Finally, it should be noted that the *o*-aminoaldehyde functionality in **2** is generated in one single reaction step, in contrast with previous routes to aromatic *o*-aminoaldehydes, where both functional groups are elaborated separately.

Experimental Section

A mixture of nicotinamide (36.5 g, 0.3 mol) and ammonium sulfamate[4] (52 g, 0.45 mol) was heated in an oil bath at 150°. After a clear melt was obtained, the temperature was raised slowly to 200°. The mixture was kept at this temperature for 6 hr, after which the content of the flask had completely solidified. Water was added and the precipitate collected and washed with ether to remove nicotinonitrile. The solid material thus obtained[6] was refluxed in 2 *N* HCl for 4 hr, made alkaline and extracted with ether. The resulting ether solution was dried (K_2CO_3) and evaporated to give pure 2-aminonicotinaldehyde (**2**) (9 g, 50%): mp 98-99° (lit.[2] 98°); ir (Nujol) 3440, 3250, 3125, 2750, 1650, 1625, 1575, 1540 cm^{-1}; nmr δ_{TMS} (DMSO-d_6) 9.96 (s, 1, HCO), 8.33 (dd, 1, H-α, $J_{\alpha-\beta}$ = 4 Hz, $J_{\alpha-\gamma}$ = 2 Hz), 8.08 (dd, 1, H-γ, $J_{\beta-\gamma}$ = 8 Hz), 7.6 (broad, 2, NH_2), 6.8 (dd, 1, H-β).

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Registry No.—**2**, 7521-41-7; nicotinamide, 98-92-0; ammonium sulfamate, 7773-06-0.

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(6) Purification of this material had no beneficial effect on the yield and purity of the final product. Its recrystallization from water gave pure **1b** (15.6 g, 50%), mp 224.

Enthalpy of the Diels-Alder Reaction of Cyclopentadiene and Maleic Anhydride

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In connection with a program of research on the energetics of cycloaddition reactions, we determined the enthalpy of the reaction between cyclopentadiene (CPD) and maleic anhydride (MA). Our report is prompted by the recent publication of similar data by Rogers and Quan.[1] These workers determined the heat for the DA reaction by standard solution calorimetric techniques. While the literature of thermal reactions abounds with kinetic data, measurement of enthalpies of reaction lags far behind. Where such data exist, they are often derived indirectly from heats of combustion or hydrogenation, or from van't Hoff data.[2] Our measurements provide an example of an application of flow calorimetry to the study of an organic reaction in solution.

The flow calorimeter and method employed have been described by Sturtevant.[3] The main components of the apparatus are a precision fluid delivery system capable of a wide range of delivery rates, a thermopile, and a massive aluminum heat sink. The reactant solutions are preequilibrated to the desired temperature and delivered through separate tubes to a junction where they are mixed just as they reach the thermopile. The heat evolved or absorbed upon mixing the solutions is quantitatively conducted through the thermopile to the heat sink. The output of the thermopile is integrated to yield the total heat transferred during a specified period.

Table I
Enthalpy of the Reaction of CPD and MA in Dioxane

Temp, °C	Run	CPD flow rate[a]	MA flow rate[a]	$-\Delta H_r$[b]
25.0	1[c]	2.8	2.8	24.14
	2	2.8	1.4	24.50
	3	2.8	1.0	24.56
	4[d]	2.0	2.0	24.92
	5	2.8	2.8	25.37
	6	1.4	1.4	24.27
	7	2.0	2.0	25.19
	8	2.8	2.8	25.24
	Average			24.8 ± 0.5[e]
40.0	1[f]	1.4	1.4	25.50
	2	2.0	2.0	25.59
	3	2.8	2.8	25.77
	4	2.0	1.4	25.62
	5	2.8	1.4	25.69
	6	1.4	2.0	25.36
	7[g]	1.4	1.4	25.78
	8	2.0	2.0	25.40
	9	2.8	2.8	25.39
	10	2.0	1.4	25.74
	11	2.8	1.4	25.45
	12	1.4	2.0	24.90
	Average			25.5 ± 0.3[c]

[a] A relative flow rate of 1 is 3.53 ml/min. [b] Kcal/mol. [c] Runs 1–3: [CPD] = 1.06 × 10^{-1} *M*; [MA] = 2.0 × 10^{-1} *M*. [d] Runs 4–8: [CPD] = 2.12 × 10^{-1} *M*; [MA] = 4.0 × 10^{-1} *M*. [e] The error is the standard deviation. [f] Runs 1–5: [CPD] = 1.88 × 10^{-1} *M*; [MA] = 4.0 × 10^{-1} *M*. [g] Runs 7–12: [CPD] = 1.98 × 10^{-1} *M*; [MA] = 4.0 × 10^{-1} *M*.

In the experiments performed, solutions of CPD (1-2 × 10^{-1} *M*)[4] and MA (2-4 × 10^{-1} *M*) in dioxane were allowed to react in the calorimeter. Upon mixing, an exothermic reaction ensued and the thermopile output increased to a steady-state value. The heat evolution was integrated for at least 5 min of the steady-state period. It should be noted that the flow rates of the two reactants were varied relative to one another, in order to demonstrate that the reaction was complete during the residence time in the calorimeter. Experiments were performed at 25 and 40°. The results of multiple runs are summarized in Table I. Control experiments indicated that there was negligible heat change on mixing of pure dioxane, or of dioxane with either reactant solution.

The enthalpy of reaction of CPD and MA in dioxane solution was found to be −24.8 ± 0.5 kcal/mol at 25.0°, and −25.5 ± 0.3 kcal/mol at 40° (the error quoted is the standard deviation). The precision of our values is not high enough to permit conclusions about the ΔC_p of this reaction, except to say that this term is probably small.

Comparison of our value of ΔH_r (25°) = −24.8 ± 0.5 kcal/mol for the reaction in dioxane and the value of Rogers and Quan of ΔH_r (25°) = −26.2 ± 0.1 kcal/mol for the reaction in dichloromethane indicates very good agreement after correction for solvent effects. Most of the data needed for solvent-effect corrections can be found in the work of Haberfield and Ray[5] as well as that of Rogers and Quan. The latter two investigators determined the heats of solution of CPD, MA, and the product *endo*-5-norbornene 2,3-dicarboxylic anhydride (N) in CH_2Cl_2.[6] The heat of solution of CPD in CH_2Cl_2 is 0.1 kcal/mol. This quantity is unknown in dioxane but it is almost certainly small, and can be assumed to be equal to the value in CH_2Cl_2 as a first approximation. The heat of solution of MA in dioxane is also known from the work of Haberfield and Ray.[5]

The enthalpy of transfer of the reactants from dioxane to CH_2Cl_2, $\delta\Delta H_{soln}$ (reactants) = ΔH^r_{soln} (CH_2Cl_2) − ΔH^r_{soln} (dioxane), is 1.2 kcal/mol. The heat of solution of N in dioxane is unknown. If it is assumed to be equal to the value in CH_2Cl_2, the small difference between our value and that of Rogers and Quan reduces to 0.3 kcal/mol, which is well within experimental error. Even if one assumes a value as large as 1 kcal/mol for the enthalpy of transfer of the product from dioxane to CH_2Cl_2, one would still find that our results are in good agreement with the values determined by standard solution calorimetry.[7]

In conclusion, we wish to emphasize that the flow calorimetric method employed is fast, convenient, and requires small amounts of sample. It is potentially applicable to measurement of enthalpies of a wide variety of fast organic reactions in solution.

Experimental Section

Materials. Maleic anhydride (Eastman Organic Chemicals) was recrystallized from $CHCl_3$, sublimed under vacuum, and stored in a desiccator until use. Dioxane was purified by refluxing over sodium followed by distillation (onto molecular sieves) immediately before use. CPD was obtained by cracking *endo*-dicyclopentadiene which had been purified by the method of Harkness, *et al.*[10]

Calorimetry. The flow calorimeter (a modified Beckman Model 190 microcalorimeter) has been described in detail elsewhere.[3,11] Calibration was accomplished by measuring the enthalpy of reaction of 1.000 × 10^{-3} *N* HCl and 2.000 × 10^{-3} *N* NaOH, employing the values given by Grenthe, *et al.*,[12] for the enthalpy of formation of water.

The temperature of the calorimeter was regulated to within ±0.005° at both temperatures at which the reaction was investigated. The output of the thermopile during the steady-state period was integrated using a ball and disk integrator. The integration precision is estimated to be better than ±1%.

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Registry No. CPD, 542-92-7; MA, 108-31-6.

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(6) A reviewer has questioned whether the product is 100% endo adduct. Although we did not determine this, the paper by Rogers and Quan[1] states that "Wilder and Gratz fractionally crystallized a kinetically determined reaction mixture and found 1.4% exo." The citation to the above experiment is erroneous, neither has this work been done by P. Wilder, Jr. (private communication). We have been unable to find the source of the report; however, even if it is substantiated, the enthalpy difference between N and X is expected to be quite small, so that the effect on our measured enthalpy is negligible.

(7) Using their data Rogers and Quan calculated a value for ΔH_r(g), and suggested an empirical equation for estimation of the heat of any DA reaction

$$\Delta H_r{}^d(g) - \Delta H_r{}^e(g) = \Delta H_H{}^d - \Delta H_H{}^e \qquad (1)$$

where $\Delta H_r{}^d$(g) is the heat of addition of any diene to dienophile (d), $\Delta H_r{}^e$(g) is the enthalpy of addition to ethylene, and $\Delta H_H{}^d$ and $\Delta H_H{}^e$ are the heats of hydrogenation of the dienophile and ethylene. Applying this equation to the reaction of CPD + MA they calculated a value for ΔH_r(g) which was 2.6 kcal/mol less exothermic than the experimental value. It should be noted that the value of $\Delta H_r{}^e$(g) is derived from the heat of formation of norbornene. The value used by Rogers and Quan of 20.6 kcal/mol has been updated by the work of Hall, *et al.*,[8] who find ΔH°_f (norbornene) = 15.1 kcal/mol. The calculated value according to eq 1 should therefore be higher than the experimental value by 2.9 kcal/mol. In addition, their conclusion that the strain energy of N contains only a small contribution from the succinic anhydride moiety (1.1 kcal/mol) now seems to be incorrect, in view of the new value for strain energy (SE) of norbornene (17.6 kcal/mol), and a revised value (4.5 kcal) for the strain contribution of a succinic anhydride moiety recently published by Eigenmann, Golden, and Benson.[9] Using the revised group additivity parameters for enthalpies of formation of oxygen-containing compounds,[9] we calculate ΔH_f(g) (N) = −111.8 kcal/mol. Comparing this value with the experimental value of −89.8 kcal/mol, the strain energy in N is 22 kcal/mol. [Note: SE (norbornene) + SE (succinic anhydride) = 22.1 kcal/mol].

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Reaction of *N*-Iodosuccinimide with Secondary Alcohols

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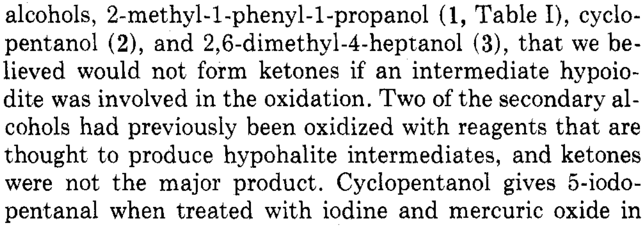
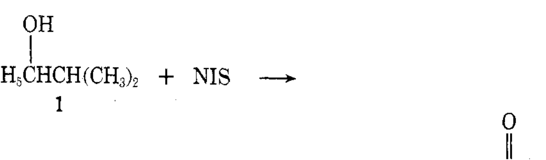
The reaction of tertiary alcohols with *N*-iodosuccinimide (NIS) has been shown to produce alkyl iodides and ketones.[1] The two products give good evidence that an alkyl hypoiodite is an intermediate in the reaction. The small number of secondary alcohols that have been oxidized with NIS produce ketones[2] and cyclic ethers.[3] The formation of a cyclic ether from a secondary alcohol and NIS suggests that an intermediate hypoiodite is probably formed (Barton-type reaction), while the production of a ketone may involve either hypoiodite formation or succinimidyl radical hydrogen abstraction.[2]

To gain more evidence for the general mechanistic pathway involved in the oxidation of secondary alcohols with NIS, NIS was allowed to react with three secondary alcohols, 2-methyl-1-phenyl-1-propanol (**1**, Table I), cyclopentanol (**2**), and 2,6-dimethyl-4-heptanol (**3**), that we believed would not form ketones if an intermediate hypoiodite was involved in the oxidation. Two of the secondary alcohols had previously been oxidized with reagents that are thought to produce hypohalite intermediates, and ketones were not the major product. Cyclopentanol gives 5-iodopentanal when treated with iodine and mercuric oxide in carbon tetrachloride[4] and 2,6-dimethyl-4-heptanol gives a furan when treated with bromine and silver acetate.[5]



$$\underset{\mathbf{1}}{C_6H_5\overset{OH}{\overset{|}{C}}HCH(CH_3)_2} + NIS \longrightarrow C_6H_5CHO + (CH_3)_2CHI + NHS + C_6H_5\overset{O}{\overset{\|}{C}}CH(CH_3)_2$$

The reaction of **1** with NIS in carbon tetrachloride at reflux in the presence of visible light[6] produced 78–87% benzaldehyde and 4–12% isobutyrophenone.[7] The 2-iodopropane product was found to be produced in 83% yield when no solvent was present. Succinimide was produced in 75–80% yield.



2