and the solid products were filtered and recrystallized from ethyl acetate. *dl*- and *meso*-succinic-d_2 acids were cyclized to the corresponding anhydrides by gentle warming with acetyl chloride.[9]

***N*-Biphenyl Succinimides.** To 0.10 g (0.001 mol) of succinic anhydride in 2 mL of anhydrous ether was added 0.169 g (0.001 mol) of 2-aminobiphenyl (Aldrich) dissolved in 1 mL of anhydrous ether. The reaction mixture was refluxed with stirring for 2 h, and then the solid amide–acid produced was filtered off.

To 0.1 g of the above solid were added 0.14 g of acetic anhydride and 0.02 g of sodium acetate, and the mixture was warmed and stirred for about 1 h until no solid was evident. The reaction mixture was cooled slowly to room temperature and then poured onto ice to yield a precipitate. This was recrystallized from a small amount of methanol to give a 60% overall yield of product, mp 135–137 °C (uncor).

Acknowledgment. Financial support from NSF Grant CHE 80 12233 is gratefully acknowledged.

Registry No. *dl*-**2**, 80655-73-8; *meso*-**2**, 80655-74-9; **3**, 80584-50-5; **4**, 80584-51-6; **5**, 80584-52-7; *dl*-succinic-d_2 acid, 21156-52-5; *meso*-succinic-d_2 acid, 21156-53-6; 2-aminobiphenyl, 90-41-5.

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[9] Blatt, A. M., Ed. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 560.

A Novel, Nonoxidative Method for the Conversion of Aldehydes to Esters

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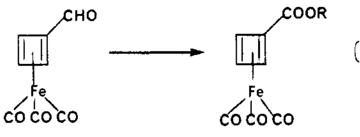
In connection with an attempted application of (cyclobutadiene)iron tricarbonyl chemistry to terpene synthesis,[2] we required a method for the conversion of the readily available[3] 1 to its esters **2a** and **2b** (eq 1). The direct



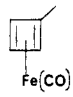
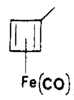
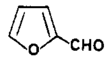
(1)

1

2a R = CH_3
2b R = isophoryl

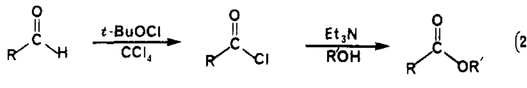
oxidation of aldehyde 1 to the corresponding acid with Ag_2O proceeds in only 1% yield.[6,7] Oxidation at the metal center is an obvious problem. We report herein a unique solution to the problem that is fairly general and represents a "nonoxidative" aldehyde oxidation.

Table I. Conversion of Aldehydes 3 to Esters 5 (eq 2)

entry	R	R′	% yield	time[d]
1		CH_3	90	3 min
2		isophoryl	39	3 min
3	Ph	CH_3	76[a]	2 h
4	PhCH=CH	CH_3	80[b]	4 h
5	*m*-OCH_3Ph	CH_3	98[c]	4 h
6		CH_3	60	4 h

[a] Ginsburg obtained benzoic acid in 96% yield.[8a] [b] The reaction of *tert*-butyl hypochlorite with cinnamaldehyde[17] *in methanol* was reported in 1941 in a paper describing the chlorination of double bonds with the reagent. 2-Chloro-3-methoxy-3-phenylpropanal was obtained in 30% yield, another example of the solvent effect. [c] Ginsburg obtained compound 7 with acetic acid as the solvent. [d] 25 °C.

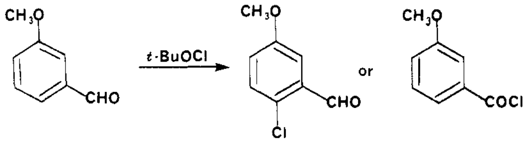
The approach takes advantage of the almost forgotten[8] selective conversion of aldehydes to acid chlorides with *tert*-butyl hypochlorite (eq 2). This reaction of aldehydes



(2)

3 4 5

was first discussed in detail in a 1951 paper by Ginsburg.[8,9] The reaction probably involves *tert*-butoxy radical abstraction of the aldehydic hydrogen. Competition between free-radical H abstraction and electrophilic chlorination results in a marked solvent effect. For example, *m*-methoxybenzaldehyde (**6**) reacts with *tert*-butyl hypochlorite in acetic acid to yield **7**, whereas we have found that in CCl_4 (see Table I) the only product is **8**. Examination of other entries in the table[10] reveals that the reaction works well for the tricarbonyliron complexes with no attack at the metal. Oxidation of aromatic aldehydes and heterocycles are not a problem.



6 7 8

Three limitations were uncovered.[11] Attempted reaction of **9** gave an ester with chlorination in the aromatic ring. Compound **10**, substituted with electron-withdrawing groups, did not react. And finally, attempts were made to convert benzaldehyde to methyl benzoate in the presence of the thioketal **11**. Unfortunately, the aldehyde was unscathed and destruction of **11** was the only observed reaction.[12]

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[1] Department of Chemistry, Indiana University, Bloomington, IN.

[2] Wilson, S. R.; Phillips, L. R.; Pelister, Y.; Huffman, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 7373–7379.

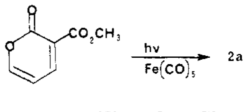
[3] Compound 1 was prepared in 64% yield as reported[4] by Vilsmeier formylation of commercially available[5] (cyclobutadiene)iron tricarbonyl.

[4] Fitzpatrick, J. D.; Watts, L.; Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3254–3255.

[5] Strem Chemicals, Inc., Newburyport, MA.

[6] Fitzpatrick, J. Ph.D. Thesis, University of Texas, Austin, TX, 1966.

[7] The inaccessibility of (cyclobutadienecarboxylic acid)iron tricarbonyl lead to another approach, based on 3-(carbomethoxy)-2-pyrone, in 21% overall yield.



Agar, J.; Kaplan, F.; Roberts, B. W. *J. Org. Chem.* **1974**, *39*, 3451–3452.

[8] (a) Ginsburg, D. *J. Am. Chem. Soc.* **1951**, *73*, 702–704. (b) Anbar, M.; Ginsburg, D. *Chem. Rev.* **1954**, *54*, 925–958.

[9] Ansell, M. F. In "The Chemistry of Acyl Halides"; Patai, S. Ed.; Interscience: New York, 1972, p 35 ff.

[10] Complete spectral data for compounds **2a** and **2b** are available as supplementary material (see supplementary material available paragraph).

[11] Although the conversion of an aliphatic aldehyde to the acid bromide with NBS has been reported[16], the reaction of heptaldehyde with *tert*-butyl hypochlorite gave extensive chlorination of the alkyl chain. The reaction with citral gave a complex mixture of products.

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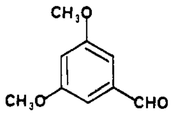
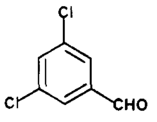
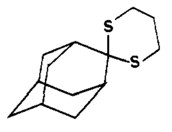


9



10



11

In summary, while the conversion of aldehyde to ester is often straightforward, the methods which effect this transformation *without the presence of a heavy metal* are rare.[13,14] We believe that the method reported here may be valuable in the oxidation of other systems sensitive to common oxidants.

Experimental Section[10]

Tricarbonyl(methyl 1-4-η-1,3-cyclobutadienecarboxylate)iron (2a). A 112.0-mg sample of aldehyde 1 in 3 mL of CCl_4 was treated with 60.0 mg of *tert*-butyl hypochlorite. After being stirred for 2 min, a mixture of 0.10 mL of CH_3OH and 0.10 mL of pyridine was added. The reaction mixture was then stirred for 30 min and poured into 10 mL of H_2O and extracted with ether; the ether was dried and evaporated. The brownish oil was distilled [60 °C (1.0 mm)] to give 114 mg (90%) of **2a**: IR (neat) 4.8, 5.0, 5.78 μm; NMR (CCl_4) δ 3.65 (s, 3 H, OCH_3), 4.3 (s, 1 H, para H), 4.6 (s, 2 H, ortho H); mass spectrum (*m/e*) 250 (28), 222 (39), 194 (41), 166 (36), 138 (18), 136 (33), 108 (100), 82 (41), 81 (27), 56 (42).

Tricarbonyl(isophoryl 1-4-η-1,3-cyclobutadienylcarboxylate)iron (2b). A 50-mg sample of 1 (0.23 mmol) and 2 mL of CCl_4 were stirred at 25 °C, while 28.0 mg of *tert*-butyl hypochlorite in 0.25 mL of CCl_4 was added. After the mixture was stirred for 2 min, 0.1 mL of pyridine and 40.0 mg (0.29 mmol) of isophorol were added. The mixture was stirred for 90 min until TLC analysis showed the reaction was complete. Then 10 mL of H_2O was added and the mixture was extracted twice with 15-mL portions of ether. After the mixture was dried with $MgSO_4$, the solvents were removed under reduced pressure, and the crude product was purified by preparative TLC (7% ether/pentane). Collection of the band at R_f 0.39 gave 32 mg (39%) of compound **2b**: IR (neat) 4.81, 5.0, 5.8, 5.95 μm (w); NMR (CCl_4) δ 0.98 (s, 3 H, CH_3), 1.0 (s, 3H, CH_3), 1.7 (br s, 3 H, CH_3), 4.18 (s, 1 H, para H), 4.42 (s, 2 H, ortho H), 5.27 (m, 1 H, vinyl H); mass spectrum, *m/e* 358 (5), 274 (8), 236 (21), 208 (62), 180 (100), 152 (37), 123 (68), 117 (83), 91 (43), 81 (33).

Methyl Cinnamate (Entry 4). To a solution of 264 mg (2mmol) of cinnamaldehyde in about 8 mL of CCl_4 was added 216 mg of *tert*-butyl hypochlorite by syringe. After the mixture was stirred for 4 h at room temperature, 25 drops of triethylamine and 25 mL of CH_3OH were added. The mixture was then refluxed for 45 min. After the mixture cooled, ether was added and the organic phase was washed with 10% HCl, saturated $NaHCO_3$ solution, and water and then dried with $MgSO_4$, and the solvents were evaporated. Distillation at 85 °C (1 mm) gave pure methyl cinnamate (79%) whose IR, NMR, and mass spectra were identical with those of an authentic sample.

Acknowledgment. We thank the National Institutes of Health (GM26039) and the Petroleum Research Fund (11243-AC1) for support of this research.

Registry No. 1, 33056-62-1; **2a**, 52571-40-1; **2b**, 80583-61-5; **3** (R = Ph), 100-52-7; **3** (R = PhCH═CH), 104-55-2; **3** (R = MeO-*m*-C_6H_4), 591-31-1; **3** (R = 2-furanyl), 98-01-1; **5** (R = Ph; R′ = Me), 93-58-3; **5** (R = PhCH═CH; R′ = Me), 103-26-4; **5** (R = MeO-*m*-C_6H4; R′ = Me), 5368-81-0; **5** (R = 2-furanyl; R′ = Me), 611-13-2; **9**, 7311-34-4; **10**, 10203-08-4; **11**, 80573-02-0; *tert*-butyl hypochlorite, 507-40-4.

Supplementary Material Available: Complete spectral data for compounds **2a** and **2b** (6 pages). Ordering information is given on any current masthead page.

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(12) *tert*-Butyl hypochlorite was reported to oxidize diphenyl sulfide to the sulfoxide: Walling, C. *J. Org. Chem.* **1967**, *32*, 286.

(13) The conversion of aldehydes to esters has been accomplished by the following. (1) Oxidation of cyanohydrins: Corey, E. J.; Gilman, N. W.; Ganem, B. E. *J. Am. Chem. Soc.* **1968**, *90*, 5616–5617. (2) Oxidation or ozonolysis of acetals: Heywood, D. L.; Phillips, B. *J. Org. Chem.* **1960**, *25*, 1699–1703. Elad, D.; Youssefyeh, R. D. *Tetrahedron Lett.* **1963**, 2189–2191. Deslongchamps, P.; Moreau, C. *Can. J. Chem.* **1971**, *49*, 2465–2467. Marvell, E. N.; Joncich, M. J. *J. Am. Chem. Soc.* **1951**, *73*, 973–975. (3) Oxidation of hemiacetals: Nishihara, A.; Kubota, I. *J. Org. Chem.* **1968**, *33*, 2525–2526. Sakuragi, H.; Tokumara, K. *Chem. Lett.* **1974**, 475–476. Loozen, H. J. J.; Godefroi, E. F.; Besters, J. S. M. M. *J. Org. Chem.* **1975**, *40*, 892–894. Sundararaman, P.; Walker, E. C.; Djerassi, C. *Tetrahedron Lett.* **1978**, 1627–1628. (4) The Tishchenko reaction (dimerization of aldehydes mediated by $Al(OR)_3$): Stammer, F. W.; Hauser, C. R. *J. Am. Chem. Soc.* **1946**, *68*, 2647–2649. Villani, F. J.; Nord, F. F. *J. Am. Chem. Soc.* **1947**, *69*, 2605–2607. Lin, I.; Day, A. R. *J. Am. Chem. Soc.* **1952**, *74*, 5133. Stapp, P. R. *J. Org. Chem.* **1973**, *38*, 1433–1434. Wagner, R. M.; Zook, H. D. "Synthetic Organic Chemistry"; Wiley: New York, 1953; p 494 ff. (5) The NBS oxidation of $ROSn(n\text{-}Bu)_3$ in the presence of aldehydes (a reaction that may be mechanistically related to the one reported here): Ogawa, T.; Matsui, M. *J. Am. Chem. Soc.* **1976**, *98*, 1629–1630. (6) By a variety of specialized methods: Stevens, C. L.; Farkas, E.; Gillis, B. *J. Am. Chem. Soc.* **1954**, *76*, 2695–2698. Riehl, J. J.; Fougerousse, A.; Lamy, F. *Tetrahedron Lett.* **1968**, 4415–4416. Ellison, R. A.; Woessner, W. D.; Williams, C. C. *J. Org. Chem.* **1972**, *37*, 2757–2759. Ho, T. L.; Wong, C. W. *Synth. Commun.* **1975**, *5*, 213–216.

(14) Related halogenations of aldehyde hydrogens to give acid halides have been reported with chlorine[15] and NBS[16].

(15) Clarke, H. T.; Taylor, E. R. "Organic Syntheses", Collect. Vol. 1; Wiley: New York, 1944; p 155.

(16) Cheung, Y. F. *Tetrahedron Lett.* **1979**, 3809–3810.

(17) Emling, B. L.; Vogt, R. R.; Hennion, G. F. *J. Am. Chem. Soc.* **1941**, *63*, 1624–1625.

Photocyclization of 1,2-Diarylethylenes in Primary Amines. A Convenient Method for the Synthesis of Dihydro Aromatic Compounds and a Means of Reducing the Loss of Methyl Groups during the Cyclization of *o*-Methylstilbenes

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One of the most useful photochemical processes in organic synthesis is undoubtedly photocyclization. Specifically, the conrotatory ring closure of *cis*-hexatrienes leading to the cyclohexadienes followed by oxidation or elimination is one of the best known and most exploited photoelectrocyclic reactions.[1,2]

The number of applications of this type of photoreaction is very large, especially for the synthesis of polycyclic aromatic compounds, the classical example being the stilbene–phenanthrene photoconversion.[3]

Nevertheless it has been shown that stilbenes which have one[4] or two[5] electron-withdrawing enolizable substituents on the double bond, when irradiated in protic solvents under nonoxidative conditions, yield 9,10-dihydrophenanthrenes. The mechanism of these reactions has been clarified recently by Laarhoven,[6,7] but their scope was restricted by the substituents required. A new method for preparation of 5,6-dihydrohexahelicenes by photocylization of 2,7-distyrylnaphthalenes under anaerobic conditions has also been recently described by the same author but "the procedure remains rather capricious due to experimental difficulties".[8]

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