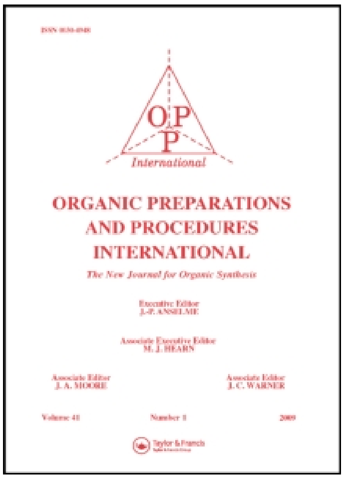

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# CARBON-CARBON COUPLING ON ATTEMPTED HYDROLYSIS OF BROMOMALEIMIDES

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# CARBON-CARBON COUPLING ON ATTEMPTED HYDROLYSIS OF BROMOMALEIMIDES[†]

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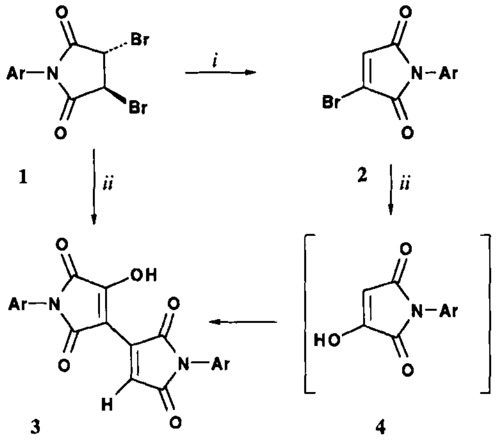
Carbon-carbon bond formation is a fundamental step for the assembly of complex organic compounds.[1] We herein report a novel aldol condensation of bromomaleimides to create a functionally rich matrix.



a) Ar = $C_6H_5$
b) Ar = $3\text{-}NO_2C_6H_4$
c) Ar = $4\text{-}MeC_6H_4$

*i*) aq. $NaHCO_3$, RT, 0.5 h
*ii*) $H_2O$, Δ, 2 hrs

In our efforts to synthesize mitosane congeners,[2] we obtained trans-dibromosuccinimides (**1a-c**) from the corresponding maleimides. These dibromides underwent dehydrobromination on treatment with aqueous sodium bicarbonate at room temperature to the corresponding bromomaleimides (**2a-c**) in quantitative yield. Earlier reports[3,4] concerning nucleophilic displacements of vinylic halogens in electrophilic olefins prompted us to examine the potential for a similar reaction in **2** to design a new approach to penicillic acid[5] using **4**. Attempts at hydrolytic displacement of the bromine in **2a-c** in boiling water to obtain **4** led instead to hydroxymaleimidoylmaleimides **3a-c**. Further attempts revealed that a one-pot conversion of **1**→**3** also occurs under the same conditions. The instability and the synthetic utility of free hydroxymaleic anhydrides[5-7] and hydroxymaleimides[8] have been reported.

## EXPERIMENTAL SECTION

Melting points are uncorrected. IR spectra were recorded in nujol on a Perkin-Elmer R-37 spectrometer ($cm^{-1}$), PMR spectra were determined in $CDCl_3$ or DMSO-$d_6$ on WH-90FT spectrometer using TMS as an internal standard (chemical shifts in δ).

*trans*-N-Aryl-3,4-dibromosuccinimides (**1**).

i) N-Bromosuccinimide Method.- A mixture of N-arylmaleimide (0.01 mole) and N-bromosuccinimide (0.02 mole) with catalytic amount of dibenzoyl peroxide in carbon tetrachloride (30 ml) was refluxed for 3 hrs. The reaction mixture was cooled to room temperature and allowed to stand for 2 hrs. The product separated as colorless crystals in quantitative yield.

ii) Bromine Method.- N-Arylmaleimide (0.01 mole) in carbon tetrachloride (30 ml) was refluxed with bromine (0.01 mole) in carbon tetrachloride (20 ml) for 45 minutes. The reaction was cooled to room temperature and allowed to stand for 2 hrs. The product separated as colorless crystals which were collected, washed with carbon tetrachloride and recrystallized from carbon tetrachloride (85-90%).

**1a**, mp. 174°. IR: 1810, 1740, 630 $cm^{-1}$. $^1$H NMR: $\delta$ 5.15 (s, 2H), 7.00-7.80 (5H).
Anal. Calcd. for $C_{10}H_7Br_2NO_2$: C, 36.03; H, 2.10. Found: C, 35.87; H, 2.19

**1b**, mp. 193°, $^1$H NMR: $\delta$ 5.30 (s, 2H), 7.30-8.40 (4H).
Anal. Calcd. for $C_{10}H_{6}Br_2N_2O_4$: C, 31.74; H, 1.58. Found: C, 31.61; H, 1.88

**1c**, mp. 171°. IR: 1820, 1740, 635 $cm^{-1}$.
Anal. Calcd. for $C_{11}H_9Br_2NO_2$: C, 38.04; H, 2.59. Found: C, 38.18; H, 2.77

N-Aryl-3-bromaleimides (**2**).- A slurry of the dibromosuccinimide (**1**, 1.0 g) and saturated solution of sodium bicarbonate (15 ml) was stirred at room temperature. The progress of the reaction was monitored by TLC. At the completion of the reaction (30 minutes), the precipitated product was collected, washed with water and recrystallized from ethanol (85-90%).

**2a**, mp. 155°. $^1$H NMR: $\delta$ 6.87 (s, 1H), 7.00-7.50 (5H).
Anal. Calcd. for $C_{10}H_6BrNO_2$: C, 47.61; H, 2.38. Found: C, 47.43; H, 2.19

**2b**, mp. 140°. IR: 1810, 1730, 1580 $cm^{-1}$. $^1$H NMR: $\delta$ 6.95 (s, 1H), 7.10-8.70 (4H).
Anal. Calcd. for $C_{10}H_5BrN_2O_4$: C, 40.40; H, 1.68. Found: C, 40.19; H, 1.82

**2c**, mp. 145°. $^1$H NMR: $\delta$ 2.37 (s, 3H), 7.00 (s, 1H),7.10-7.40 (4H).
Anal. Calcd. for $C_{11}H_8BrNO_2$: C, 49.62; H, 3.00. Found: C, 49.79; H, 3.06

Hydroxymaleimidoylmaleimides (**3**).- A slurry of **1** or **2** (500 mg) in water (100 ml) was heated at regular for 2 hrs. The progress of the reaction was indicated by dissolution of the reactants followed by gradual separation of the product from the hot solution. The product was collected, washed with water and recrystallized from ethanol (yields, 70-75% for **3a-c**).

**3a**, mp. 225°. $^1$H NMR: $\delta$ 5.85 (s, 1H), 7.00-7.70 (10H), 9.80 (s, 1H, exchangeable).
Anal. Calcd. for $C_{20}H_{12}N_2O_5$: C, 66.66; H, 3.33. Found: C, 66.55; H, 3.47

**3b**, mp. 234°. IR: 3275, 1755, 1715, 1650, 1625 $cm^{-1}$. $^1$H NMR: $\delta$ 5.95 (s, 1H), 7.40-8.40 (8H), 10.35 (s, 1H, exchangeable).
Anal. Calcd. for $C_{20}H_{10}N_4O_9$: C, 56.87; H, 2.36. Found: C, 56.63; H, 2.17

**3c**, mp. 217°. IR: 3270, 1765, 1710, 1655, 1630 $cm^{-1}$. $^1$H NMR: $\delta$ 2.30 (s, 3H), 2.36 (s, 3H), 5.74 (s, 1H), 7.10-7.50 (8H), 9.80 (s, 1H, exchangeable).

Anal. Calcd. for $C_{22}H_{16}N_2O_5$: C, 68.04; H, 4.12. Found: C, 67.88; H, 4.01

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## REFERENCES

† Reactions of Cyclic Anhydrides, Part XXI.

1. W. Carruthers, "Some Modern Methods of Organic Synthesis", 3rd Edition, Cambridge University Press, 1986; R. K. Mackie, D. M. Smith and R. A. Aitken, "Guidebook to Organic Synthesis", 2nd Edition, Longmans, New York, 1990.
2. V. Balasubramaniyan and N. P. Argade, Tetrahedron, 45, 835 (1989).
3. J. W. Hancock, C. E. Morrel and D. Rhom, Tetrahedron Lett., 987 (1962).
4. J. March, "Advanced Organic Chemistry", 3rd Edition, Wiley Eastern Reprint, New Delhi, 1986, p. 295.
5. C. L. Yeh, W. T. Colwell and J. I. DeGraw, Tetrahedron Lett., 3987 (1978).
6. R. E. Ireland and W. J. Thompson, J. Org. Chem., 44, 3041 (1979) and **references** cited therein.
7. S. Kaneko, J. Biochem., 28, 1 (1938).
8. M. Augustin and P. Jeschke, Z. Chem., 27, 211 (1987).

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# A CONVENIENT SYNTHESIS OF 5,7-DIHYDROXYCHROMONE

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*National Center for Agricultural Utilization Research*
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5,7-Dihydroxychromone (3) is a flavanoid decomposition product[1] that has been found as a constituent in certain plant extracts[2,3] and is a germination and growth inhibitor.[3] Purification of gram