Mechanism and Linear Free Energy Relationships in the Kinetics of Formation of Bicyclo[3.3.1]nonane Derivatives from 1,3,5-Trinitrobenzene, Benzoylacetones, and Base

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The kinetics and mechanism of cyclication of the anionic σ complex obtained from the reaction of sym-trinitrobenzene (TNB) and benzoylacetone (BA) in the presence of triethylamine (NEta) have been studied in Me₂SO-H₂O (80% v/v). The order of the reaction has been found to be zero in TNB, unity in BA, fractional in NEt_3 , and negative and nonintegral in H⁺NEt₃. When the solvent is changed from Me₂SO-H₂O (80% v/v) to CH₃CN the order with respect to TNB is zero, BA is unity, NEt₃ is unity, and H^+NEt_3 is negative and nonintegral. The fractional order with respect to NEt₃ in Me₂SO-H₂O (80% v/v) was found to be due to the involvement of Me₂SO in proton abstraction and hence in cyclization. DMF also brought about the cyclization in a similar manner. The plot of rate constants for the formation of bicyclic complexes from substituted benzoylacetones and TNB vs. σ^+/σ concaved downward indicating a change in the rate determining step.

Strauss et al. have examined the kinetics and mechanism of formation and cyclization of some carbanionic σ complexes and reported that all cyclizations are mechanistically similar.^{2,3} Previous studies in our laboratories⁴ on the cyclization of 1:1 Meisenheimer adduct derived from 1,3,5-trinitrobenzene (TNB) and acetoacetanilide in the presence of NEt₃ have also established the same mechanistic picture as that of Strauss et al. However the cyclization process of the 1:1 Meisenheimer adduct derived from TNB and benzoylacetone (BA) in the presence of excess NEt₃ differs to a certain extent mechanistically, as suggested and confirmed by the different kinetic data. Since the ketone selected for the present investigation has highly acidic hydrogen atoms, the reaction is initiated and cyclization completed by highly basic solvents such as Me₂SO and DMF even in the absence of an external base such as NEt_3 . We report here the kinetics of the cyclization of 1:1 TNB-BA complex in Me₂SO-H₂O (80% v/v, a basic solvent) and CH₃CN, a solvent with lower basicity than Me₂SO. A kinetic study of cyclization of TNB-BA and Meisenheimer adduct brought about by Me_2SO was also made. This is the first report in which a solvent brings about σ complex formation which is followed by cyclization. In all the experiments pseudo-first-order conditions were maintained and good kinetic plots resulted. The results are reproducible within 5% error.

Only one report has so far appeared on the structurereactivity correlations in the conversion of σ complexes to bicyclo[3.3.1]nonane derivatives.⁵ In order to expand the scope of correlation analysis in this field, in the present investigation, rate constants were correlated with substituent constants for the formation of bicyclic complexes from carbanions derived from different benzoylacetones and TNB in the presence of NEt₃ in CH₃CN and in the absence of NEt₃ in Me₂SO.

The addition of excess of NEt₃ to a solution of BA and TNB in Me₂SO-H₂O (80% v/v) gives rise immediately upon mixing to a visible spectrum with two maxima at 473 and 584 nm characteristic of 1:1 Meisenheimer complex and this rapidly changes to give a peak at 515 nm owing to the formation of the bicyclic adduct. These spectral changes, are illustrated in Figure 1. As reported earlier,³

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in the present study, the slow disappearance of 1:1 Meisenheimer complex has been followed at 570 nm.

Results and Discussion

In Me₂SO-H₂O (80% v/v), at 40 °C, the cyclization rate was observed to be zero order in TNB (Figure 2, line A), first order in BA (Figure 2, line B, slope 0.99, and line c, slope 0.99), fractional order in NEt₃ (Figure 2, line D, slope 0.66, and line E, slope 0.78), and negative nonintegral order in H⁺NEt₃ (Figure 3, curve A, slope \sim -0.47, and curve B, slope ~ -0.40) and increased by increasing ionic strength (Figure 3, line c). A similar rate picture was noticed even at lower temperatures and at 580 nm. When the same cyclization process was carried out in a less basic solvent, CH₃CN, the rate was found to be zero order in TNB (Figure 4, line B), first order in BA (Figure 4, line A, slope 0.96), first order in NEt₃ (Figure 4, line C, slope 0.97), and

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Figure 1. Visible spectral changes on conversion of 1 to 4. Repeated scans at 1 min intervals at 35 °C.



Figure 2. Effect of TNB, BA, and NEt₃ concentrations on the rate of stage II in Me₂SO-H₂O [80%, v/v] at 40 °C. (A) \odot , 4 + log [TNB] vs. 2 + log k_{obad} ; [BA] = 0.04 M; [NEt₃] = 0.05 M; [H⁺NEt₃Cl⁻] = 0.003 M; [⁺NEt₄Cl⁻] = 0.015 M. (B) \equiv , 2 + log [BA] vs. 2 + log k_{obad} ; [TNB] = 0.0008 M; [NEt₃] = 0.03 M. (C) \triangle , 2 + log [BA] vs. 3 + log k_{obad} ; [TNB] = 0.0008 M; [NEt₃] = 0.04 M; [NEt₃Cl⁻] = 0.005 M. (D) \blacklozenge , 2 + log [NEt₃] vs. 2 + log k_{obad} ; [TNB] = 0.0008 M; [BA] = 0.04 M; [H⁺NEt₃Cl⁻] = 0.005 M. (D) \blacklozenge , 3 + log [NEt₃] vs. 3 + log k_{obad} ; [TNB] = 0.0008 M; [BA] = 0.04 M; [H⁺NEt₃Cl⁻] = 0.005 M.

negative nonintegral order in H^+NEt_3 (Figure 4, curve E, slope ~ -0.57) and increased by increasing ionic strength (Figure 4, line D). Our latter observations are consistent with the detailed mechanism illustrated in Scheme I.

Since methylene protons of BA are highly acidic, step 1 is significant and enters into the kinetic picture and hence, the rate expression for this reaction is different from that of Strauss.³ The rate of formation of 4 can be given as

$$\frac{d[4]}{dt} = -\frac{d[1]}{dt} = k_3[3]$$
(5)

For the sequence of reactions under stage II outlined in Scheme I, two rate limiting expressions can be derived. On the basis of steady-state treatment

$$\frac{d[4]}{dt} = -\frac{d[1]}{dt} = \frac{K_1 k_2 k_3 [1] [NEt_3] [BA]}{k_{-2} [H^+ NEt_3] [BA^-] + k_3 [BA^-]}$$
(6)

On the basis of preequilibrium treatment

$$\frac{d[4]}{dt} = -\frac{d[1]}{dt} = \frac{K_1 K_2 k_3 [1] [\text{NEt}_3] [\text{BA}]}{[\text{H}^+ \text{NEt}_3] [\text{BA}^-]}$$
(7)



0.6

Figure 3. Effect of H⁺NEt₃Cl⁻ and ⁺NEt₄Cl⁻ concentrations on the rate of stage II in Me₂SO-H₂O [80% v/v] at 40 °C. (A) \odot , 3 + log [H⁺NEt₃Cl⁻] vs. 2 + log k_{obsd} ; TNB = 0.0008; BA = 0.03 M; NEt₃ = 0.06 M. (B) \Box , 4 + log [H⁺NEt₃Cl⁻] vs. 2 + log k_{obsd} ; [TNB] = 0.0008 M; [BA] = 0.03 M; [NEt₃] = 0.04 M; [⁺NEt₄Cl⁻] = 0.05 M. (C) \triangle , 3 + log [⁺NEt₄Cl⁻] vs. 2 + log k_{obsd} ; [TNB] = 0.008 M; BA = 0.03 M; [NEt₃] = 0.025 M.



Figure 4. Effect of BA, TNB, NEt₃, ⁺NEt₄Cl⁻, and H⁺NEt₃Cl⁻ concentrations on the rate of stage II in CH₃CN at 30 °C. (A) \odot , 2 + log [BA] vs. 2 + log k_{obsd} ; [TNB] = 0.0005 M; [NEt₃] = 0.1 M; [H⁺NEt₃Cl⁻] = 0.00878 M; [⁺NEt₄Cl⁻] = 0.2296 M. (B) \Box , 4 + log [TNB] vs. 3 + log k_{obsd} ; [BA] = 0.1 M; others same as A. (C) \triangle , 2 + log [NEt₃] vs. 4 + log k_{obsd} ; others same as B. (D) \oplus , 3 + log [⁺NEt₄Cl⁻] vs. 3 + log k_{obsd} ; [TNB] = 0.0004 M; BA = 0.1 M; [NEt₃] = 0.1 M. (E) \blacktriangle , 3 + log [H⁺NEt₃Cl⁻] vs. 2 + log k_{obsd} ; others same as B.

According to eq 6 and 7 the reaction rate should be zero order in TNB, first order in BA, and first order in NEt₃. A plot of first-order rate coefficients vs. $[H^+NEt_3]$ is curvilinear (Figure 4, curve E, slope ~-0.57) and hence rate expression 6 is applicable for the cyclization process. When H⁺NEt₃ is constant (equal to the initially added TNB) and ⁺NEt₄ is varied, little effect on the rate of cyclization is seen (Figure 4, line D). This is expected for a reaction in which charge is neither created nor destroyed. The very slight increase in rate with increasing salt concentration can be attributed to the stabilization of 3 which is formed from the neutral entity 2.

Protonation of 1 at C₄ results in 5. One would expect adduct 5 to undergo a similar type of reaction as 2 as represented in Scheme I to give bicyclic adduct 6. Formation of adduct 6 has been ruled out due to the following reasons: (i) An NMR spectrum of the isolated adduct has a peak at δ 5.7 due to a bridging proton and a peak at δ 8.4 due to the propenide proton. These protons are absent in adduct 6. (ii) Adduct 4 is more stable than adduct 6 due to its delocalized charge.

We have also considered the possibility of proton transfer from the highly acidic methylene group of the side



chain to the ring in 1, followed by intramolecular attack on the resultant dinitro diene function of 3. This mechanism can be dismissed on the ground that the kinetic data are consistent with the reaction sequence specified in Scheme I.

In Me₂SO-H₂O (80% v/v) eq 6 holds except that order with respect to NEt₃ is fractional. This is due to the fact that Me₂SO also initiates proton abstraction and carbanionic σ complex formation and also effects the cyclization process.

Cyclization Process Catalyzed by Me₂SO. In the absence of NEt₃, when a solution of TNB in Me₂SO was mixed with excess BA in Me₂SO, two absorption maxima were noticed at 473 and 584 nm immediately in the visible spectrum, which changed to give a peak at 515 nm. These spectral changes (Figure 5) are similar to those illustrated in Figure 1 and clearly indicate that the same type of adducts are formed in the absence and in the presence of NEt_3 in Me_2SO . Since the basicity of Me_2SO is less than that of NEt_3 , the amount of 1:1 Meisenheimer adduct produced by the former is also less as indicated by smaller optical density values at 473 and 584 nm. Hence in the present study the rate of cyclization catalyzed by Me₂SO has been conveniently measured by observing the increase in absorbance at 510 nm rather than the decrease in absorbance at 570 nm.

Double logarithmic plots of k_{obsd} with concentration of TNB (Figure 6, line A) and BA (Figure 6, line B) are linear with slopes 0 and 0.96, respectively. It has also been noticed that the cyclization rate decreased with decreasing percentage of Me₂SO. Repeated attempts to isolate 7 were unsuccessful. Since the cyclization process of the TNB-BA-NEt₃ system is catalyzed by both NEt₃ and Me₂SO in Me₂SO-H₂O, log-log plots of NEt₃ concentration vs. k_{obsd} have slopes less than unity, 0.66 and 0.78 in the absence and presence of added salt, respectively.



Substituent Effect. The rate constants for the formation of bicyclic adducts from the 1:1 Meisenheimer adducts of TNB and various substituted benzoylacetones in the presence of NEt₃ in CH₃CN and those in the absence of NEt₃ in Me₂SO at three different temperatures are presented in Table I. Figure 7, curve B, reflects good correlation at 35 °C between the rate constants of the NEt₃ catalyzed cyclization reaction and σ (r = 0.99, s = 0.10, ρ = 2.82) and Figure 7, curve A, indicates excellent corre-



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Figure 5. Visible spectral changes on conversion of 1 to 4 for the Me₂SO catalyzed cyclization reaction. Repeated scans at 15-min intervals at 35 °C.



Figure 6. Effect of TNB and BA concentrations on the rate of stage II of the Me₂SO catalyzed cyclization reaction at 40 °C. (A) \odot , 5 + log [TNB] vs. 3 + log k_{obsd} ; [BA] = 0.1 M; [⁺NEt₄Cl⁻] = 0.00887 M. (B) \Box , 2 + log [BA] vs. 4 + log k_{obsd} ; [TNB] = 0.00005 M; [⁺NEt₄Cl⁻] = 0.00887 M.



Figure 7. (A) \odot , σ^+ vs. 4 + log k_{obsd} . Substituent effect in Me₂SO catalyzed cyclization reaction at 35 °C. (B) Δ , σ vs. 4 + log k_{obsd} . Substituent effect in NEt₃ catalyzed reaction; solvent, CH₃CN; temperature, 35 °C.

lation when rate constants of the Me₂SO catalyzed reaction are plotted against σ^+ (r = 0.99, $s = 0.05 \rho = 1.14$) at 35 °C.

The point of interest in the present investigation is that the plot of log k_{obsd} vs. substituent constant in either the NEt₃ catalyzed cyclization reaction or Me₂SO catalyzed

	$k_{\text{obsd}}, a \min^{-1}$			$k_{\rm obsd}$, $b \min^{-1}$		
substituents	25 °C	30 °C	35 °C	35 °C	40 °C	45 °C
p-OCH ₃	0.0036	0.0055	0.0082	0.00033	0.00053	0.00084
p-NHCOCH ₃				0.00046	0.00074	0.0011
p-CH ₃	0.0130	0.0145	0.0161	0.0010	0.0012	0.0013
Ĥ	0.0444	0.0531	0.0633	0.0018	0.0021	0.0023
p-Cl	0.1102	0.1256	0.1425	0.0031	0.0035	0.0039
p-Br	0.1862	0.2015	0.2175	0.0035	0.0036	0.0046
m-Cl	0.0724	0.0942	0.1219	0.00093	0.0017	0.0030
m-Br	0.1253	0.1401	0.1560	0.00095	0.0017	0.0032
m-NO ₂	0.0007	0.0008	0.0009			
p-NO ₂	0.0004	0.0006	0.0008			

^a For the NEt₃ catalyzed cyclization reaction; solvent, CH₃CN; [TNB] = 0.005 M; [benzoylacetones] = 0.1 M; [NEt₃] = 0.1 M; [⁺Net₄Cl⁻] = 0.2296 M; [H⁺NEt₃Cl⁻] = 0.0176 M. ^bFor the Me₂SO catalyzed cyclization reaction; [TNB] = 0.0001 M; [benzoylacetones] = 0.1 M; $[^{+}NEt_{4}Cl^{-}] = 0.00221 \text{ M}.$



Figure 8. (A) \odot , $-\Delta S^*$ eu vs. $\Delta H^* \times 10^{-4}$ cals/mol for the Me₂SO catalyzed cyclization reaction at 35 °C. (B) \Box , $-\Delta S^*$ eu vs. ΔH^* × 10⁻⁴ cals/mol for the NEt₃ catalyzed cyclization reaction; solvent, CH₃CN; temperature, 35 °C. (C) Δ , $\sigma^+ - \sigma$ vs. 1/ $\rho \log k/k_0 - \sigma$ for the Me₂SO catalyzed cyclization reaction.

reaction is not linear but has a maximum at the point corresponding to (p-bromobenzoyl)acetone. Since the curve concaves downward, the break in the Hammett equation arises due to the change of the rate determining step. When electron donating and weakly electron withdrawing substituents are present in the phenyl ring of BA, proton abstraction is the rate determining step, and when strongly electron withdrawing substituents are present, cyclization is the rate determining step. Electron donating substituents reduce the positive charge density on the carbonyl carbon and hence tighten the C-H bond in the adjacent position so much that breakage of the C-H bond forms the slower rate determining step. On the contrary, strongly electron withdrawing groups render the carbonyl carbon highly positive and thus weaken the C-H bond which ruptures easily and cyclization becomes the slower rate determining step. A plot of ΔH^* vs ΔS^* is linear (Figure 8, lines A and B) in both reactions adding support to the fact that the reaction proceeds through a single mechanism throughout the series. The entropy of activation is negative in both reactions indicating that the freedom of motion in the side chain of the σ complex is hindered in the transition state due to cyclization.

In the presence of NEt₃, the bicyclic complexes of (pnitrobenzoyl)acetone and (m-nitrobenzoyl)acetone undergo cleavage and hence they show marked deviation from the correlation line. Even for the cyclization process catalyzed by Me₂SO, the plot of $\log a/a - x$ vs. time is not linear in the case of (p-nitrobenzoyl)- and (m-nitrobenzoyl)acetone systems, indicating the possibility of some other interfering reaction.

When proton abstraction is rate determining, the removal of the proton leaves behind a carbanionic center and hence ρ is positive. When cyclization is rate determining, the unit negative charge on the carbonionic center gets delocalized, the negative charge density per unit area decreases, and hence the ρ value is negative. Since the reaction site is only one atom away from the ring carrying substituents, the ρ values are reasonably high.

In the polarized form 8, since there is a positive charge adjacent to the ring, a +M group (OCH_3, CH_3, etc) is likely to be in conjugation and hence in resonance interaction with the carbonyl group. It is probable that the carbonyl group is in a highly polarized form in Me₂SO and hence the rate constants show excellent correlation with σ^+ , whereas in CH₃CN the carbonyl group is comparatively less polarized than in Me₂SO and hence rate constants show good correlation only with σ values.



For the Me₂SO catalyzed reaction the plot of $[1/\rho \log$ $k/k_0 - \sigma$] vs $[\sigma^+ - \sigma]$ is linear with a slope of unity (Figure 8, line c, r = 0.99, s = 0.03), indicating that a thorough resonance treatment of the substituent effect is justifiable.

Experimental Section

Purification of Reagents. Me₂SO (Baker analytical reagent), DMF (Mallinkrodt analytical reagent), and CH₃CN (Merck) were dried over molecular sieves type 4A, distilled, and used. Triethylamine (reagent grade) was distilled from small quantities of phenyl isocyanate.⁶ Triethylammonium chloride was recrystallized from absolute ethanol and dried under vacuum. Tetraethylammonium chloride (Fluka AG) was used as such. Benzoylacetones were prepared from the corresponding acetophenones and acetic anhydride by using boron trifluoride.⁷ TNB was prepared by known procedures^{8,9} and was repeatedly re-

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crystallized from ethanol-water solutions with decolorizing carbon.

Kinetic Runs in 80% Me₂SO and CH₃CN. Stock solutions of TNB, BA, NEt₃, and the salts were prepared in either of the solvents and thermostated at the experimental temperature, and the quantities for each run were pipetted into volumetric flasks and diluted to the required volume. The decrease in absorbance as a function of time was then recorded at 570 nm against solvent blank by employing a nonrecording Carl-Zeiss VSU2-P spectrophotometer.

Kinetic Runs in Me₂SO. Kinetics of the cyclization process catalyzed by Me₂SO were followed by mixing the appropriate solutions (preequilibrated to required temperature) and transferring the reaction mixture to a thermostated cell in a Carl-Zeiss VSU2-P spectrophotometer. The increase in absorbance as a function of time was then recorded at 510 nm against solvent blank. Figures 1 and 5 were obtained on a Carl-Zeiss UV-vis specord

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Registry No. 1:1 TNB-(p-OCH₃)BA complex, 95346-53-5; 1:1 TNB-(p-NHCOCH₃)BA complex, 95346-54-6; 1:1 TNB-(p-CH₃)BA complex, 95346-55-7; 1:1 TNB-BA complex, 95346-56-8; 1:1 TNB-(p-Cl)BA complex, 95346-57-9; 1:1 TNB-(p-Br)BA complex, 95346-58-0; 1:1 TNB-(m-Cl)BA complex, 95346-59-1; 1:1 TNB-(m-Br)BA complex, 95346-60-4; 1:1 TNB-(m-NO₂)BA complex, 95346-61-5; 1:1 TNB-(p-NO₂)BA complex, 95346-62-6; NEt₃, 121-44-8.

Direct Synthesis of 5-Methyl-3-aryl-1,2,4-oxadiazoles from Aryl Aldehydes. Nitroethane, and Ammonium Acetate

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The condensation of 2,5-dimethoxybenzaldehyde (1b) with nitroethane and ammonium acetate in glacial acetic acid has been found to give three different products, depending on reactant ratio and reaction time. At an aldehyde:nitroethane:ammonium acetate ratio of 1:1.5:0.8 a normal Knoevenagel condensation occurred, vielding 1-(2,5-dimethoxyphenyl)-2-nitropropene. At a reactant ratio of 1:3:2 (same reactant sequence), the primary product was 2.5-dimethoxybenzonitrile, and at a reactant ratio of 1:40:8, with extended reflux time, the major product was 3-(2,5-dimethoxyphenyl)-5-methyl-1,2,4-oxadiazole (8b). This last reaction served as a prototype for a new oxadiazole synthesis which was then extended to include six additional 5-methyl-3-aryl-1,2,4-oxadiazoles (8a,c-g; where aryl = Ph, 2,5-dimethoxyphenyl, 2,4-dichlorophenyl, m-chlorophenyl, p-tolyl, 3,5-dimethoxyphenyl, and p-carboxyphenyl), whose structures were assigned on the basis of ${}^{13}C$ NMR characteristics of known reference compounds. Benzonitrile also reacted with excess nitroethane and ammonium acetate to yield 5-methyl-3phenyl-1,2,4-oxadiazole (8a). The overall mechanism of oxadiazole formation is shown to be dependent on a preliminary reaction wherein the nitroalkane, in the presence of ammonium acetate and acetic acid, is first transformed into the corresponding alkanoic acid and hydroxylamine. Hydroxylamine then converts the aromatic aldehyde, via the intermediary nitrile, to the oxadiazoles following reactions of established precedent.

Major synthetic routes to the 1,2,4-oxadiazoles have been recently reviewed by Clapp,¹ who pointed out that 95% of the practical preparations are encompassed by two general methods; viz., (a) the condensation of amidoximes with carboxylic acid derivatives, and (b) the dipolar cycloaddition of nitrile oxides to nitriles. Subsequently, Lin and co-workers² reported a new general method in which N'-acyl-N.N-dimethylamides react with hydroxylamine to form 3,5-disubstituted or 5-monosubstituted 1,2,4-oxadiazoles in high yields.

We have now observed a new and unusual formation of 5-methyl-3-aryl-1,2,4-oxadiazoles (8a-g, Table I) from the reaction of aromatic aldehydes with nitroethane in the presence of ammonium acetate and report here several examples of the synthesis along with evidence concerning the mechanism of the transformation (Scheme I).

The Henry (Knoevenagel) condensation of aromatic aldehydes with nitroalkanes is by now a classical route to β -nitrostyrenes.³ In a particular application of this process

Table I. ¹H and ¹³C NMR Resonance Assignments^a for the 5-Methyl-3-aryl-1,2,4-oxadiazoles 8a-g 0

 CH_3

N Ar										
		δ (¹ H)	δ (¹³ C)							
8	Ar	5-Me	5-Me	C-3	C-5					
a	phenyl	2.54	11.8	168.0	176.1					
b	2,5-dimethoxyphenyl	2.65	12.2	166.8	175.4					
С	2,4-dichlorophenyl	2.68	12.0	166.2	176.0					
d	<i>m</i> -chlorophenyl	2.64	12.3	167.4	176.8					
е	p-tolyl	2.38	12.2	168.3	176.2					
f	3,5-dimethoxyphenyl	2.46	12.4	168.4	176.5					
g	p-carboxyphenyl	2.70	12.0	167.0	177.7					

^a δ values are ppm with respect to Me₄Si.

we had prepared 1-(2,5-dimethoxyphenyl)-2-nitropropene (2b) from 2,5-dimethoxybenzaldehyde (1b), nitroethane, and ammonium acetate (ratio 1:1.5:0.8) via a 3-h reflux in acetic acid essentially as described in the literature.⁴ While the yield was quite adequate (70%), an attempt was made to improve it by altering the proportions of 1b:

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