methylnitrosobenzene, 623-11-0; 2-nitrosobiphenyl, 21711-71-7; 4-chloronitrosobenzene, 932-98-9; sodium nitrite, 7632-00-0; 4-aminocarbazole, 18992-64-8.

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Synthesis of 1-α-Cumyl-1,2,3,6-tetrahydropyridazine-3,6-dione

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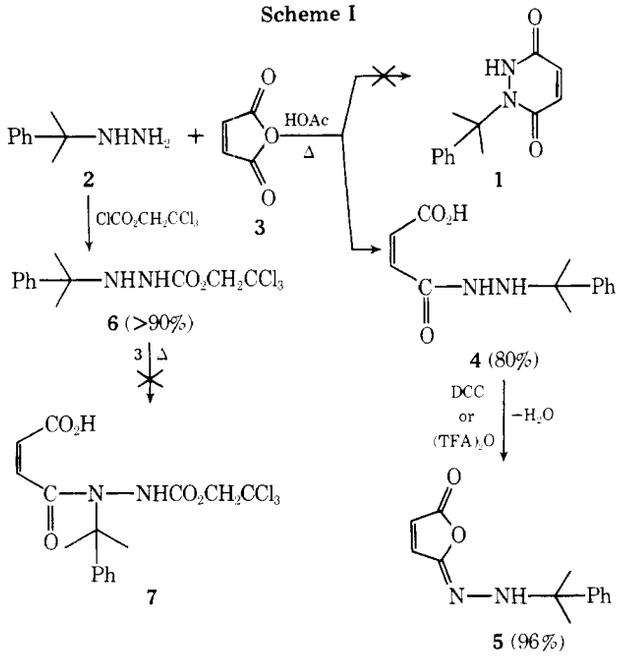
The title compound **1** cannot be prepared from reaction of α-cumylhydrazine (**2**) and maleic anhydride (**3**) in a manner analogous to the preparation of the 1-phenyl analogue. Instead, this reaction affords maleamic acid **4** and, after dehydration, isomaleimide **5**. When the unsubstituted nitrogen of **2** is protected by conversion to the trichloroethyl carbazate **6**, the substituted nitrogen is inert toward maleic anhydride, but not toward the more reactive maleoyl chloride **10**. The latter can be prepared by the reaction of lithium trichloroethoxide with excess maleic anhydride, followed by treatment with phosphorus trichloride. Maleic anhydride, which is unreactive toward 2,2,2-trichloroethanol, affords the isomeric fumarate **9** when treated with excess alkoxide ion. Treatment of carbazate **6** with maleoyl chloride **10** affords maleamate **11**. The latter diectly affords the desired tetrahydropyridazinedione **1** upon treatment with zinc in acetic acid.

1-α-Cumyl-1,2,3,6-tetrahydropyridazine-3,6-dione[1-4] (**1**), a precursor of a cyclic diacylhydrazyl radical which we desired, could not be prepared from α-cumylhydrazine[5] (**2**) and maleic anhydride (**3**). This unsuccessful approach is similar to that used to prepare the analogous 1-phenyltetrahydropyridazinedione[6] from phenylhydrazine. However, in the present case, α-cumylaminomaleamic acid (**4**) is obtained as the only product (Scheme I). Dehydration of **4** with either dicyclohexylcarbodiimide or trifluoroacetic anhydride affords the yellow isomaleimide **5** rather than the desired tetrahydropyridazinedione **1**. NMR chemical shifts (δ 6.13 and 7.20 ppm), vinyl coupling constant (J = 5.5 Hz), and ir carbonyl (1784 and 1757 cm^{-1}) and imine (1618 cm^{-1}) absorption peaks are in agreement with those observed for other isomaleimides.[7]

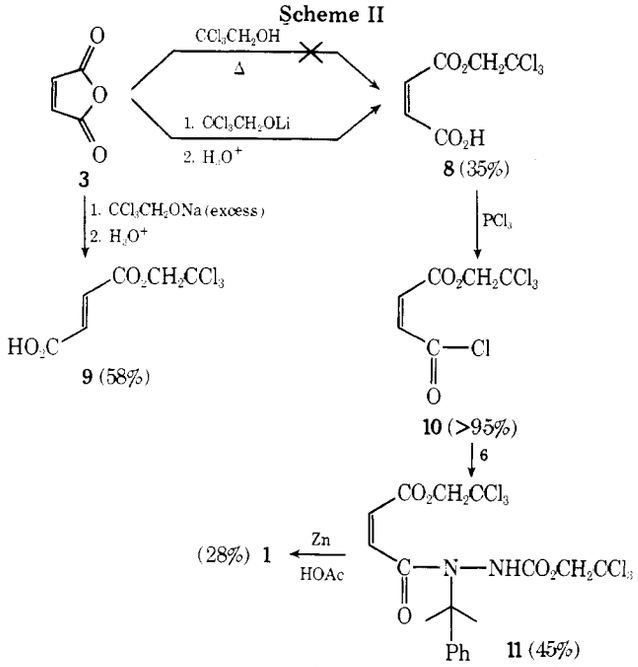
Scheme I



At this point, we felt that if the unsubstituted nitrogen of the hydrazine were protected, the maleic anhydride would be forced to react at the less reactive substituted nitrogen. Trichloroethoxycarbonyl[8] was chosen for this role since it could be removed under mild conditions that would not affect any of the other functionality present. To this end, α-cumylhydrazine was treated with 2,2,2-trichloroethyl chloroformate affording trichloroethyl carbazate **6** as a light, brown oil that could not be crystallized or distilled. The NMR spectrum of the oil is consistent with the assigned structure and showed it to be relatively pure. Reaction of carbazate **6** with maleic anhydride in refluxing toluene for 3 days failed to produce any detectable (NMR) quantity of the desired product **7**; extensive decomposition of the carbazate, however, was indicated.

We thought that a more reactive form of maleic acid could be obtained by protecting one carboxyl group and converting the other to the acid chloride. The trichloroethyl ester was chosen as the protecting group since this would allow removal of both protecting groups in one step. Heating maleic anhydride with trichloroethanol at 100 °C for 1 h (Scheme II) failed to produce any reaction (as judged by NMR), although methanol or ethanol react under these conditions.[9] Continued heating at 150 °C for 5 h afforded a colorless solid having an NMR spectrum inconsistent with that expected of the desired maleate **8**. Treatment of the anhydride with excess sodium trichloroethoxide affords the isomeric trichloroethyl hydrogen fumarate **9** [NMR, J_{vinyl} = 16.1 Hz (trans **HC**=**CH**);[10] ir 982 cm^{-1} (trans C=C)[11]]. Presumably, excess alkoxide ion allows the maleate isomerize to the sterically less congested fumarate

Scheme II



through reversible Michael addition to the double bond. When the reaction was carried out using the lithium alkoxide and excess maleic anhydride, the desired trichloroethyl hydrogen maleate **8** [NMR, J_{vinyl} = 12.4 Hz (cis **HC=H**);[10] ir 722 cm^{-1} (cis C=C)[11]] was obtained. Treatment of maleate **8** with phosphorus trichloride[12] affords maleoyl chloride **10** [NMR, J_{vinyl} = 12.0 Hz (cis **HC=CH**[10]] as a colorless, fuming liquid.

Treatment of trichloroethyl carbazate **6** with maleoyl chloride **10** affords maleamate **11** [NMR, J_{vinyl} = 12.0 Hz (cis **HC=CH**)[10]]. Finally, removal of the two protecting groups with zinc in acetic acid provides the desired α-cumyltetrahydropyridazinedione **1** as a colorless solid. NMR (δ 6.72 and 7.07 ppm, J_{vinyl} = 9.8 Hz) and ir (1665 and 1585 cm^{-1}) spectral data are in accord with that reported for other tetrahydropyridazinediones.[7] When heated in a capillary tube immersed in an oil bath, the amorphous solid changes without melting at ca. 220–230 °C into needles which then melt at 315–316 °C dec. When immersed into hot (250 °C) oil, **1** melts, bubbles, solidifies and does not melt again below 300 °C. Presumably, pyridazinedione **1** loses α-methylstyrene to afford 1,2,3,6-tetrahydropyridazine-3,6-dione (lit. mp >300[13a] and 300–310 °C dec[13b]).

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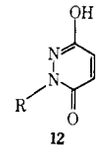
Registry No.—**2**, 3178-39-0; **3**, 108-31-6; **4**, 60498-79-5; **5**, 60498-80-8; **6**, 60498-81-9; **8**, 60498-82-0; **9**, 60498-83-1; **10**, 60498-84-2; **11**, 60498-85-3; **12** (R = α-cumyl), 60498-86-4; 2,2,2-trichloroethyl chloroformate, 17341-93-4; sodium trichloroethoxide, 60498-87-5; lithium trichloroethoxide, 60498-88-6.

Supplementary Material Available. Spectral data (NMR, ir, and mass spectra), elemental analyses, and procedures for the preparation of compounds **1**, **4–6**, and **8–11** (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This name and the associated structural formula are used in view of the relationship of **1** to other diacylhydrazines. Numerous studies[2-4] suggest that the structure of **1** would doubtlessly be more accurately portrayed as **12**.



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Synthesis of ω-Methoxy-1,2-dihydronaphthalenes. Gas Phase Pyrolysis of 1-(2′-, 3′-, and 4′-Methoxyphenyl)-1,3-butadienes

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Gas-phase pyrolysis of 1-(2′-methoxyphenyl)-1,3-butadiene yields 5-methoxy-1,2-dihydronaphthalene. Likewise, pyrolysis of 1-(3′-methoxyphenyl)-1,3-butadiene yields a mixture of 6-methoxy- and 8-methoxy-1,2-dihydronaphthalene. Pyrolysis of 1-(4′-methoxyphenyl)-1,3-butadiene yields 7-methoxy-1,2-dihydronaphthalene. Finally, pyrolysis of 2-(4′-methoxyphenyl)-2,4-pentadiene yields 7-methoxy-4-methyl-1,2-dihydronaphthalene. A mechanism for these pyrolysis reactions is discussed.

We should like to report the results of the following gas-phase pyrolysis reactions: 1-(2′-methoxyphenyl)-1,3-butadiene (I)[1] yields 5-methoxy-1,2-dihydronaphthalene (II, 68%);[2] 1-(3′-methoxyphenyl)-1,3-butadiene (III)[3] yields a mixture of 6-methoxy-1,2-dihydronaphthalene (IV, 28%)[4] and 8-methoxy-1,2-dihydronaphthalene (V, 42%);[2] 1-(4′-methoxyphenyl)-1,3-butadiene (VI)[1,5] yields 7-methoxy-1,2-dihydronaphthalene (VII, 62%);[6-8] and finally 2-(4′-methoxyphenyl)-2,4-pentadiene (VIII) yields 7-methoxy-4-methyl-1,2-dihydronaphthalene (IX, 96%)[9-13] (Scheme I).

These results are consistent with the three-step mechanism