# σ Amination of Biphenyl and Naphthalene with Trichloramine–Metal Halide. Products and Relative Rates[1a]

PETER KOVACIC AND A. K. HARRISON[1b]

*Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106*

*Received February 7, 1966*

Direct amination of biphenyl in *o*-dichlorobenzene or 1,2-dichloroethane with trichloramine in the presence of aluminum chloride or aluminum bromide gave 3-aminobiphenyl. With naphthalene in *o*-dichlorobenzene, a mixture of 40% α- and 60% β-amino derivatives was obtained from the reaction catalyzed by aluminum chloride or titanium tetrachloride. In 1,2-dichloroethane the isomeric composition was 66% α- and 33% β-naphthylamines. High concentrations of reactants in this solvent favored β substitution. Relative rate studies revealed the order: biphenyl/toluene (0.75–0.84), *p*-xylene/biphenyl (7.5), naphthalene/toluene (42–46), and naphthalene/biphenyl (54). Fluorene provided extremely low yields of basic product.

Earlier reports from this laboratory[2-5] on the direct amination of aromatic compounds with trichloramine–aluminum chloride have been concerned with benzene and its alkyl derivatives. For example, toluene yielded *m*-toluidine as the predominant basic product. Evidence has been presented which supports a σ-substitution mechanism.[2-5] In the present communication this reaction has been extended to include biphenyl and naphthalene. The nature of the products, the effect of changes in concentration, solvent, and catalyst, and relative rate data are discussed. A brief investigation of fluorene was also carried out.

## Results and Discussion

**Biphenyl.**—When biphenyl was caused to react with trichloramine in *o*-dichlorobenzene in the presence of aluminum chloride at 5–10°, 3-aminobiphenyl was obtained in 27% yield (Table I). No change in organic product composition occurred when water was added to the reaction mixture or from the introduction of dry hydrogen chloride. It is not surprising that the quantity of isolated amine was decreased by these additives since hydrogen chloride destroys trichloramine,[6] and water hydrolyzes aluminum chloride which is required in substantial amounts.[2] No organic base was formed with titanium tetrachloride as the catalyst. A reduced yield (12%) was recorded when 1,2-dichloroethane served as the solvent. In all cases the only aromatic amine found to be present was 3-aminobiphenyl.

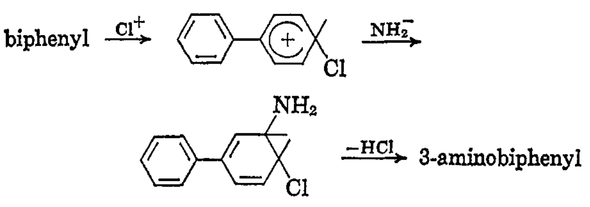
TABLE I

AMINATION OF BIPHENYL[a]

| $o$-$C_6H_4Cl_2$, moles | Additive | Temp, °C | 3-Aminobiphenyl yield, % |
|---|---|---|---|
| 1.24 | ... | 5–10 | 27 |
| 1.24 | ... | 50 | 13 |
| 1.24 | ... | −25 | 23 |
| 1.24 | HCl[b] | 5–10 | 20 |
| 1.24 | $H_2O$[c] | 5–10 | 15 |
| 3.3 | ... | 5–10 | 0[d] |
| ...[e] | ... | 5–10 | 12 |

[a] 0.75 mole. [b] Hydrogen chloride gas was passed into the reaction mixture. [c] 1 g. [d] Titanium tetrachloride (0.1 mole) was used in place of aluminum chloride. [e] A solution of trichloramine (0.05 mole) in 1,2-dichloroethane (100 ml) was used, with additional 1,2-dichloroethane (3.65 moles) as solvent.

The formation of this isomer fits well into the addition–elimination mechanism (σ substitution) postulated for the amination reaction.[4,5] Since the actual nucleophile is not known, amide ion is used for the sake of simplicity. Although both rings of the σ complex



(1)

should theoretically be susceptible to nucleophilic attack, specificity is indicated by the absence of the 2- and 4-amino isomers.

With the knowledge that exclusive *meta* orientation is novel with biphenyl, we anticipate that σ amination will prove synthetically useful in this series.

**Naphthalene.**—When naphthalene reacted with trichloramine in *o*-dichlorobenzene in the presence of aluminum chloride, a 30% yield of isomeric naphthylamines was obtained (Table II). This mixture was shown to be 40% α- and 60% β-naphthylamine by infrared spectroscopy. With 1,2-dichloroethane as the solvent the same yield of basic product resulted, but the isomer distribution was now 66% α and 33% β. With naphthalene, electrophilic attack occurs preferentially at the α position. In connection with the present work, there are several pertinent, prior studies in-

TABLE II

AMINATION OF NAPHTHALENE

| Naphthalene, mole | Solvent | Moles | Naphthylamine, % Yield | α | β |
|---|---|---|---|---|---|
| 0.75 | $o$-$C_6H_4Cl_2$ | 1.42 | 30 | 40 | 60 |
| 0.75[a] | $o$-$C_6H_4Cl_2$ | 2.64 | 32 | 40 | 60 |
| 0.75[b] | $o$-$C_6H_4Cl_2$ | 2.3 | 29 | 40 | 60 |
| 0.75 | $ClCH_2CH_2Cl$ | 3.05 | 30 | 66 | 33 |
| 0.375 | $ClCH_2CH_2Cl$ | 1.22[c,d] | 15 | 70 | 30 |
| 0.375 | $ClCH_2CH_2Cl$ | 3.05[d,e] | 14 | 50 | 50 |

[a] α-Chloronaphthalene was the sole chlorinated product. [b] Titanium tetrachloride (0.15 mole) as catalyst. [c] Sufficient to maintain homogeneity; trichloramine (0.025 mole) in additional 1,2-dichloroethane (50 ml). [d] $AlCl_3$, 0.1 mole. [e] Trichloramine (0.025 mole) in additional 1,2-dichloroethane (100 ml).

---

[1] (a) Paper IV: Chemistry of N-Halamines. (b) Postdoctoral Research Associate, 1964–1965.

[2] P. Kovacic, C. T. Goralski, J. J. Hiller, Jr., J. A. Levisky, and R. M. Lange, *J. Am. Chem. Soc.*, **87**, 1262 (1965).

[3] P. Kovacic, R. M. Lange, J. L. Foote, C. T. Goralski, J. J. Hiller, Jr., and J. A. Levisky, *ibid.*, **86**, 1650 (1964).

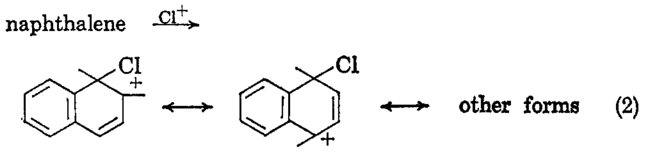
[4] P. Kovacic, J. A. Levisky, and C. T. Goralski, *ibid.*, **88**, 100 (1966).

[5] P. Kovacic and J. A. Levisky, *ibid.*, **88**, 1000 (1966).

[6] W. A. Noyes, *ibid.*, **42**, 2173 (1920).

volving halogenation,[7] hydrogen exchange,[8] and nuclear coupling.[9,10]

Stabilization of the intermediate σ complex by delocalization is again possible in the amination scheme.



(2)

As discussed previously, the subsequent steps would be (a) attack by the nucleophile at either the α or β position and (b) elimination of hydrogen chloride. From this it is seen that the formation of both α- and β-naphthylamines can be explained by fixation of the electrophile at the α position. Some support for this suggestion was found by analysis of the neutral products. Only α-chloronaphthalene was found, with no evidence for presence of the β isomer. A similar general argument has been advanced recently to interpret the results of nuclear coupling of naphthalene[9] by metal halides, and formation of 2,2′-binaphthyl and polymer from decarbonylation of 1,4-dihydro-1-naphthoyl chloride in the presence of aluminum chloride.[10]

**Solvent Effect.**—The isomer distribution in naphthalene amination was influenced by the nature of the medium. Thus, the α/β ratio was 66:33 in 1,2-dichloroethane, and 40:60 in *o*-dichlorobenzene (Table II). This finding is reminiscent of the situation in naphthalene acylation.[11,12] Bassilios and co-workers observed that the proportion of α isomer from acetylation varied with solvent as indicated, 1,2-dichloroethane (91%), *o*-dichlorobenzene (65%), and nitrobenzene (25%).[13] The change in orientation with solvent has been ascribed to differences in the kinetic order,[11] reaction reversibility,[12] solubility phenomena,[12] and dipole moment of the diluent.[13]

**Concentration Effect.**—Further similarities to prior investigations are apparent from a scrutiny of the results from variation in concentration. It was found that high concentrations of reactants in 1,2-dichloroethane (the aromatic/$AlCl_3$/$NCl_3$ ratio was kept constant) favored the formation of α-naphthylamine (Table II). A similar observation has been reported in acylation studies of naphthalene in this same solvent.[14] Substitution at the α position is the preferred route at high concentrations (which introduces a third-order term) of the acyl halide–catalyst complex, whereas lower concentrations (second-order expression) increased the amount of β substitution.

**Catalyst Effect.**—When naphthalene was treated with trichloramine in *o*-dichlorobenzene in the presence of titanium tetrachloride a 29% yield of the isomeric naphthylamines was realized, consisting of 40% α and 60% β (Table II). In contrast, biphenyl did not give a basic product under these conditions. There is ample evidence that titanium tetrachloride is generally a weaker catalyst than aluminum chloride.[15] Presumably, in the biphenyl–titanium tetrachloride system, the weaker electrophile yields a σ complex of insufficient carbonium ion character to undergo nucleophilic attack. In relation to the role of catalyst, evidence has been presented for σ-complex formation by direct interaction of naphthalene and the metal halide.[16]

**Relative Rate Studies.**—Competitive aminations were carried out in an attempt to gain further insight into this unusual reaction. The problems associated with determination of relative rates in aromatic amination have been discussed in detail elsewhere.[5] Similar control of reaction conditions was exercised in the present study to provide the necessary basis for gathering meaningful results.

At a 1:1 molar ratio of biphenyl/toluene in *o*-dichlorobenzene with aluminum chloride catalyst, $k_{\text{biphenyl}}/k_{\text{toluene}}$ was found to be 0.75–0.84 (Table III). The same result was observed with aluminum bromide as promoter. With a biphenyl/toluene ratio of 1:2 a relative rate value of 0.76 was obtained. This result indicates that the reaction is first order in aromatic reactant.[6] A further check on the validity of this method was obtained by determination of the relative rate of amination of *p*-xylene *vs.* biphenyl. The ratio found was 7.5 which is good agreement with that calculated (7.4) by use of previously determined rate data: $k_{p\text{-xylene}}/k_{\text{toluene}} = 5.8^5$ and $k_{\text{biphenyl}}/k_{\text{toluene}} = 0.78$.

TABLE III

COMPETITIVE AMINATIONS, $k_{\text{biphenyl}}/k_{\text{ArH}}$

| Biphenyl, mole | ArH | Mole | *o*-$C_6H_4Cl_2$, moles | $k_{\text{biphenyl}}/k_{\text{ArH}}$ Obsd | Calcd |
|---|---|---|---|---|---|
| 0.5 | Toluene | 0.5 | 1.5[a] | 0.84 | 0.84 |
| 0.75[b] | Toluene | 0.75 | 2.56 | 0.75 | 0.75 |
| 0.5[c] | Toluene | 0.5 | 1.5 | 0.78 | 0.78 |
| 0.5 | Toluene | 1.0 | 1.5 | 0.38 | 0.76 |
| 0.5[d] | *p*-Xylene | 0.5 | 2.12 | 0.13 | 0.13 |

[a] A small residue (1–2 g) was noted. [b] $AlCl_3$ (0.15 mole) and $NCl_3$ (0.05 mole) in *o*-$C_6H_4Cl_2$ (100 ml). The relative rate of chlorimation (Table V) was determined in this run. [c] $AlBr_3$ (0.1 mole) as catalyst. [d] $NCl_3$ (0.05 mole) in *o*-$C_6H_4Cl_2$ (100 ml).

In an extension of the kinetic aspects the $k_{\text{rel}}$ for naphthalene/toluene was ascertained. This resulted in the ratio, 42–43, with an isomer distribution for naphthylamine of 40% α and 60% β (Table IV). A

TABLE IV

COMPETITIVE AMINATIONS, $k_{\text{naphthalene}}/k_{\text{ArH}}$

| Naphthalene, mole | ArH | Mole | $k_{C_{10}H_8}/k_{\text{ArH}}$ Obsd | Calcd |
|---|---|---|---|---|
| 0.5[a] | Toluene | 0.5 | 42 | 42 |
| 0.5[b] | Toluene | 0.5 | 43 | 43 |
| 0.5 | Toluene | 1.0 | 23 | 46 |
| 0.5 | Biphenyl | 0.5 | 54 | 54 |

[a] The relative rate of chlorination (Table V) was determined in this run. [b] A small deposit (1–2 g) was present both before and after reaction.

---

(7) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution. Nitration and Halogenation," Academic Press Inc., New York, N. Y., 1959, p 173.

(8) C. Eaborn and R. Taylor, *J. Chem. Soc.*, 1012 (1961).

(9) P. Kovacic and F. W. Koch, *J. Org. Chem.*, **30**, 3176 (1965).

(10) A. T. Balaban and C. D. Nenitzescu, "Friedel-Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 989.

(11) F. R. Jensen and G. Goldman, "Friedel-Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 36.

(12) P. H. Gore, ref 11, Chapter 31.

(13) H. F. Bassilios, S. M. Makar, and A. Y. Salem, *Bull. Soc. Chim. France*, **21**, 72 (1954).

(14) Reference 11, p 1027.

(15) G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 11.

(16) H. H. Perkampus and T. Kranz, *Z. Physik. Chem.*, **34**, 213 (1962).

similar determination of the relative rate for naphthalene *vs.* biphenyl gave the value (54) in close agreement with that (55) calculated.

Comparison of the relative rates of amination and chlorination in these systems proves highly illuminating. Thus, in a competitive reaction in which $k_{rel} = 0.75$ (amination) for biphenyl *vs.* toluene, a value of 1.06 was obtained for chlorination (Table V). A very similar ratio for halogenation was observed with chlorine in acetic acid.[17] In contrast, for naphthalene *vs.* toluene, the value of 42 pertained to amination, and 8 to chlorination.

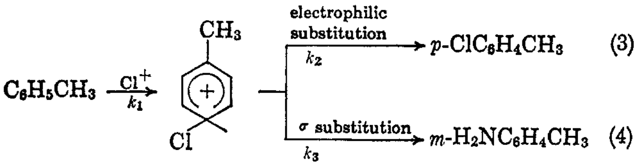
TABLE V

COMPETITIVE CHLORINATIONS

| ArH | Mole | ArH′ | Mole | $k_{ArH}/k_{ArH'}$ Obsd | $k_{ArH}/k_{ArH'}$ Calcd |
|---|---|---|---|---|---|
| Biphenyl | 0.75 | Toluene | 0.75 | 1.06[a] | 1.06 |
| Naphthalene | 0.5 | Toluene | 0.5 | 8.0 | 8.0 |

[a] The $^1/_2$ *ortho/para* ratio for the chlorobiphenyls was 0.32; *cf.* the value of 0.3 resulting from use of chlorine in acetic acid: G. H. Beaven, P. B. D. de la Mare, M. Hassan, E. A. Johnson, and N. V. Klassen, *J. Chem. Soc.*, 2749 (1961).

There are two pathways available for further transformation of the intermediate σ complex (illustrated with toluene). Although $k_1$ appears to be rate determining,[5] the $k_2/k_3$ ratio would control the amount of aminated product formed. Furthermore, it is reasonable to expect variation in $k_2/k_3$ with the nature of the aromatic substrate.



**Fluorene.**—σ amination of fluorene gave surprisingly poor results. Crude basic product, which was not further characterized, was isolated in less that 5% yield. In contrast, electrophilic substitution with this hydrocarbon is known to proceed in good yield.[18] The neutral portion of the reaction mixture was found to contain 2-chlorofluorene. It may be that the nucleophile perferentially attacks the 9 position of fluorene,[19] or else that proton loss is favored from the unusually stable[20] σ complex.

## Experimental Section[21]

**Warning.**—Exercise the necessary precautions in working with N-halamines.

**Materials.**—*o*-Dichlorobenzene and 1,2-dichloroethane were fractionally distilled from phosphorus pentoxide. The other reagents were high purity commercial materials which were used as obtained.

**Preparation of Trichloramine.**—The previous procedure[2] was followed with *o*-dichlorobenzene or 1,2-dichloroethane solvent. The trichloramine concentration was determined iodometrically.[2]

**General Procedure for Amination.**—The apparatus consisted of a 1-l., three-neck flask fitted with a stirrer, condenser, thermometer, and dropping funnel. The cold solution of trichloramine (0.05 mole) in solvent (100 ml) was added during 15 min to a mixture of the aromatic compound, solvent, and aluminum chloride (0.1 mole) at 5–10°. After an additional 0.5 hr the homogeneous reaction mixture was stirred with ice-dilute hydrochloric acid. After standing (usually overnight), the neutral organic phase was separated from the acidic, aqueous layer and washed with dilute hydrochloric acid, and the combined aqueous portions were extracted with ether. Treatment of the acidic, aqueous phase with just sufficient sodium hydroxide to ensure complete solution of the aluminum hydroxide precipitate liberated the basic product. After extraction of the amine with ether, the extract was washed with water, dried, and then freed of solvent by evaporation. Yields are based on an equimolar relationship between trichloramine and the basic product.

The products were identified by comparison with authentic samples by means of infrared spectroscopy and gas chromatography. In the biphenyl studies[22] (Table I), the crude basic product contained 90–95% 3-aminobiphenyl (glpc column 2, 180°, 60 ml of He/min). In the case of naphthalene[22,23] (Table II), the crude basic product consisted of 90–95% naphthylamines (glpc column 2, 200°, 60 ml of He/min). The isomer distributions were determined on samples isolated by glpc.

**Amination of Fluorene.**—The general procedure was followed with fluorene (0.057 mole), trichloramine (0.0375 mole), aluminum chloride (0.075 mole), and *o*-dichlorobenzene (1.75 moles). After work-up the crude base was obtained in 4% yield. The product, which was not characterized, appeared to be a mixture of amines.

A similar result[24] was noted in methylene chloride solvent. Work-up of the neutral portion by distillation yielded a fraction of 2-chlorofluorene contaminated with fluorene. The 2-chlorofluorene was collected by glpc and characterized by comparison (infrared spectrum and glpc retention time) with an authentic sample.[25]

**Competitive Aminations.**—Essentially the same procedure was used in the competitive runs as described in the preceding section. However, prior to addition of the trichloramine solution, the solvent–catalyst–aromatic mixture was filtered to remove traces of insoluble material, thus ensuring homogeneity. In some cases the product mixture was filtered to determine whether any precipitate had formed. In most cases, however, visual observation of the crude product mixture was sufficient. Reaction mixtures were homogeneous unless otherwise stated. The general procedure was used for work-up. The crude reaction products were identified by glpc and infrared spectroscopy. Duplicate runs were made which were in satisfactory agreement.

Competitive aminations involving biphenyl were carried out at 5° with a solution of trichloramine (0.0375 mole) in *o*-dichlorobenzene (75 ml) and aluminum chloride catalyst (0.1 mole; Table III). The products were analyzed by glpc (column 2, 190°, 60 ml of He/min).

In similar studies with naphthalene at 5°, a solution of trichloramine (0.05 mole) in *o*-dichlorobenzene (100 ml) was used. The aromatic reactants were diluted with 250 ml of *o*-dichlorobenzene, and aluminum chloride (0.1 mole) was added (Table IV). Product analysis was accomplished by glpc (column 2, 180°, 60 ml of He/min).

**Competitive Chlorinations.**—The organic phase remaining after extraction of the crude reaction mixture with aqueous hydrocloric acid was washed neutal with water and dried over sodium sulfate. The chlorinated products were identified by glpc in comparison with authentic materials. Satisfactory checks were realized from duplicate determinations.

**Analytical Procedures.**—Analysis by glpc was made on the undistilled crude products. The indicated columns were (1) 12 ft × 0.25 in., Apiezon L (14%) on Chromosorb P (5% NaOH wash); (2) 1-ft column as in (1); (3) 15-ft column as in (1). Use was made of calibration curves obtained with authentic materials. Estimated precision of the data is ±3%.

---

[17] Reference 7, p 159.

[18] W. E. Kuhn, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p 447.

[19] We are grateful to one of the referees for this suggestion.

[20] P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, *J. Chem. Soc.*, 5317 (1964); H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **84**, 1238 (1962).

[21] Aminations of biphenyl and fluorene have recently been effected by use of N-chlorodimethylamine–ferrous sulfate: F. Minisci, V. Trabucchi, and R. Galli. We wish to thank Professor Minisci for making available these unpublished results.

[22] The assistance of Dr. John J. Hiller in the scouting work is acknowledged.

[23] We wish to thank Dr. Roger Hopper for contributing to the preliminary studies.

[24] We are grateful to Dr. Sohan S. Chaudhary for this experimental contribution.

[25] J. Buffle, *Helv. Chim. Acta*, **15**, 1483 (1932).

The infrared spectra were recorded on Beckman IR-5A or IR-8 spectrophotometers either neat or, where necessary, as a solution in carbon disulfide. Analysis of the naphthylamine products was made by reference to a graph constructed from known mixtures of the isomeric naphthylamines in carbon disulfide.

**Isomerization Studies.**—A mixture of 4-aminobiphenyl (1 g) in *o*-dichlorobenzene (20 ml) containing aluminum chloride (0.6 g) was treated with hydrogen chloride gas and 1 drop of water. The reaction mixture was stirred at 10° for 2 hr, and then worked up by the standard procedure. The starting material was recovered unchanged in quantitative yield. A similar study of the isomeric naphthylamines was carried out. In both cases the isomers were recovered unchanged in essentially quantitative yield.

**Acknowledgment.**—We gratefully acknowledge support for this work by the National Institutes of Health, U. S. Public Health Service.

---

# Chemistry of Dimethylketene Dimer. VI. Reactions of the β-Lactone Dimer of Dimethylketene with Enamines[1]

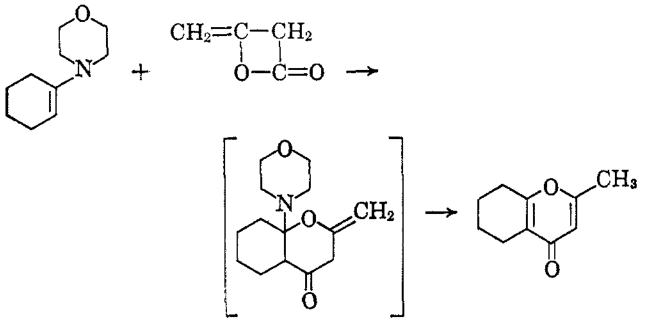
JAMES C. MARTIN, ROBERT D. BURPITT, AND HANS U. HOSTETTLER

*Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee*

*Received August 2, 1966*

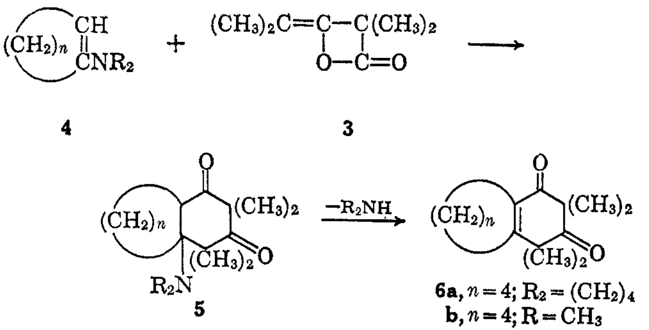
Enamines containing one β-hydrogen atom react with the lactone dimer of dimethylketene to form aminocyclohexanediones. These adducts lose amine to give cyclohexenediones. An enamine, a ketene O,N-acetal, and a ketene aminal, each containing two β-hydrogen atoms, were all acylated at the β carbon by the dimethylketene dimer. Enamines with no β hydrogen did not react.

Hünig, *et al.*, reported that 4-(1-cyclohexen-1-yl)-morpholine reacts with diketene to give 5,6,7,8-tetrahydro-2-methylchromone (**1**)[2]. They suggested a reaction mechanism involving acylation of the enamine and ring closure to an intermediate **2**, which stabilized itself by loss of amine and isomerization of the exocyclic double bond.



**2** **1**

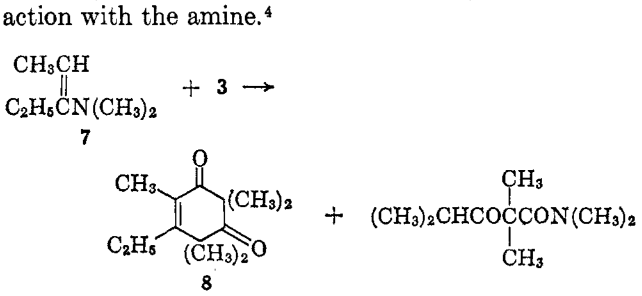
We found that the reaction of cyclohexenylamines with the lactone dimer of dimethylketene (**3**) differs from the behavior with diketene in that an alternate closure occurs to form a carbocyclic ring, and the intermediate adduct with the amine moiety is isolable. 1-(1-Cyclohexen-1-yl)pyrrolidine (**4a**) and **3**, heated on a steam bath for several hours, gave hexahydro-2,2,4,4-tetramethyl-4a-(1-pyrrolidinyl)-1,3(2H,4H)-naphthalenedione (**5a**) in 80% yield, and similar treatment of N,N-dimethyl-1-cyclohexen-1-ylamine (**4b**) with **3** gave the dimethylamino analog **5b**. The adduct **5a** showed variable stability;[3] one sample, stored at room temperature, changed slowly to a mixture of 5,6,7,8-tetrahydro-2,2,4,4-tetramethyl-1,3(2H,4H)-naphthalenedione (**6c**) and pyrrolidine. Distillation afforded pure **6c** in 88% yield. This elimination of amine was catalyzed by strong bases; **5a**, as well as the more stable **5b**, was converted rapidly into **6c** when refluxed



**6a**, $n = 4$; $R_2 = (CH_2)_4$
**b**, $n = 4$; $R = CH_3$
**c**, $n = 4$
**d**, $n = 3$

in benzene containing a small amount of sodium methoxide.

Further work demonstrated that stability of the adduct **5** depends not only on the nature of the amine, but even more on the structure of the enamine involved. Treatment of enamines **4d** derived from cyclopentanone with the dimethylketene dimer **3** did not give the intermediate adducts **5**, but only the unsaturated diketone **6d**. Reaction of **3** with the acyclic enamine **7** likewise produced the cyclohexenedione **8** without detection of an intermediate. In these cases in which the amine was evolved during the addition reaction, some ketene dimer **3** was expended by reaction with the amine.[4]



The cyclic diketone structures of **5**, **6**, and **8**, rather than 4-pyranone derivatives **9** and **10** corresponding to the Hünig products, were indicated by nmr spectra.

---

[1] Paper V in this series: R. H. Hasek, R. D. Clark, E. U. Elam, and R. G. Nations, *J. Org. Chem.*, **27**, 3106 (1962).

[2] S. Hünig, E. Benzing, and K. Hübner, *Chem. Ber.*, **94**, 486 (1961).

[3] Stability is associated with purity, in that more carefully purified samples were unchanged during prolonged storage.

[4] R. H. Hasek, R. D. Clark, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **27**, 60 (1962).