tified by their parent masses of 352 and their UV spectra[30] as the two isomeric benzonaphthofluoroanthenes (I and II, see earlier). These same products were also reported in the $SbCl_3$-catalyzed pyrolysis of An[11,12] and are the expected condensation products of the major dimer, 2,9-$An_2$.

Gel permeation chromatography of pyrolysis mixtures from reaction at 440 °C for 1 h showed two well-defined peaks corresponding to the dianthracenes and to An. Only a very small peak was observed before the rather sudden onset of the dimer peak, suggesting the near absence of trimeric and larger products.

**Acknowledgment.** This work was supported by a grant from the Gas Research Institute. We thank Dr. Buchanan from Oak Ridge National Laboratories for providing us with UV spectra for bianthracenyls. A sample of 1-anthraldehyde was kindly provided by Professor M. Platz, Ohio State University.

**Registry No.** An, 120-12-7; $AnH_2$, 613-31-0; 2,9-$An_2$, 67263-10-9; 1,9-$An_2$, 1055-23-8; naphthalene, 91-20-3; phenanthrene, 85-01-8; biphenyl, 92-52-4; diphenyl ether, 101-84-8.

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# The Question of Friedel–Crafts Transformylations. Acid-Catalyzed Reactions of Aromatic Aldehydes with Arenes

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The reactions of aromatic aldehydes with various arenes in the presence of Lewis and Brønsted acids have been examined with the aim of determining if transformylations occur. No evidence for such transformylations was obtained. The major initial reaction is nucleophilic addition of the arene to the carbonyl group of the aldehyde to produce a diarylmethanol, followed by reaction with a second molecule of arene with elimination of water to produce a triarylmethane. Further reactions include (1) reversible dealkylations/realkylations of triarylmethanes to yield di- and triarylmethanes having aromatic nuclei corresponding to those of both the initial aldehyde and the arene and (2) alkylation, cyclialkylation, and dealkylation reactions that result in the formation of anthracene and/or substituted anthracenes and dihydroanthracenes. The anthracene and dihydroanthracene derivatives are produced in significant amounts only when aluminum chloride is the acid catalyst. The mechanisms of the reactions of aromatic aldehydes with arenes in the presence of aluminum chloride are discussed and compared with reactions of aromatic ketones.

In previous papers[1,2] we have described the occurrence of certain Friedel–Crafts transacylations and transsulfonylations. The results of these investigations led us to consider the possibility of analogous transformylations—reactions of aromatic aldehydes with nucleophilic arenes that result in the transfer of a formyl group from one aromatic nucleus to another. Although the reactions of aromatic ketones and sulfones with arenes in the presence of Lewis and protonic acids had not received much attention until recently, the analogous reactions of aldehydes have been investigated rather extensively. The addition of benzene to benzaldehyde in the presence of $AlCl_3$ or $FeCl_3$ was reported by Schaarschmidt et al.[3] to give triphenylmethane and anthracene. Further work by Hey[4] and Ungnade[5] showed that substituted triphenylmethanes and anthracenes were formed by the reactions of other aromatic aldehydes with aromatic hydrocarbons such as toluene and xylenes in the presence of excess $AlCl_3$. For example, reaction of *p*-tolualdehyde with benzene in the presence of $AlCl_3$ gave triphenylmethane, anthracene, and toluene.[4a] The results of these studies were interpreted as indicating that the aldehyde provides the meso carbons of the anthracene molecules and the methinyl carbon of the triphenylmethane molecules, whereas the hydrocarbon rings supply the two end rings of the anthracene molecules and the three rings in the triphenylmethane molecules.

The initial step in these reactions was considered by Hey and Ungnade to be the decarbonylation of the aldehyde, the reverse of a Gattermann–Koch reaction,[6,7] rather than a transformylation. The aldehyde expected from a transformylation reaction was never detected. The carbon monoxide produced by the decarbonylation was presumed to react with the aromatic hydrocarbons in some unspecified way to produce the triarylmethanes and anthracenes.

In view of the transacylations and transsulfonylations that we had recently observed, it became of interest to us to investigate the possibility that transformylations may actually occur in the reactions of aromatic aldehydes of the types described by Hey and Ungnade and that the aldehyde produced by transformylation may be an intermediate in these reactions although it has gone undetected. The present work was designed to determine whether or not such a transformylation may occur, with the hope that

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(1) El-Khawaga, A. M.; Roberts, R. M.; Sweeney, K. M. *J. Org. Chem.* **1985**, *50*, 2055.

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(3) Schaarschmidt, A.; Hermann, L.; Szemzo, B. *Ber.* **1925**, *58*, 1914.

(4) (a) Hey, J. D. *J. Chem. Soc.* **1935**, 72. (b) Hey, J. D.; Ellison, H. *J. Chem. Soc.* **1938**, 1847.

(5) (a) Ungnade, H. F.; Crandall, E. W. *J. Am. Chem. Soc.* **1949**, *71*, 2209. (b) Ungnade, H. F.; Kline, E. F.; Crandall, E. W. *J. Am. Chem. Soc.* **1953**, *75*, 333.

(6) (a) Gattermann, J.; Koch, J. A. *Ber.* **1897**, *30*, 1622. (b) Olah, G. A. Friedel–Crafts and Related Reactions; Wiley Interscience: New York, 1964; Vol. III, Chapter 38.

(7) The kinetics of decarbonylation were studied extensively by Schubert. See: (a) Schubert, W. M.; Latourette, H. K. *J. Am. Chem. Soc.* **1952**, *74*, 1879. (b) Burkett, H.; Schubert, W. M.; Schultz, F.; Murphy, R. B.; Talbott, R. *J. Am. Chem. Soc.* **1959**, *81*, 3923.

**Table I. Reactions of Benzaldehyde with Various Arenes and Catalysts**

| entry | arene | molar ratio, BA/arene/cat.[a] (catalyst) | temp, °C | time, h | observed products (%)[b] |
|---|---|---|---|---|---|
| 1 | toluene[c] | 1.0/3.5/2.1 ($AlCl_3$) | 60 | 6 | benzene (7)<br>toluene (14)<br>benzaldehyde (3)<br>methylanthracenes[d] (2)<br>dimethylanthracenes[d] (22)<br>triarylmethanols[e] (3)<br>diarylmethanes[e] (27) |
| 2 | toluene[c] | 1.0/3.0/2.1[f] ($AlCl_3$) | 60 | 1 | benzene (8)<br>toluene (50)<br>xylene (8)<br>benzaldehyde (8)<br>ditolylmethane[d] (3)<br>tolylxylylmethane[e] (3)<br>methylanthracenes[d] (3)<br>dimethylanthracenes[d] (13)<br>phenylditolylmethane[d] (3)<br>tritolylmethane[d] (3) |
| 3 | toluene | 1.0/1.0/2.1 ($AlCl_3$) | 60 | 5 min | benzene (2)<br>toluene (11)<br>benzaldehyde (50)<br>ditolylmethanes (4)<br>tritolylmethane (4) |
| 4 | toluene | 1.0/1.0/2.1 ($AlCl_3$) | 60 | 0.5 | benzene (2)<br>toluene (5)<br>benzaldehyde (43)<br>ditolylmethane (2)<br>anthracene (3)<br>methylanthracenes[e] (12)<br>dimethylanthracenes[d] (27)<br>triarylmethanes[e] (3) |
| 5 | toluene | 1.0/1.0/2.1 ($AlCl_3$) | 60 | 1 | benzene (6)<br>toluene (15)<br>xylene (3)<br>benzaldehyde (2)<br>diphenylmethane (2)<br>phenyltolylmethane[d] (2)<br>ditolylmethane (8)<br>anthracene (2)<br>methylanthracenes[e] (23)<br>dimethylanthracenes[d] (34) |
| 6 | toluene | 1.0/1.0/2.1 ($CF_3SO_3H$) | 60 | 5 min | toluene (28)<br>benzaldehyde (50)<br>benzoic acid (9)<br>phenylditolylmethane (13) |
| 7 | toluene | 1.0/1.0/2.1 ($CF_3SO_3H$) | 60 | 0.5 | toluene (11)<br>benzaldehyde (26)<br>benzoic acid (3)<br>tolylphenylmethane (11)<br>phenylditolylmethane[e] (24)<br>phenylditolylmethanol[d] (23) |
| 8 | toluene | 1.0/1.0/2.1 ($CF_3SO_3H$) | 60 | 1 | toluene (7)<br>benzaldehyde (26)<br>benzoic acid (2)<br>phenyltolylmethane (15)<br>phenylditolylmethane[e] (20)<br>phenylditolylmethanol[d] (32) |
| 9 | diphenylmethane | 1.0/1.0/2.1 ($AlCl_3$) | 60 | 5 min | benzene (21)<br>toluene (2)<br>benzaldehyde (46)<br>diphenylmethane (21)<br>dibenzylbenzene[e] (6) |
| 10 | diphenylmethane | 1.0/1.0/2.1 ($AlCl_3$) | 60 | 1 | benzene (12)<br>toluene (5)<br>benzaldehyde (35)<br>diphenylmethane (10)<br>ditolylmethane (3)<br>dihydroanthracene (2)<br>anthracene (15)<br>methylanthracenes[d] (8) |
| 11 | anisole | 1.0/3.0/1.2 ($AlCl_3$) | 100 | 1 | anisole (62)<br>phenol (2)<br>anisylphenylmethane (22)<br>dianisylphenylmethane (2) |

**Table I (Continued)**

| entry | arene | molar ratio, BA/arene/cat.[a] (catalyst) | temp, °C | time, h | observed products (%)[b] |
|---|---|---|---|---|---|
| 12 | anisole | 1.0/3.0/1.2 ($AlCl_3$) | 0 | 1 | anisole (35)<br>anisylphenylmethane (18)<br>dianisylphenylmethane (27)<br>dianisylphenylmethanol (16) |
| 13 | anisole | 1.0/3.0/1.2 ($ZnCl_2$) | 25 | 6 | anisole (61)<br>benzaldehyde (30)<br>anisylphenylmethane (3)<br>dianisylphenylmethane (2) |
| 14 | anisole | 1.0/3.0/1.2 ($SnCl_4$) | 25 | 6 | anisole (71)<br>benzaldehyde (28)<br>dianisylphenylmethane (3) |
| 15 | mesitylene | 1.0/3.5/2.1 ($AlCl_3$) | 25 | 1 | mesitylene (10)<br>benzaldehyde (16)<br>tetramethylbenzene (3)<br>diphenylmethane (2)<br>phenyltolylmethane (2)<br>ditolylmethane (3)<br>mesitylphenylmethane (22)<br>mesitylxylylmethane (8)<br>mesityltolylmethane (2)<br>dimesityltolylmethane (3) |
| 16 | mesitylene | 1.0/3.5/2.1 ($CF_3SO_3H$) | 25 | 1 | mesitylene (24)<br>benzaldehyde (10)<br>mesitylphenylmethane (25)<br>phenyl(tetramethylphenyl)methane (3)<br>mesitylxylylmethane (19) |

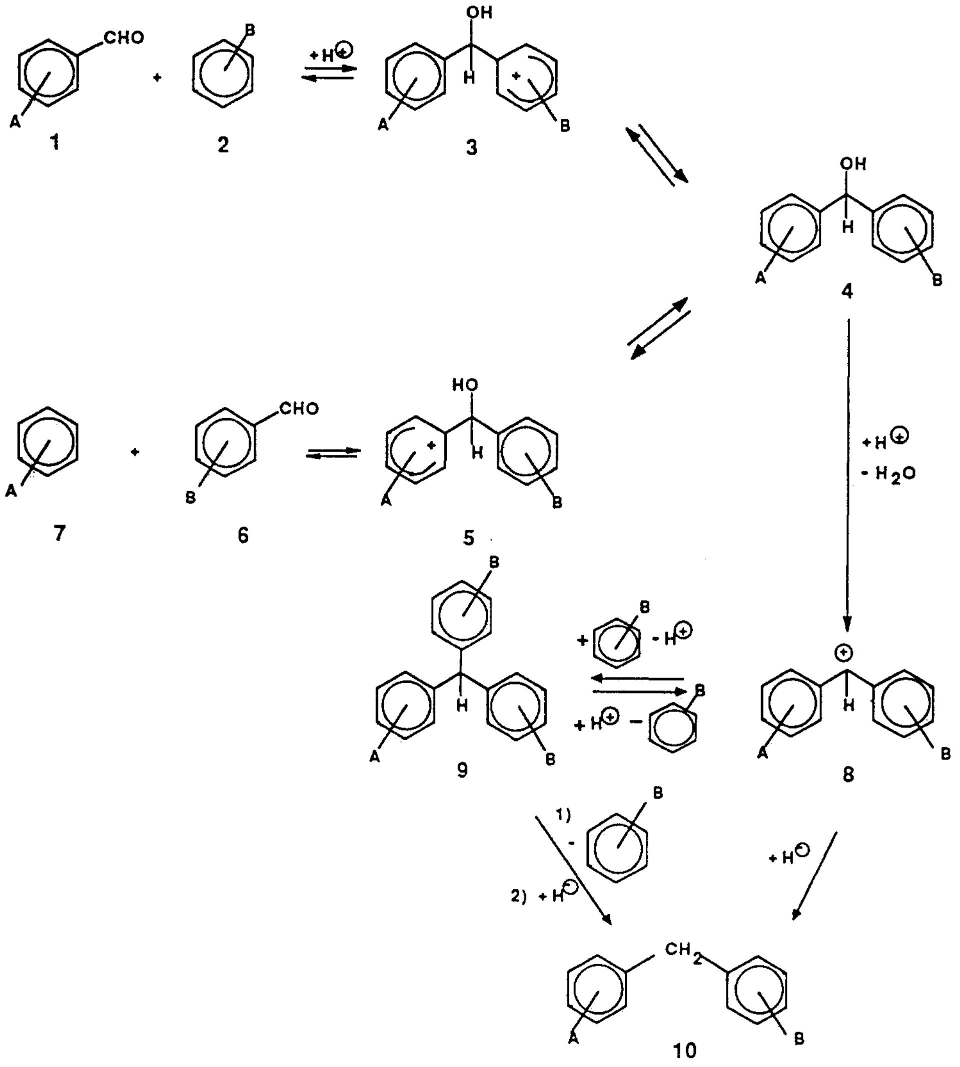
[a] BA = benzaldehyde, cat. = catalyst. [b] Results from GC/MS analysis. Since unidentified products and identified products in amounts of 1% or less are not included, the sum of the percentages is usually less than 100%. [c] This experiment carried out according to the procedure of Hey.[4a] [d] Two isomers observed. [e] Three or more isomers observed. [f] With 1.2 mol of $AlCl_3$ at 0 °C and 60 °C only starting materials were recovered.

**Table II. Reactions of Various Aldehydes with Various Arenes and $AlCl_3$**

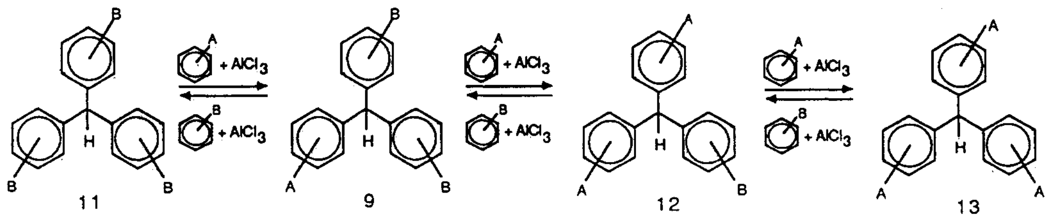
| entry | aldehyde[a] | arene | molar ratio AL/arene/cat.[b] | temp, °C | time, h | observed products (%)[c] |
|---|---|---|---|---|---|---|
| 1 | TOL | toluene | 1.0/3.5/2.5 | 25 | 1 | toluene (8)<br>P-tolualdehyde (74)<br>tritolylmethane (5) |
| 2 | TOL | toluene | 1.0/3.5/2.1 | 60 | 6 | benzene (8)<br>toluene (20)<br>diphenylmethane (7)<br>phenyltolylmethane (15)<br>ditolylmethane (5)<br>dihydrodimethylanthracenes[e] (6)<br>dimethylanthracenes[e] (5)<br>trimethylanthracenes[e] (10) |
| 3 | AN | toluene | 1.0/3.0/2.1[d] | 60 | 1 | toluene (23)<br>xylene (7)<br>*p*-hydroxybenzaldehyde (6)<br>anisaldehyde (5)<br>ditolylmethanes[e] (9)<br>anisyltolylmethane (5)<br>dimethylanthracenes[e] (12)<br>(hydroxyphenyl)tolylmethane (16)<br>anisylditolylmethane (2) |
| 4 | AN | phenetole | 1.0/3.0/1.2 | 60 | 1 | anisole (21)<br>phenetole (50)<br>anisaldehyde (2)<br>bis(*p*-ethoxyphenyl)methane (9)<br>anisyl(*p*-ethoxyphenyl)methane (7)<br>anisylbis(*p*-ethoxyphenyl)methane (4) |
| 5 | 3,4-DMB | anisole | 1.0/3.0/2.1 | 60 | 1 | anisole (50)<br>dihydroxybenzaldehyde (34)<br>3,4-dimethoxybenzene (5)<br>dianisylmethane[e] (4)<br>anisyl(3,4-dimethoxyphenyl)methane[e] (4)<br>trianisylmethane[e] (4) |
| 6 | 3,4-DCB | anisole | 1.0/1.0/1.2[f] | 60 | 1 | anisole (35)<br>dichlorobenzene (2)<br>anisyl(3,4-dichlorophenyl)methane (39)<br>dianisyl(3,4-dichlorophenyl)methane (23) |

[a] Aldehydes: TOL = *p*-tolualdehyde, AN = anisaldehyde, 3,4-DMB = 3,4-dimethoxybenzaldehyde, 3,4-DCB = 3,4-dichlorobenzaldehyde. [b] AL = aldehyde, cat. = catalyst. [c] Results from GC/MS analysis. Since unidentified products and identified products in amounts of 1% or less are not included, the sum of the percentages is usually less than 100%. [d] When 1.2 mol of $AlCl_3$ was used, the same products were found but only 1% of dimethylanthracenes was produced. [e] Several possible isomers observed. [f] $CF_3SO_3H$ gave similar results.

Scheme I



Scheme II



if it does the intermediate aldehyde may be detected before it undergoes subsequent reactions to form triarylmethanes and anthracenes. Whether or not the transformylation could be detected, we considered it important to gain more insight into the mechanism of formation of the triarylmethanes and anthracenes. To this end we have explored the reactions of a number of aromatic aldehydes with a variety of arenes and Lewis and Bronsted acid catalysts, including repetition of some of the experiments of Hey and Ungnade, under a variety of experimental conditions, and we have examined the reaction mixtures by means of capillary GC/MS analysis.

The results from reactions of benzaldehyde with toluene, diphenylmethane, and anisole are presented in Table I. The experiments of entries 1 and 2 were carried out according to the procedure of Hey.[4a] Note that we observed methylanthracene as well as dimethylanthracenes as products. Hey described the identification of 2,6- and 2,7-dimethylanthracene, but he reported that no monomethylanthracene could be detected in the product. We also observed unsubstituted anthracene as a product when a lower ratio of toluene/benzaldehyde was used (entries 4, 5). No diaryl- or triarylmethanes were reported by Hey. With triflic (trifluoromethanesulfonic) acid as catalyst (entries 6–8), di- and triarylmethanes were produced, but no anthracenes. Ungnade reported triphenylmethanol as a product and no triphenylmethane.[5a] Triphenylmethane is known to be oxidized by air in the presence of $AlCl_3$ to triphenylmethanol,[8] and there was ample opportunity for such an oxidation in Ungnade's procedure. We detected triarylmethanols in several of our experiments.

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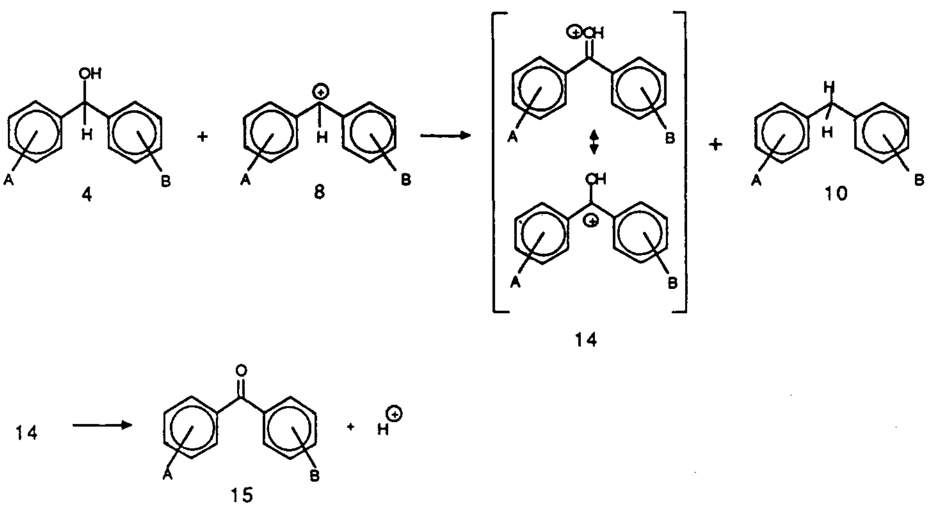
[8] Norris, J. F.; MacLeod, G. *Am. Chem. J.* **1901**, *26*, 502. See also Kantner and Kreevoy (Kantner, S. S.; Kreevoy, M. M. *J. Org. Chem.* **1977**, *42*, 865), who showed that the reaction of triphenylmethane with triflic acid, followed by quenching with water, gives triphenylmethanol.

**Scheme III**

III A:



III B:

$$Ar_3CH + H^+ \rightarrow Ar_2CH^+ + ArH$$

$$Ar_2CH^+ + Ar_3CH \rightarrow Ar_2CH_2 + Ar_3C^+$$

$$Ar_3C^+ + H_2O \rightarrow Ar_3COH + H^+$$

The reaction of benzaldehyde with diphenylmethane and aluminum chloride (entries 9 and 10) produced anthracene very quickly. Reactions between benzaldehyde and anisole produced di- and triarylmethanes but no anthracenes (entries 11–14). Reactions performed by using the milder catalysts ($ZnCl_2$ and $SnCl_4$) and lower temperatures resulted mainly in recovery of starting materials, although some triarylmethanes were produced. Reactions between benzaldehyde and mesitylene gave a variety of di- and triarylmethanes with both aluminum chloride and triflic acid as catalysts. The major product with aluminum chloride catalyst was mesitylphenylmethane, but the other products demonstrated extensive transmethylations between the aryl groups. In none of the reactions of benzaldehyde with various arenes was more than a trace of the aldehyde expected from transformylation detected, but significant amounts of benzene were produced in most of the reactions.

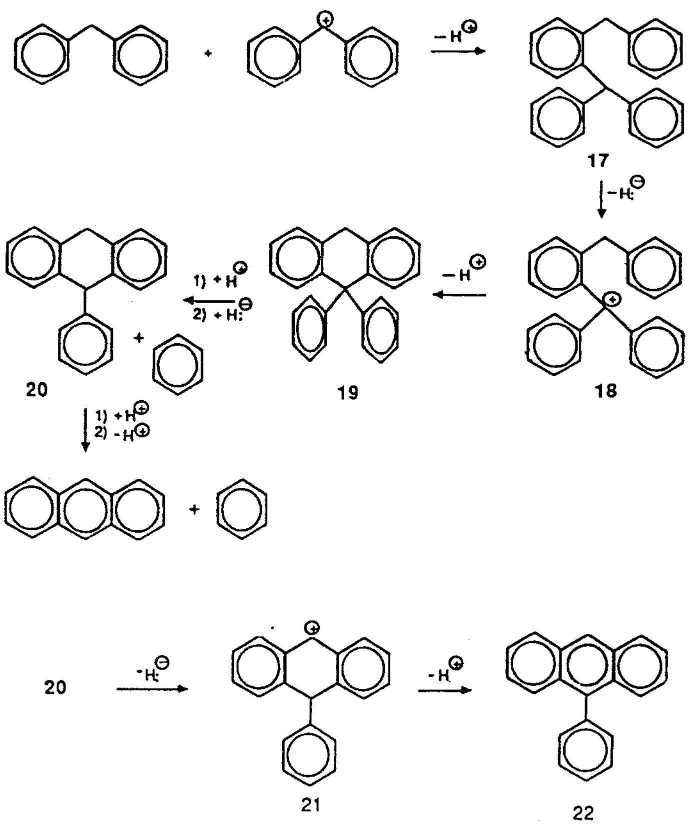
Results from experiments with other aromatic aldehydes are presented in Table II. *p*-Tolualdehyde and anisaldehyde reacted with toluene in the presence of aluminum chloride to give a variety of products, including di- and triarylmethanes and methyl-substituted anthracenes. No methoxy-substituted anthracenes were produced. Anisaldehyde, 3,4-dimethoxybenzaldehyde, and 3,4-dichlorobenzaldehyde gave no anthracenes with either anisole or phenetole and aluminum chloride. As in the experiments of Table I, no aldehyde corresponding to the transformylation product was detected.

**Mechanistic Implications.** In view of the observed transacylations and transsulfonylations we have reported,[1,2] we were surprised to find little or no evidence for aldehydes produced by transformylation, even under mild reaction conditions and with a sensitive method of identification (GC/MS). However, examination of the products formed from the reactions of the aldehydes and arenes in acidic media suggests that the pathways for competing reactions are much more favorable in the case of the aldehydes than in the case of the ketones and sulfones. Indeed, the aldehydes gave significant amounts of triarylmethanes under milder conditions than those producing transacylations of ketones. This may possibly be explained in terms of Schemes I and II. The intermediate diarylmethanol **4** apparently undergoes protonation, followed by loss of a water molecule to produce cation **8** in preference to protonation of the A ring that would produce **5** and thus lead to transformylation product **6** (the "other aldehyde"). In comparing the different behaviors of aromatic aldehydes and ketones, two factors should be noted. One is that the steric hindrance produced by the ortho methyl groups in the ketones that favors their transacylation[1,2] would be less pronounced in the corresponding aromatic aldehydes. Another is that the intermediate cation **8** is less stable and thus more reactive than the corresponding tertiary cation from a ketone. Reaction of the cation **8** with the arene **2** produces the triarylmethane **9**, which may then undergo a dealkylation to produce a diarylmethane, **10**, and reversible dealkylation/realkylation reactions to produce other triarylmethanes, **11**, **12**, and **13**, as indicated in Scheme II.

The fact that in many of the reactions of Tables I and II triarylmethanes were observed that did not contain the aromatic moiety corresponding to the original aldehyde might be interpreted as evidence for the initial formation of the "other aldehyde" (**6**) by transformylation, followed by subsequent addition reactions to produce the triarylmethanes. However, these results are equally compatible with the mechanisms outlined in Schemes I and II, and it should be noted that an argument that the "other aldehyde" is produced by transformylation but then undergoes subsequent reactions so rapidly that it cannot be detected is not viable in view of the fact that substantial amounts of the initial aldehyde were usually recovered.[9]

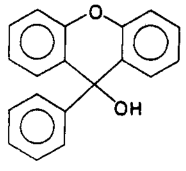
The GC/MS analyses of some of the reactions carried out for different time periods indicated that diarylmethanes as well as triarylmethanes are produced and the

Scheme IV



triarylmethanes do not persist in the reaction mixtures as long as the diarylmethanes (entries 3–5 and 6–8 in Table I). Referring to Scheme I, we suggest that diarylmethanes (e.g., **10**) may be produced directly from diarylmethyl cations (**8**) by hydride abstraction, or from triarylmethanes (**9**) by dealkylation followed by hydride abstraction. In either case, a source of hydride must be postulated. One attractive possibility is depicted in Scheme III, part A: hydride transfer from **4** to **8** produces a diphenylmethane, **10**, and the conjugate acid (**14**) of a diaryl ketone (**15**). Diaryl ketones were detected among the products from a number of the reactions. Another possibility is outlined in part B of Scheme III: a triarylmethane may simply react with an acid catalyst to produce a diarylmethane and a triarylmethyl cation, in which case a second molecule of triarylmethane serves as the hydride source. Upon workup with water the triaryl cation would be converted into a triarylmethanol. Triarylmethanols were also often found among reaction products.

As mentioned earlier, Hey[4] and Ungnade[5a] both proposed that the formation of anthracene and its derivatives involved the preliminary cleavage of carbon monoxide from the original aldehyde and the subsequent incorporation of the carbon of the carbon monoxide into the meso (9,10) positions of the anthracenes. Later work by Hey[5b] showed that benzyl alcohol or benzhydrol (diphenylmethanol) could be substituted for benzaldehyde in reaction with diphenyl ether and aluminum chloride to produce compound **16**.



**16**

Still later, Tsuge and Tashiro[10] reported that diphenylmethane reacted with aluminum chloride to give toluene, methyldiphenylmethane, dimethyldiphenylmethane, and anthracene. This work showed that the presence of an aldehyde is not necessary for the formation of anthracene and its derivatives. We suggest that the function of the aldehyde in the reactions of Hey and Ungnade that gave anthracenes is not to provide carbon monoxide by decarbonylation but to produce a diarylmethanol by nucleophilic addition of an arene to the aldehyde, a process compatible with the nucleophilic addition of arenes to reactive aromatic ketones that we reported earlier.[1] The diarylmethanol reacts as suggested in Scheme III to yield a diarylmethane, which leads to anthracenes by the Friedel–Crafts steps of alkylation, cyclialkylation, and dealkylation outlined in Scheme IV. Note that the carbonyl carbon of the aldehyde does end up in the 9- and 10-positions of the anthracene molecule, but not because it was eliminated from the aldehyde and later reacted in some unspecified way with the arenes to produce anthracene. The first step is the alkylation of diphenylmethane by a diphenylmethyl cation to produce the triarylmethyl

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(9) Although the ditolylmethanes and tritolylmethanes produced from benzaldehyde and toluene (entries 2, 4, 5, Table I) can be explained by transmethylations between tolyl and phenyl rings (and it is obvious from the presence of xylenes and trimethylbenzenes in some reaction mixtures (entries 2, 4, Table I, and entry 3, Table II) that these occur), transfer of ethoxy groups would not be expected in the reactions of anisaldehyde and phenetole (entry 4, Table II).

(10) Tsuge, O.; Tashiro, M. *Koru Taru* **1962**, *14*, 513; *Chem. Abstr.* **1964**, *60*, 433e.

**Table III. Reactions of Di- and Triphenylmethanes with Benzene and Acid Catalysts**

| entry | reactants | molar ratio, DPM or TPM[a]/benzene (catalyst) | temp, °C | time, h | observed products (%)[b] |
|---|---|---|---|---|---|
| 1 | DPM,[a] benzene | 1.0/5.0/2.1 ($AlCl_3$) | 60 | 1 | benzene (79)<br>toluene (5)<br>anthracene (12)<br>9-phenylanthracene (1) |
| 2 | TPM[a] | 1.0/0.0/2.1 ($AlCl_3$) | 60 | 2 | diphenylmethane (1)<br>benzophenone (2)<br>anthracene (7)<br>triphenylmethanol (55)<br>9-phenylanthracene (5) |
| 3 | DPM[a] | 1.0/5.0/2.1 ($CF_3SO_3H$) | 60 | 1 | benzophenone (19)<br>triphenylmethane (1)<br>tolyldiphenylmethane[c] (78) |
| 4 | TPM[a] | 1.0/0.0/2.1 ($CF_3SO_3H$) | 25 | 1 | diphenylmethane (10)<br>triphenylmethane (3)<br>triphenylmethanol (60)<br>9-phenylanthracene (4) |

[a] DPM = diphenylmethane, TPM = triphenylmethane. [b] Results from GC/MS analysis. Since unidentified products and identified prducts in amounts of 1% or less are not included, the sum of the percentages is usually less than 100%. [c] Several isomers observed.

compound 17. This intermediate undergoes cyclialkylation to produce 9,9-diphenyl-9,10-dihydroanthracene, 19. The cyclialkylation that converts 17 into 19 requires hydride abstraction of the tertiary hydrogen of 17 to produce the carbocation intermediate 18; the intramolecular cyclialkylation that follows is analogous to some we have observed previously.[11] Fonken[12] has demonstrated that although tetraarylmethanes are difficult to isolate, they do exist in equilibrium with triarylmethanes and arenes in the presence of aluminum chloride. One might expect that the cyclic tetraarylmethane 19 would be formed more readily than an acyclic analogue, but that dealkylation might also take place readily to produce 9,10-dihydro-9-phenylanthracene, 20. The formation of anthracene may be completed by dealkylation from benzene at the 9-position and aromatization of the central ring by loss of a proton.

In support of this proposed mechanism for the formation of anthracenes, we report the results presented in Tables III and IV. The reaction of diphenylmethane and benzene with aluminum chloride (entry 1, Table III) gave anthracene as the major product and a small amount of 9-phenylanthracene (22 in Scheme IV).[13] With triflic acid as catalyst (entry 3, Table III), no anthracene or 9-phenylanthracene was produced, but the major products observed were benzophenone and tolyldiphenylmethane.[14] Triphenylmethane and aluminum chloride (entry 2, Table III) also gave anthracene and 9-phenylanthracene, but the major product was triphenylmethanol, which has been reported before as an oxidation product of triphenylmethane in the presence of aluminum chloride.[8] Reaction of triphenylmethane with triflic acid as catalyst (entry 4, Table III) also gave triphenylmethanol as the major product and almost as much 9-phenylanthracene as when aluminum chloride catalyst was used.

According to Scheme I, a diarylmethanol formed initially by nucleophilic addition of an arene to an aromatic aldehyde is the prime intermediate for the production of both triarylmethanes and diarylmethanes containing aryl groups different from that of the original aldehyde, and for the production of anthracene and its derivatives. From the result of the reaction of diphenylmethanol with toluene and aluminum chloride at 60 °C (entry 1, Table IV), it may be seen that dimethylanthracenes were the major products, as they were in the reactions of benzaldehyde with toluene (entries 1, 2, 4, 5, Table I). At 25 °C, reaction of phenylanisylmethanol with toluene and aluminum chloride gave a complex mixture, with mixed diarylmethanes as the major products (entry 2, Table IV). No anthracene or its derivatives were detected. Reaction of diphenylmethanol with diphenylmethane and aluminum chloride at 60 °C (entry 3, Table IV) gave mainly anthracene and its derivatives, one of which was 9,10-dihydro-9-phenylanthracene, 20. Reaction of the same starting materials in the same proportions, but with triflic acid instead of aluminum chloride (entry 4, Table IV), gave no anthracene, but a high yield of three (diphenylmethyl)diphenylmethane isomers (17 plus the two isomers in which the diphenylmethyl group is meta and para to the benzyl group of the other diphenylmethane moiety).

These results from the reactions outlined in Tables III and IV confirmed our belief that the mechanisms of Schemes I–IV represent a reasonable rationale for the reactions of aromatic aldehydes with arenes in the presence of aluminum chloride. We noted that anthracene and its derivatives were produced in the reactions of aldehydes and arenes and diarylmethanes and/or diarylmethanols in only trace amounts when catalysts other than aluminum chloride were used. It is also significant that anthracene was not produced from the reaction of benzaldehyde or tolualdehyde with anisole or phenetole, even with aluminum chloride at 60 °C. Undoubtedly the alkoxy groups of these aromatic ethers complexed with aluminum chloride in such a way as to deactivate it. In agreement with

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(11) Roberts, R. M.; Anderson, G. P., Jr.; Khalaf, A. A.; Low, C.-E. *J. Org. Chem.* **1971**, *36*, 3342.

(12) Fonken, G. J. *J. Org. Chem.* **1963**, *28*, 1909.

(13) We are indebted to Dr. Ben M. Benjamin, who served as a referee for this paper, for correctly identifying as 9-phenylanthracene a product that we had previously incorrectly identified as its isomer, 9,10-dihydro-9,10-[1′,2′-benzeno]anthracene ("triptycene"). The mass spectra of these isomers are very similar, as might be expected, but comparison of the spectrum of an authentic sample of 9-phenylanthracene with that of the product isolated by GC/MS shows clearly that they are identical.

(14) The production of a significant amount of benzophenone from diphenylmethane was surprising, but may be rationalized as follows: Dealkylation of diphenylmethane yields benzene and benzyl cation, which abstracts hydride from a second molecule of diphenylmethane, producing toluene and diphenylmethyl cation. The latter cation alkylates benzene to give triphenylmethane, which is oxidized to triphenylmethanol. Triphenylmethanol undergoes dearylation to benzene and protonated benzophenone; loss of a proton yields benzophenone. The toluene produced in the second step reacts with triphenylmethane to yield tolyldiphenylmethane, a major observed product.

**Table IV. Reactions of Diarylmethanols with Arenes and Acid Catalysts**

| entry | DAM[a] | arene | molar ratio DAM/arene/catalyst (catalyst) | temp, °C | time, h | observed products (%)[b] |
|---|---|---|---|---|---|---|
| 1 | DPM[c] | toluene | 1.0/3.0/2.1 (AlCl$_3$) | 60 | 6 | benzene (29) |
| | | | | | | toluene (30) |
| | | | | | | xylenes (13) |
| | | | | | | dimethylanthracenes[d] (13) |
| | | | | | | trimethylanthracenes[d] (3) |
| 2 | PAM[e] | toluene | 1.0/3.0/2.1 (AlCl$_3$) | 25 | 1 | benzene (4) |
| | | | | | | anisole (8) |
| | | | | | | diarylmethanes[d,f] (31) |
| | | | | | | diarylketones[d,f] (16) |
| | | | | | | triarylmethanes[d,f] (3) |
| | | | | | | anisylditolylmethanol (2) |
| 3 | DPM[c] | diphenylmethane | 1.0/1.0/2.1 (AlCl$_3$) | 60 | 1 | toluene (6) |
| | | | | | | benzophenone (15) |
| | | | | | | 9,10-dihydroanthracene (2) |
| | | | | | | anthracene (6) |
| | | | | | | methylanthracenes[d] (13) |
| | | | | | | dimethylanthracenes[d] (3) |
| | | | | | | 9-phenylanthracene (2) |
| | | | | | | 9,10-dihydro-9-phenylanthracene (2) |
| 4 | DPM[c] | diphenylmethane | 1.0/1.0/2.1 (CF$_3$SO$_3$H) | 60 | 1 | benzaldehyde (3) |
| | | | | | | (diphenylmethyl)diphenylmethane[g] (97) |

[a] DAM = diarylmethanol. [b] Results from GC/MS analysis. Since unidentified products and identified products in amounts of 1% or less are not included, the sum of the percentages is usually less than 100%. [c] DPM = diphenylmethanol. [d] Several isomers observed. [e] PAM = phenylanisylmethanol. [f] Aryl groups included phenyl, tolyl, and anisyl. [g] Three isomers observed.

this conclusion, it is interesting to note that some dimethylanthracene was produced in the reaction of anisaldehyde with toluene (entry 3, Table II), but in this experiment there was a molar excess of aluminum chloride over the amount of the anisaldehyde, which contained the methoxy group. We believe that the greater catalytic effect of aluminum chloride with respect to the formation of anthracene, in comparison with triflic acid, zinc chloride, and stannic chloride, is due to the greater hydride-abstracting capability of aluminum chloride.[11,15,16] This is required for the steps of which **18** is produced from **17** and **21** is produced from **20** (Scheme IV). Triflic acid and the other catalysts are able to induce (by proton donations) the dealkylations and realkylations leading to mixed diarylmethanes and triarylmethanes, but they are less effective in the hydride abstractions necessary for the formation of anthracene and its derivatives.

## Experimental Section

**Method of Analysis.** All qualitative and quantitative GC/MS analyses were performed on a Finnigan 4023 quadrupole system equipped with a Model 4500 source upgrade. Chromatographic separations were performed on a 50-m DB-1 fused silica WCOT capillary column with a film thickness of 0.25 μm. Quantitative analyses were performed on the product mixtures from several representative reactions using standard curves and on-column injection techniques as described previously;[1] the other analyses were carried out under similar conditions on the same instrument. The percentages reported are those computed by the instrument by integration of the ion currents within the peak areas that were selected manually.

**Reaction of Benzaldehyde with Toluene and AlCl$_3$.** The general procedure for this reaction was that described by Hey.[4a] Benzaldehyde (53 g, 0.50 mol) was added slowly to a mixture of toluene (160 g, 1.74 mol) and AlCl$_3$ (150 g, 1.13 mol). The mixture was allowed to react at 60 °C for 6 h and then quenched by pouring over ice. The mixture was extracted with ethyl ether and the ether extract was washed sequentially with water, 10% NaHCO$_3$, and water, and then dried over CaCl$_2$. GC/MS analysis of the reaction mixture showed the products listed in Table I, entry 1. Experiments in which different proportions of reactants, different reaction temperatures, and different reactions times were used are described in Table I, entries 2–5.

**Reactions of Benzaldehyde with Various Arenes and Catalysts.** These reactions were conducted in an appropriately sized round-bottomed flask fitted with a magnetic stirrer and a reflux condenser protected with a drying tube. The benzaldehyde, arene, and catalyst were allowed to react and then the reaction mixtures were quenched by pouring over ice. The ratios of benzaldehyde to arene used were 1:3 and 1:1. The arenes tested were toluene, anisole, mesitylene, and diphenylmethane. The catalysts used were AlCl$_3$, ZnCl$_2$, SnCl$_4$, and triflic acid. Temperatures ranged from 0 °C to 100 °C, times from 5 min to 6 h. The quenched reaction mixtures were then extracted with either chloroform or ethyl ether. The organic extracts were washed sequentially with water, saturated NaHCO$_3$, and water and then dried over CaCl$_2$. The extracts were subjected to qualitative or quantitative GC/MS analysis. The results are presented in Table I, entries 6–16.

**Reactions of Various Aldehydes with Various Arenes and AlCl$_3$.** In the previously described apparatus were mixed the aldehyde, arene, and catalyst. The aldehydes tested were *p*-tolualdehyde, anisaldehyde, and 3,4-dimethoxybenzaldehyde. The arenes were toluene, anisole, and phenetole. The catalyst used was AlCl$_3$. The reactions were allowed to proceed for 1 to 6 h at temperatures of 25 °C and 60 °C and then quenched by ice–water. The reaction workup was as described previously. Both qualitative and quantitative GC/MS analyses of these reaction mixtures were performed with the results depicted in Table II.

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(15) Khalaf, A. A.; Roberts, R. M. *J. Org. Chem.* **1970**, *35*, 3717.

(16) Olah, G. A. In *Friedel–Crafts and Related Reactions*; Olah, G. A., Ed.; Interscience: New York, 1963; Vol. 1, pp 214, 215. Nenitzescu has ascribed the hydride-abstracting capability of aluminum chloride to its ability to form a conjugate acid with water, H$^+$ (AlCl$_3$OH)$^-$, the initial step of a chain hydride abstraction process being effected by the proton of this powerful Bronsted acid (Nenitzescu, C. D.; Avram, M.; Sliam, E., *Bull. Soc. Chim. Fr.* **1955**, 1266).

**Reactions of Di- and Triphenylmethanes with Benzene and Acid Catalysts.** Diphenylmethane and triphenylmethane were allowed to react with $AlCl_3$ or triflic acid for 1 or 2 h at temperatures of 25 °C or 60 °C in the presence or absence of benzene. The reaction workup and analysis were as described previously; the results are depicted in Table III.

**Reactions of Diarylmethanols with Arenes and Acid Catalysts.** Diphenylmethanol and *p*-anisylphenylmethanol were allowed to react for 1 or 6 h with $AlCl_3$ at temperatures of 25 °C or 60 °C with or without toluene as solvent. The reaction workup and analysis were as described previously. The results are depicted in Table IV.

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# *Notes*

## New 2-Pyridone Derivatives via 1,3-Dipolar Cycloadditions of Novel Mesoionic Compounds

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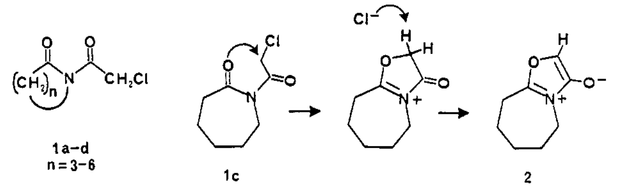
Mesoionic compounds were first reported in 1935[1] and were recently reviewed.[2] Isolable munchnones and isomunchnones were first described in 1964[3] and 1974,[4] respectively. Our interest in the chemistry of mesoionic compounds stems from the discovery of the polymerization of a new family of isomunchnones.[5] *N*-chloroacetyl lactams **1b–d** (but not **1a**) were found to spontaneously form low molecular weight polymers through the intermediacy of isomunchnone **2**.[6]



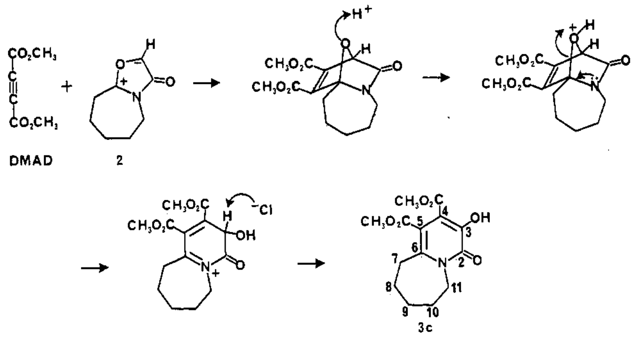
1a–d
n = 3–6

1c

2

During our attempts to observe and trap this intermediate, we became intrigued by several aspects of the chemistry of this family of mesoionic heterocycles. They represent the first bicyclic isomunchnones as well as the first possessing only alkyl substituents; aryl substituents have been used routinely to stablize charge in isomunchnones as well as munchnones. The synthesis of **2** involved the readily available and inexpensive starting materials caprolactam and chloroacetyl chloride. Previous syntheses of isomunchnones involved carbene intermediates to effect the ring closure[4] or ring closure of *N*-benzoylphenylglyoxanilide using triphenyl phosphite.[7] Conventional ring-closure approaches to isomunchnones have proven unsuccessful due to various rearrangements,[8] and it was of interest to examine the synthetic utility of $\alpha$-chloroacetimides as precusors to isomunchnones and their cycloadducts.

Scheme I



### Results and Discussion

*N*-chloroacetyl lactams **1a–d** were examined for reaction with several dienophiles known to undergo 1,3-dipolar cycloadditions.[1] The pyrrolidone derivative **1a** was unexpectedly stable and failed to react even with prolonged heating at 150 °C. Compounds **1b** and **1c** reacted readily with both dimethyl acetylenedicarboxylate (DMAD) and *N*-phenylmaleimide (NPM), two of the more reactive dienophiles.[1] The products obtained resulted from rearrangement of the initially formed adduct by two distinct mechanisms, both of which are apparently catalyzed by the HCl liberated during formation of the isomunchnone; e.g., in the formation of **2** from **1c**. The proposed general mechanism for DMAD addition and rearrangement is given in Scheme I, while the overall process for reaction with NPM is outlined in Scheme II.

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[2] Potts, K. T. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Chapter 8.

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