-3} *M* (5.1%). Inspection of Table I shows that this computer calculated value of the catalyst concentration together with the computer calculated values of k_1 and k_2 gives a very accurate reproduction of the amount of conjugated ketone **3** produced as a function of time over the entire course of the reaction. In the 20% sodium amide reaction, extrapolation of the logarithm of the concentration of starting dienol **1** vs. time plot to the initial concentration of dienol **1** yields a concentration of 81.3% and, therefore, 18.7% (8.1×10^{-3} *M*) as the effective catalyst concentration. This value is exactly the same as that obtained from the linear least-squares computer program for the effective catalyst concentration. The mean concentration of catalyst as calculated from the difference between the measured and calculated amounts of unconjugated ketone **2** for all points is 17.4%; the average of the last four data points is 19%, in good agreement with the extrapolated value and the computer generated value of 18.7%.

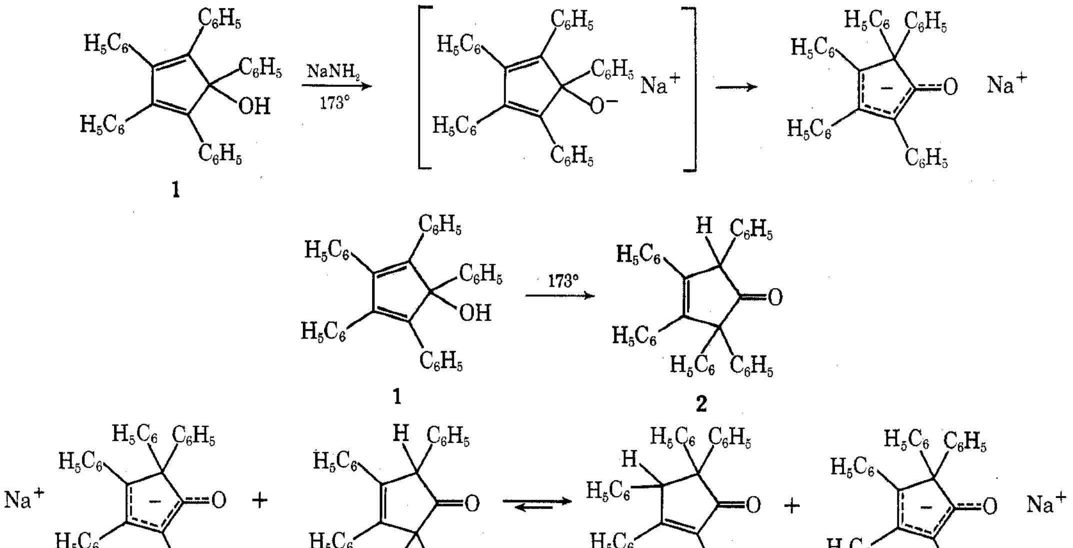
If the conversion of unconjugated ketone **2** to conjugated ketone **3** is essentially base catalyzed, then the ratio $k_2(20\%)/k_2(10\%)$ should equal the ratio of the catalyst concentrations for the two reactions. The ratio of catalyst concentrations 19/5 = 3.8 can be compared with $5.31 \times 10^{-4}/1.24 \times 10^{-4} = 4.2$. The agreement between these ratios confirms the base catalysis quantitatively. In view of the medium effect previously noted for the k_1 values, it is reasonable to suppose that a portion of the variation between the two ratios obtained for the k_2's is due to a small difference in the temperature of the boiling IAE solution.

Although chemical experiments previously published[3,4] indicate that the conversion of unconjugated ketone 2 to conjugated ketone 3 is reversible, the data reported here indicate that the equilibrium constant for this conversion must be greater than 20 and, in these runs, indeterminable.

The possibility that the conversion of the conjugated base of dienol 1 (initial anion) to the rearranged anion was important was tested by taking a sample at relatively long times and quenching it at the reaction temperature (173°) followed by analysis. Such high-temperature quenches had previously[3] been shown to favor the formation of conjugated ketone 3 over unconjugated ketone 2. Results of this quench established that conjugated ketone 3 was increased and unconjugated ketone 2 was decreased over their concentrations in a sample treated normally under the same conditions, but the remaining dienol 1 was unaffected and therefore no conjugate base of the dienol 1 was present under either analytical conditions at long times. The rearrangement reaction of the anion appears to be quite rapid at these temperatures and thus the catalyst is not the added sodium amide but is indeed the rearranged anion.

The kinetic data rule out the possibility of unconjugated ketone 2 or conjugated ketone 3 being obtained via the quench of the rearranged anion catalyst by the starting dienol 1. The formation of conjugated ketone 3 results from the quenching of the rearranged anion catalyst by the intermediate unconjugated ketone 2 and indeed requires that the conversion of dienol 1 to conjugated ketone 3 take place via the intermediate unconjugated ketone 2.

These results give rise to the following mechanism for the reaction of isoamyl ether (IAE) solutions of dienol 1 with sodium amide, which is simpler and slightly different from the mechanism previously proposed.[3]



Experimental Section

General. The gas–liquid partition chromatographic (GLC) analysis of samples was performed on a Bendix Model 2600 (flame) gas chromatograph and a Bendix Model 1200 recorder. The GLC was equipped with a 3 ft × 0.25 in. column packed with 3% QF-1 on Chromosorb W (H.P., mesh 100/120) support. Operating conditions were as follows: temperature of inlet 210°, detector 255°, injector 255°, column 210°, and He carrier gas flow rate of 80 ml/min. The retention times and relative molar response to a flame ionization detector, based on 100 for dienol 1, for the materials involved were as follows: dienol 1, 6 min 15 sec, 100; unconjugated ketone 2, 13 min 45 sec, 80; conjugated ketone 3, 15 min 45 sec, 86. The temperature of the reaction mixture was maintained at the temperature reported ±1° by means of a thermostatically controlled oil bath. Extreme care was exercised to remove impurities, especially water, from the IAE solvent used. The solvent was distilled, under nitrogen, from lithium aluminum hydride ($LiAlH_4$), chromatographed under nitrogen, on alumina and redistilled, under nitrogen, from $LiAlH_4$ directly into the reaction flask, which was oven baked, flamed, and cooled under nitrogen. The reaction flask containing the IAE was then continuously swept with nitrogen. Although ultrahigh-purity nitrogen was used, it was passed through a BTS catalyst (pelleted form of finely divided copper on an inert support). The nitrogen was passed successively through a column of molecular sieves, a column of BTS catalyst heated by means of a heating tape, and finally through another column of molecular sieves. The output gas had an oxygen and water content each below 1 ppm. These precautions were utilized because in several initial experiments where these precautions were not taken the results obtained were found to be irreproducible. This irreproducibility was not observed when the above described precautions were taken. To ensure against premature hydrolysis of the sodium amide used, vials containing preweighed base were prepared in a drybox and were opened immediately before introduction to the IAE solution.

Kinetic Runs. Reaction of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol (1) with 10% (Molar Ratio) of Sodium Amide. Into a 100-ml, three-necked, round-bottomed flask equipped with a reflux condenser, a serum cap, a magnetic stirrer, and a nitrogen inlet tube was placed 50 ml of purified isoamyl ether (IAE), which was then heated to 173° under nitrogen. At this point 1.0 g (2.16 mmol) of the dienol 1 was added as a solid all at once. After solution occurred (almost instantaneously), 8.0 mg (0.2 mmol) of preweighed sodium amide was added all at once. At this point a vigorous reaction occurred but the reaction mixture was contained by the confines of the flask. While the mixture was refluxing, samples of 1 ml each were taken at various times (Table I) by inserting a hypodermic syringe through the serum cap. The samples thus removed were placed in a flask containing twice the volume of water and well shaken. To this mixture was added 1 ml of benzene, the solution was shaken, and the organic layer was removed. The remaining water solution was extracted a second time with another 1 ml of benzene, the benzene solutions were combined, and then dried over anhydrous magnesium sulfate. All samples removed were treated as described above. After all the required samples were collected, GLC analysis was carried out using the instrument and conditions described above. For each kinetic run the peak areas of the three peaks corresponding to the dienol 1, the unconjugated ketone 2, and the conjugated ketone 3 were determined by triangulation[5] and the percent concentrations represented by these peak areas, corrected for the flame response ratios, were then calculated (Table I) and plotted on the same graph vs. time (Figure 1). Using analytical GLC on all kinetic samples and from previous-

Table I
Isomerization Reaction of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol in Isoamyl Ether at 173° with Various Molar Ratios of Sodium Amide

Reaction time,	Ratio, %[b]			[Ketone 3/	[Ketone 3/	
min	Dienol 1	Ketone 2	Ketone 3	(dienol 1)$_0$][c]	(dienol 1)$_0$]$_{calcd}$[d]	[Ketone 2]$_{calcd}$[d]
30[a]	89.0	11.0	Trace	0.0	0.9	8.0
60	82.5	15.2	2.3	2.4	3.4	13.8
90	74.2	18.4	7.4	7.7	7.0	17.7
120	66.2	20.6	13.2	13.8	11.3	20.2
150	61.7	22.8	15.5	16.3	16.0	21.7
180	59.3	22.7	18.0	18.9	20.9	22.3
210	51.0	22.6	26.4	27.7	26.0	22.4
240	48.8	21.9	29.3	30.8	31.0	22.1
300	39.6	20.2	40.4	42.5	40.6	20.5
360	32.9	19.8	47.3	49.7	49.4	18.5
420	28.0	20.0	52.0	54.7	57.2	16.2
480	22.9	17.5	59.6	62.7	64.0	14.0
540	17.7	14.9	67.4	70.9	69.8	11.9
660	11.8	13.0	75.2	79.1	79.0	8.5
750	9.3	11.2	79.5	83.6	84.0	6.5
30[e]	75.6	18.4	5.0	6.1	3.4	6.0
60	66.8	21.8	11.3	13.8	10.3	7.8
90	57.6	27.7	15.8	19.4	18.0	7.9
150	49.5	27.3	22.8	28.0	32.5	6.9
210	40.8	23.3	35.9	44.1	44.7	5.7
270	33.2	22.0	44.9	55.2	54.7	4.7
270[f]	37.0	12.8	50.3			

[a] 10% sodium amide; results reported are for three kinetic runs which were reproducible to within 1% of each other. [b] Amounts reported are corrected for flame response ratios. [c] Concentration of ketone 3 used in nonlinear least-squares computer program to obtain rate constant k_2. [d] Computer generated values. [e] 20% sodium amide; results reported are for three kinetic runs which were reproducible to within 1% of each other. [f] Sample of kinetic solution quenched at 173° with water.

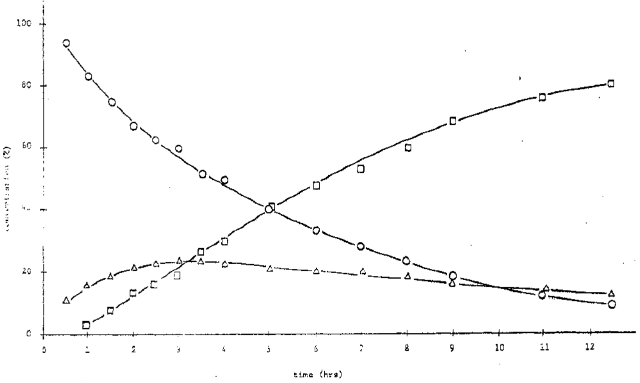


Figure 1. Variation with time of concentration of dienol **1**, unconjugated ketone **2**, and conjugated ketone **3** at 173° in isoamyl ether with 10% (molar ratio) sodium amide: ○, dienol **1**; △, unconjugated ketone **2**; □, conjugated ketone **3**.

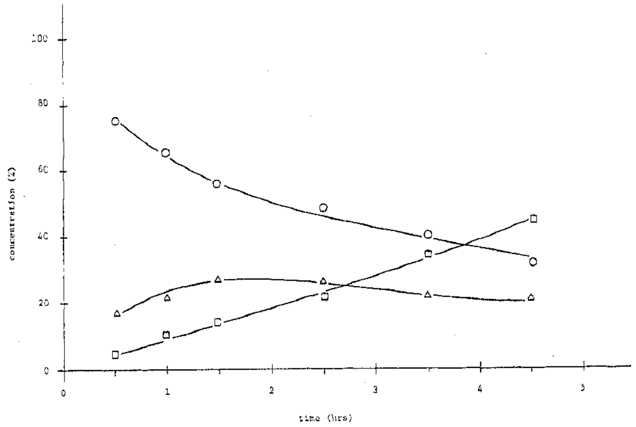


Figure 2. Variation with time of concentration of dienol **1**, unconjugated ketone **2**, and conjugated ketone **3** at 173° in isoamyl ether with 20% (molar ratio) sodium amide: ○, dienol **1**; △, unconjugated ketone **2**; □, conjugated ketone **3**.

ly reported[3,4] synthetic experiments the results indicate that only three species are present in each kinetic sample, dienol **1**, unconjugated ketone **2**, and conjugated ketone **3**. This information established a mass balance for each kinetic sample and for the overall reaction of approximately 100%.

Reaction of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol (1) with 20% (Molar Ratio) of Sodium Amide. This experiment was performed exactly as described above except that 16 mg (0.4 mmol) of sodium amide was used. After all the required samples were removed from the kinetic run and were treated as described above, water was added dropwise to the refluxing reaction mixture remaining in the flask so that a quench at 173° could be performed. After this high-temperature quench was completed, the mixture was cooled to room temperature, extracted with benzene, the organic layer was separated, dried over anhydrous magnesium sulfate, and analyzed on the GLC using the same instrument and conditions previously described for the kinetic samples. The results of this kinetic run and the high-temperature quench are reported in Table I and Figure 2.

Registry No.—**1**, 2137-74-8; **2**, 34759-47-2; **3**, 34759-48-3; sodium amide, 7782-92-5.

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