Anal. Calcd for $C_{12}H_{17}N_3$: C, 70.90; H, 8.43; N, 20.67. Found: C, 70.79; H, 8.58; N, 20.52.

3,4,5-Triaminotoluene (14). A mixture of 3.9 g (0.020 mol) of **7**, 9.0 g of mossy tin, and 60 ml of concentrated hydrochloric acid was placed in a three-necked 500-ml round-bottomed flask, fitted with a condenser and overhead stirrer, and heated on a steam bath for 1 hr. The cooled mixture was made basic with 80 g of 50% NaOH, then extracted four times with 50-ml portions of $CHCl_3$. The combined $CHCl_3$ layers were dried over Na_2SO_4, filtered, and evaporated leaving behind a white solid. Recrystallization of the solid from benzene afforded 1.7 g (63%) of **14** as white needles, mp 100–102.5° (lit.[15] 105°).

4-Amino-2,6-dimethylbenzimidazole Monohydrate (13). A mixture of 3.7 g (0.027 mol) of **14** and 25 ml of acetic anhydride was heated in a 250-ml round-bottomed flask on a steam bath for 15 min. After cooling the mixture, 50 ml of 3 *N* hydrochloric acid was added, and the reaction was heated under reflux for 2 hr. The mixture was cooled, made basic with concentrated NH_4OH, and extracted four times with 40-ml portions of $CHCl_3$. Evaporation of the combined $CHCl_3$ layers yielded an oily residue, which was treated with 60 ml of 6 *N* hydrochloric acid and heated under reflux for 3 hr. The cooled mixture was made basic with concentrated NH_4OH, and allowed to sit in the refrigerator for 3 hr, resulting in the formation of 3.0 g (62.5%) of **13** as long light gold needles, mp 97–98.5° (lit.[16] 100°). This was used without further purification.

4-Propionamide-2,6-dimethylbenzimidazole (15). A mixture of 3.0 g (0.017 mol) of **13** and 50 ml of propionic acid was heated under reflux for 6 hr. The mixture was poured into 100 ml of ice water, and made basic with concentrated NH_4OH. The resulting precipitate was removed by filtration and washed liberally with water. After drying the solid it was recrystallized from tetrahydrofuran to yield 2.7 g (75.7%) of **15** as a white crystalline solid, mp 139° dec.

Anal. Calcd for $C_{12}H_{15}N_3O$: C, 66.34; H, 6.96; N, 19.34. Found: C, 65.98; H, 6.98; N, 19.27.

2,6-Dimethyl-4-*N*-propylaminobenzimidazole (3). A three-necked 250-ml round-bottomed flask, fitted with a condenser, addition funnel, and septum, was charged with 20.5 ml (20.5 mmol) of a 1 *M* borane–THF solution. A solution of 1.77 g (8.20 mmol) of **15** in 80 ml of hot dry THF was added to the mixture over a 10-min period and the reaction was heated under reflux for 3.5 hr. To the cooled mixture 60 ml of 6 *N* hydrochloric acid was added slowly. The THF was removed by distillation at atmospheric pressure. Sodium hydroxide pellets were added to saturate the aqueous phase and the latter was extracted three times with a total of 60 ml of ether. The ether was evaporated leaving behind an oil which was treated with 60 ml of 6 *N* hydrochloric acid and heated at reflux for 2 hr. After cooling sodium hydroxide pellets were added until the mixture was basic and the latter was extracted a total of three times with 60 ml of ether. After drying with Na_2SO_4, the ether was evaporated leaving behind a solid. Recrystallization from 40% $EtOH–H_2O$ afforded 1.0 g (60.2%) of **3** as a white amorphous solid, mp 87–88°.

Anal. Calcd for $C_{12}H_{17}N_3 \cdot 0.5H_2O$: C, 67.89; H, 8.55; N, 19.79. Found: C, 68.19; H, 8.86; N, 19.94.

Acknowledgment. The authors wish to express appreciation to Ciba-Geigy, Greensboro, N.C., for their encouragement and assistance during this investigation.

Registry No.—**1**, 53369-82-7; **2**, 53369-83-8; **3**, 53369-84-9; **4**, 53369-85-0; **6**, 2078-03-7; **7**, 6393-42-6; **8**, 5264-65-3; **9**, 53369-86-1; **10**, 53369-87-2; **11**, 53369-89-4; **13**, 19364-67-1; **14**, 27530-48-9; **15**, 53369-88-3; *n*-propylamine, 107-10-8; *n*-propyl bromide, 106-94-5; propionic acid, 79-09-4.

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Aril Azines. III.[1] Reaction of Benzil Benzal Monoazine with Sodium Methoxide

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Received September 26, 1974

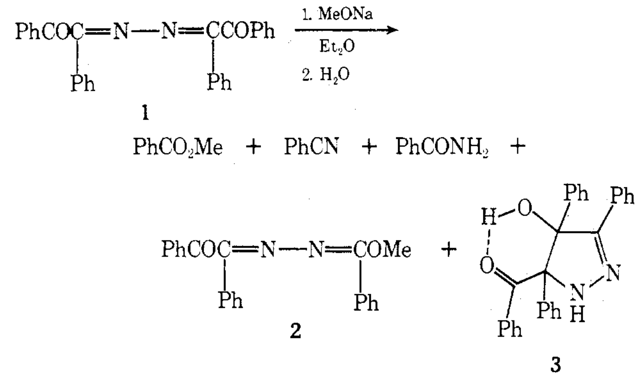
Reaction of benzil benzal monoazine (5) with sodium methoxide in ether gives as the major product benzil diazine (9). Several other products are formed, which include benzonitrile, benzamide, benzoic acid, 5-methoxy-1,2,5-triphenyl-3,4-diaza-2,4-pentadien-1-one (2), 3,4,5-triphenylpyrazole (6), *N*-benzylbenzamide (7), and a dihydro derivative of benzil diazine (10). It is suggested that the products are formed *via* two primary reaction pathways: (i) nucleophilic attack by methoxide ion on the benzal carbon atom of 5, and (ii) abstraction of a proton from this carbon atom by methoxide ion.

The reaction of benzil monoazine (1) with sodium methoxide in ether has been shown to give the products depicted in Scheme I.[2] A possible pathway for the formation of the dihydro product **3** has been proposed to be that shown in Scheme II.[2] This postulate has led us to attempt to generate the anionic species **4** in an alternative fashion.

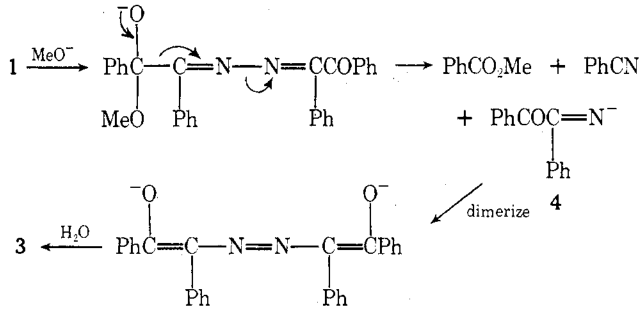
To this end the reaction of benzil benzal monoazine (**5**) with sodium methoxide was investigated in the hope that reaction might proceed, at least in part, by removal of the azomethine proton followed by fragmentation to benzonitrile and the anion **4**. In the event, treatment of **5** with sodium methoxide in boiling ether led to the rapid development of a blue coloration that later became dark red-brown; after 5 days aqueous work-up gave a plethora of products, which did not include **3**. These are shown in Scheme III; only **9** was isolated in major amount (35%).

Compounds **2** and **6** were identified by direct comparison with samples of those compounds that had been obtained previously in our work with benzil monoazine.[2] *N*-Benzylbenzamide (**7**) was identified by comparison with an au-

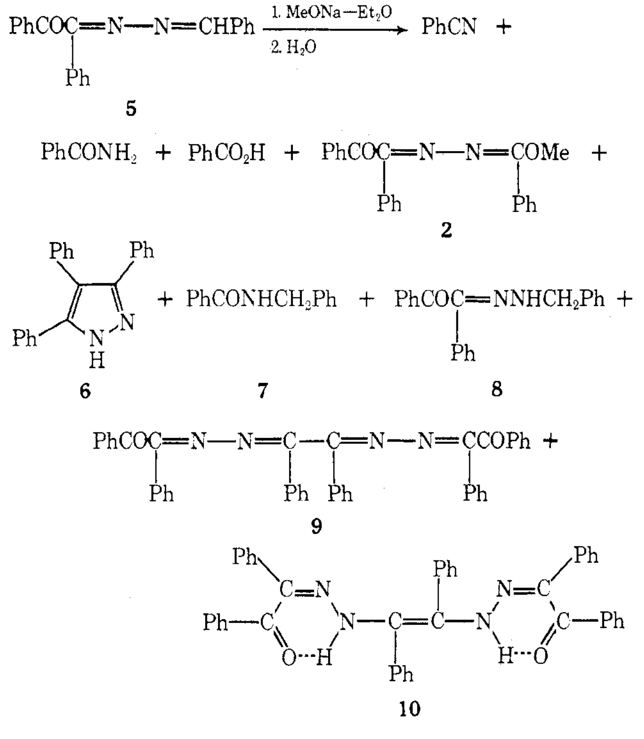
Scheme I



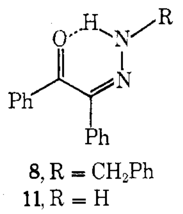
Scheme II



Scheme III



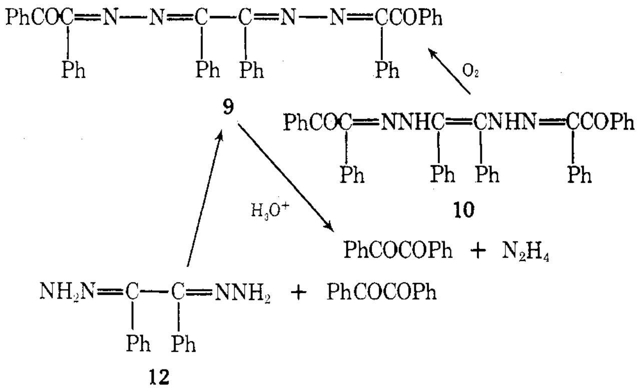
thentic sample prepared by treatment of benzoyl chloride with benzylamine.[3] The structural assignment 8 is tentative, since insufficient material was available for full characterization; it is made on the basis of the similarity of the ir spectrum of this product with that of benzil monohydrazone (11).



8, R = CH_2Ph
11, R = H

The structure of the yellow diazine 9 was assigned on the basis of the close similarity of its ir spectrum to that of benzil monoazine (1) and its hydrolysis to benzil and hydrazine. The assignment was confirmed by the independent preparation of 9 from benzil dihydrazone (12) and benzil (Scheme IV). Compound 10 separated from the original reaction mixture as an orange-red solid at the water–ether interface after treatment of the reaction mixture with water. It could not be purified by recrystallization since the red solutions formed in organic solvents rapidly turned yellow in air, giving the diazine 9.[4] A sample of the solid after thorough washing with ether and water gave elemental analytical data corresponding to the composition $C_{42}H_{32}N_4O_2 \cdot 0.5H_2O$; mass spectrometry corroborated the assignment of the formula $C_{42}H_{32}N_4O_2$. This formulation and its very facile oxidation to 9 suggested that it is a dihydro derivative of 9, and structure 10 (or the geometrical isomer at the ethylenic bond) is proposed on the basis of the relationship of its ir spectrum to the ir spectra of 8 and 11.

Scheme IV

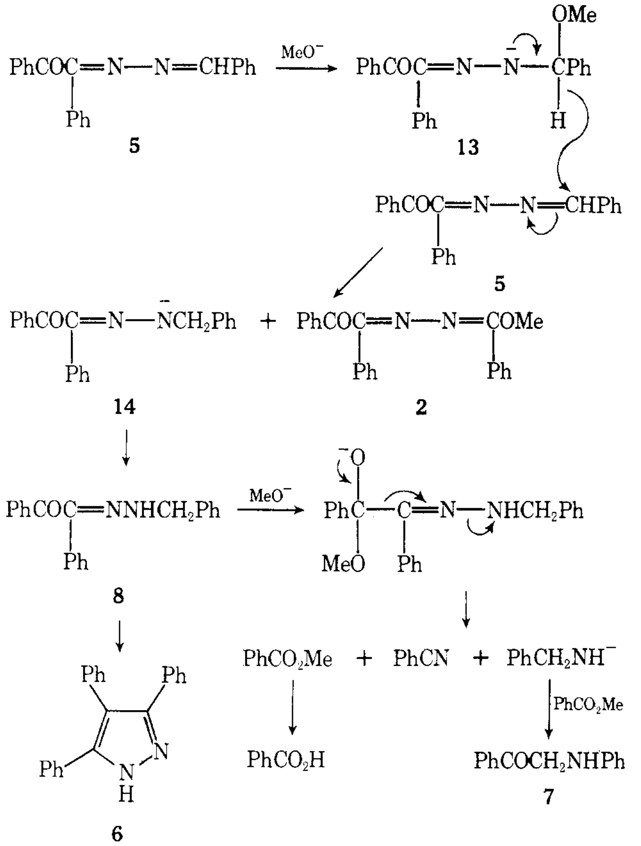


The formation of the products other than 9 and 10 from 5 and sodium methoxide can be envisaged as occurring *via* initial attack of methoxide ion to give the anion 13 (Scheme V). Hydride transfer from 13 to a second molecule of 5 would produce 2 and the anion 14, which could serve as the source of products 6, 7, and 8 and the smaller fragments observed (Scheme V). Alternatively, the anion 14 could arise *via* hydride or electron transfer from methoxide ion to 5. Scheme V involves the protonation of 14 before work-up; the proton source is considered to be methanol formed by proton abstraction from 5 (*vide infra*). The isolation of benzoic acid but not of methyl benzoate is attributed to hydrolysis of the latter by hydroxide ion formed in the conversion of 8 to 6.

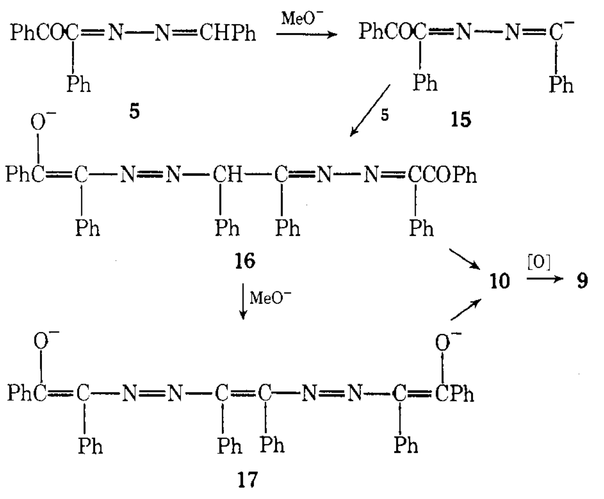
The formation of products 9 and 10 is postulated to involve a different primary reaction—proton abstraction by methoxide ion of the azomethine hydrogen of 5 to give the anion 15 (Scheme VI). Reaction of this with a second molecule of 5 would serve as a source of 10, *via* formation of its anion 16 or its dianion, 17; it is possible that the initial blue color of the reaction mixture is due to the latter species.[5] The azine 9 is considered to arise by oxidation of 10, either during the course of the reaction or during work-up.

The fact that compound 3 was not observed among the products from the reaction of 5 with sodium methoxide fails to provide evidence concerning the intermediacy of 4 in the formation of 3 from 1 and sodium methoxide. For,

Scheme V



Scheme VI



although the possibility exists that **4** might be formed from **5** *via* elimination of benzonitrile from **15**, there is no evidence that this occurs.

Experimental Section

Benzil Benzaldehyde Monoazine (5).[6] Benzil monohydrazone (17.0 g, 0.077 mol) was added to a solution of benzaldehyde (9.4 g, 0.088 mol) in absolute ethanol (550 ml) and the solution was refluxed for 3 hr. The solution was concentrated to *ca.* 100 ml and cooled to give yellow plates (15.25 g), mp 139–146°. Further concentration and cooling gave a second crop (5.30 g), mp 149–150.5°. The combined crops were dissolved in a mixture of benzene (50 ml) and ethanol (50 ml), and the solution was concentrated to 75 ml to give benzil benzaldehyde monoazine (20.2 g): mp 149–150° (lit.[6] mp 150°); λ_{max} ($CHCl_3$) 5.94 μ; λ_{max} (EtOH) 260 (log ϵ 4.23), 306 nm (log ϵ 4.46); δ ($CDCl_3$) 7.43 (m, 11 H), 7.92 (m, 4 H), 8.57 (s, 1 H).

Reaction of 5 with Sodium Methoxide. Benzil benzaldehyde monoazine (14.4 g) and dry sodium methoxide (9.06 g) in dry ether (1.2 l.) were stirred under a blanket of dry nitrogen. After 24 hr the solution was deep blue, and after 5 days red-brown. The red-brown reaction mixture was shaken with water (300 ml). The red-orange solid at the water–ether interface and suspended in the aqueous phase was filtered, washed with water and ether, and dried. This solid, compound **10** (0.52 g), had mp 184.5–185° dec; λ_{max} ($CHCl_3$) 3.01, 6.14 μ; *m/e* (%) 624 (4), 519 (6), 491 (5), 415 (28), 414 (58), 402 (5), 387 (6), 311 (10), 310 (24), 297 (10), 194 (5), 178 (10), 165 (10), 150 (10), 134 (14), 110 (7), 109 (55), 108 (17), 107 (13), 106 (27), 105 (100), 104 (65), 103 (29).

Anal. Calcd for $C_{42}H_{32}N_4O_2 \cdot 0.5H_2O$: C, 79.60; H, 5.25; N, 8.85. Found: C, 79.70; H, 5.40; N, 8.86.

The aqueous solution was extracted with ether, and the extracts were combined with the red ethereal solution, whose color rapidly changed to yellow. This process was not dependent on light. The aqueous solution was acidified to give benzoic acid (1.04 g, 7%); this was recrystallized to give material, mp 119–120°; mmp 120–121°.

The combined ethereal solutions were concentrated to *ca.* 150 ml and on standing for 5 days gave a mixture of crystals (4.11 g) from which a white crystalline solid, mp 165–173°, was separated manually. This was crystallized from ether to give material: mp 178–179° dec; λ_{max} ($CHCl_3$) 2.99, 3.04 (complex), 5.98 μ; solutions of this material in hot carbon tetrachloride or chloroform were red. Consistent elemental analytical and mass spectral data could not be obtained for this substance.

The residual yellow crystalline solid had mp 164–180°. Several recrystallizations from ethanol–benzene gave material, mp 184–186°. An analytical sample, mp 184.5–185.5°, was prepared by several recrystallizations of this material from acetic acid: λ_{max} ($CHCl_3$) 5.98 μ; λ_{max} (CH_2Cl_2) 258 (log ϵ 4.59), 318 nm (log ϵ 4.67); δ ($CDCl_3$) 7.15–7.55 (m, 26 H), 7.97 (m, 4 H).

Anal. Calcd for $C_{42}H_{30}N_4O_2$: C, 81.01; H, 4.86; N, 9.00. Found: C, 80.73; H, 4.85; N, 9.11.

This was identified as benzil diazine (**9**) by mmp 184–185° with an authentic sample (*vide infra*), mp 184–185°. Its mixture melting point with benzil monoazine was 169–175° and with benzil benzaldehyde monoazine, 141–144°.

The original ethereal solution was evaporated, and the residue was taken up in benzene–petroleum ether and chromatographed on alumina (B.D.H.; 480 g). Elution with benzene–petroleum ether (1:1) gave an oil (1.01 g) that contained mainly benzonitrile, identified by ir and nmr spectroscopy and by odor.

Further elution with benzene–petroleum ether (1:1) gave an oil (0.62 g), which was crystallized from ether to give crystalline material, mp 121–123°; this was recrystallized from ether to give needles, mp 124–125°. It was shown to be 1,2,5-triphenyl-5-methoxy-3,4-diaza-2,4-pentadien-1-one (**2**) by ir spectral comparison and by mixture melting point comparison with an authentic sample.[2]

Further elution with benzene–petroleum ether (1:1, 3:1, and 9:1) and benzene gave additional benzil diazine (2.56 g; total, 6.06 g), mp 184–185°.

Elution with ether–benzene (1:99) gave an orange oil (0.62 g) that crystallized from benzene to give *N*-benzylbenzamide (**7**): mp 104–105° and mmp 104–105° with an authentic sample (*vide infra*), mp 103.5–104°; λ_{max} (CCl_4) 3.05, 6.00 μ; δ ($CDCl_3$) 4.43 (d, *J* = 6 Hz, 2 H; s after D_2O treatment), 7.17 (m, 9 H; 8 H after D_2O treatment), 7.73 (m, 2 H).

Elution with ether–benzene (1:9) gave a green gum (0.78 g), which was rechromatographed under the same conditions to give material (0.54 g) that crystallized from ethanol as a solid, mp 125–135°; after recrystallization from ethanol this gave greenish needles, mp 147–148°; λ_{max} ($CHCl_3$) 3.01, 6.09 μ.

Anal. Calcd for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.91. Found: C, 79.89; H, 6.33; N, 8.95.

Elution with ether gave a white solid (0.57 g) from which 3,4,5-triphenylpyrazole (**6**), mp 265–266.5°, was obtained by crystallization from ethanol; it had mmp 265–266.5° with an authentic sample,[2] mp 265–266.5°.

Elution with methanol–chloroform (1:1) gave a black oil (0.57 g) that had an ir spectrum characteristic of benzamide and crystallized from water to give benzamide, mp 121–124°.

Hydrolysis of 9. Compound **9** (0.65 g) was heated in aqueous 66% sulfuric acid (75 ml) for 20 min. The mixture was poured into water (500 ml) and continuously extracted with ether for 2 days. The ethereal solution was dried and evaporated to give benzil (0.58 g, 88%), which after crystallization from ethanol had mp 90–93.5°. The aqueous acidic solution was treated with excess salicylaldehyde to detect hydrazine.[7] The solution became fluorescent and on standing salicylalazine crystallized and was filtered to give fluorescent needles (0.42 g, 96%), mp 214–216° (lit.[8] mp 213°); mmp 214–216° with an authentic sample, mp 214–216°, prepared from salicylaldehyde and hydrazine dihydrochloride in water. The ir spectra of the two samples were indistinguishable.

Conversion of 10 to 9. Compound **10** (58 mg) was dissolved in dichloromethane and the red solution was allowed to stand in the air until the color had changed to yellow. The solution was evaporated, and the residue was crystallized from acetic acid to give yellow crystals (44 mg, 78%) of benzil diazine, mp 182–184°; mmp 182–184°.

***N*-Benzylbenzamide (7).** Benzoyl chloride (1.40 g, 0.0100 mol) in dry ether was added to a solution of benzylamine (2.14 g, 0.0200 mol) in dry ether (50 ml). White crystals formed, which were filtered and washed well with ether. The filtrate and washings were evaporated to give a white solid, which was crystallized from benzene to give *N*-benzylbenzamide (1.50 g, 50%), mp 103.5–104° (lit.[3] mp 105–106°).

Benzil Dihydrazone. (12). Benzil dihydrazone was prepared by boiling a solution of benzil and 2 equiv of hydrazine hydrate in 1-propanol under reflux for 60 hr: mp 151.5–152.5° (lit.[9] mp 152–153°); λ_{max} ($CHCl_3$) 2.90, 3.03; 6.19, 6.30 μ; δ ($CDCl_3$) 5.67 (br s, 4 H), 7.2–7.7 (m, 10 H).

Benzil Diazine (9). Benzil dihydrazone (2.38 g, 0.0100 mol) and benzil (4.20 g, 0.0200 mol) were heated under reflux in 1-propanol for 5 hr with a few drops of concentrated hydrochloric acid. A yellow crystalline mass, mp 171–180°, crystallized on cooling. Three crystallizations from glacial acetic acid gave benzil diazine, mp 184–185°.

Acknowledgment. We thank the National Research Council of Canada for support of this work.

Registry No.—**2,** 53555-48-9; **5,** 53555-49-0; **6,** 18076-30-7; **7,** 1485-70-7; **8,** 53555-51-4; **9,** 53555-50-3; **10,** 53555-52-5; **12,** 4702-78-7; sodium methoxide, 124-41-4; benzoyl chloride, 98-88-4; benzylamine, 100-46-9; benzil, 134-81-6; hydrazine, 302-01-2; benzil monohydrazone, 5344-88-7; benzaldehyde, 100-52-7.

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(2) P. Yates, E. M. Levi, and B. L. Shapiro, *Can. J. Chem.*, **52**, 3343 (1974).
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(4) In contrast to the autoxidation of **3**,[2] this autoxidation does not appear to be photochemically induced; this is explicable in terms of the pathway proposed for the oxidation of **3**, wherein the photochemical step involves its conversion to an intermediate analogous to **10**.
(5) In the light of our considerations relating to the possible dimerization of **4**,[2] it is of interest to note that **17** could arise by dimerization of **15**.
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Diazotization of *endo*-7-Aminomethylbicyclo[3.3.1]nonan-3-ols and *endo*-7-Aminomethylbicyclo[3.3.1]non-2-ene[1]

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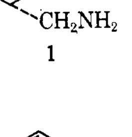
Received August 21, 1974

Diazotization of *endo*-7-aminomethylbicyclo[3.3.1]nonan-*exo*-3-ol (**3**) with aqueous nitrous acid produced 3-methylbicyclo[3.3.1]non-2-en-*exo*-7-ol (**7**), *exo*-7-methylbicyclo[3.3.1]nonan-3-one (**8**), and presumably *exo*-8-hydroxybicyclo[4.3.1]dec-2-ene (**9**) as major products. Exposure of *endo*-7-aminomethylbicyclo[3.3.1]nonan-*endo*-3-ol (**2**) to both protic (acetic acid or water) and aprotic (benzene) deamination resulted mainly in formation of 1-methyl-2-oxaadamantane (**19**) and 4-oxahomoadamantane (**20**) in addition to a component tentatively identified as *endo*-8-hydroxybicyclo[4.3.1]dec-3-ene (**21**). Compound **2** yielded *endo*-7-aminomethylbicyclo[3.3.1]non-2-ene (**4**) with dilute sulfuric acid. Deamination of **4** under conditions used for **2** provided 2-adamantanol (**28**) and 2-adamantyl acetate (**29**) as principal products. Elimination, transannular interactions, and apparently ring expansion comprise the dominant reaction routes. **7** gave **8** with sulfuric acid. The preparations of the isomeric 7-methylenebicyclo[3.3.1]nonan-3-ols (**10**) and *endo*-7-methylbicyclo[3.3.1]nonan-3-one (**11**) from reduction of 7-methylenebicyclo[3.3.1]nonan-3-one (**12**) are described. Endo alcohol **10b** provided **19** under acidic conditions. Mechanistic aspects of the investigation are treated.

Previous reports from this laboratory have described the preparation[5] of *endo*-7-aminomethylbicyclo[3.3.1]nonan-3-one (**1**) and its versatility as a precursor to various bicyclo[3.3.1]nonane derivatives.[6] Reduction of **1** with $NaBH_4$ in alcoholic solvents provided the corresponding alcohols,[7] **2** (endo) and **3** (exo). Keeping in mind the possibility for transannular interaction with the hydroxyl and alkenyl moieties, we intended to determine the response of **2** and **3**, as well as the aminoalkene **4**, toward various deaminating systems. Attention was devoted to mechanistic aspects.



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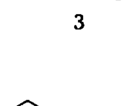

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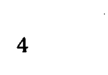

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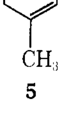

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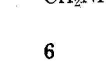

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In related studies,[8] diazotization of **1** yielded 4-protoadamantanone and 3-methylbicyclo[3.3.1]non-2-en-7-one (**5**). *endo*-3-Aminomethylbicyclo[3.3.1]nonane (**6**) produced 3-methylbicyclo[3.3.1]non-2-ene, 3-methylenebicyclo[3.3.1]nonane, *endo*-3-acetoxymethylbicyclo[3.3.1]nonane, and *endo*-3-hydroxymethylbicyclo[3.3.1]nonane.

Results and Discussion

The isomeric amino alcohols **2** and **3** were subjected to deamination in three solvent systems. The major products resulted from elimination and transannular interactions. In addition, there was indication of ring expansion to the bicyclo[4.3.1]decene system.