72% yield: mp 154–157° ($CHCl_3$–n-pentane); ir (KBr) 3240 (NH), 1692, 1640, 1515 cm^{-1}; nmr ($CDCl_3$) τ 1.68 (NH, exchangeable with D_2O), 2.5–2.8 (m, 10 H), and 7.90 (s, 3 H); mass spectrum m/e (per cent) 278 (60, $M^{\cdot +}$), 236 (100, $M^{\cdot +} - CH_2CO$, m* at m/e 200.3), 235 (11, $M^{\cdot +} - CH_3CO\cdot$).

Anal. Calcd for $C_{17}H_{14}N_2O_2$ (278): C, 73.37; H, 5.07; N, 10.07. Found: C, 73.65; H, 5.08; N, 9.93.

Thermolysis of 4b. When a toluene solution of **4b** (1.0 g in 5 ml) was heated at 98–100° and then cooled, compound **5b** was obtained in 98% yield: mp 148–149.5° (1:1 $CHCl_3$–ether); ir (KBr) 3270 (NH), 1680, 1642, 1530 cm^{-1}; nmr ($CDCl_3$) τ 1.00 (NH, exchangeable with D_2O), 1.8–2.2 (m, 2 H), 2.25–2.75 (m, 8 H), and 7.98 (s, 3 H); mass spectrum m/e (per cent) 278 (54, $M^{\cdot +}$), 175 (16, $M^{\cdot +} - PhCN$), 105 (100, $PhCO^+$).

Anal. Calcd for $C_{17}H_{14}N_2O_2$ (278): C, 73.37; H, 5.07; N, 10.07. Found: C, 73.06; H, 5.08; N, 10.00.

Independent Synthesis of 5a. α-Benzoyl phenylacetonitrile (**10**, 0.02 mol), prepared by the method of Levine and Hauser,[9] was dissolved in pyridine (7 ml) and treated with $NH_2OH \cdot HCl$ (0.02 mol) at room temperature for 24 hr. The suspension was poured into ice–water, and the precipitate was filtered, washed with water, and dried over P_2O_5 to give **11** in 56% yield. Crystallization from water–EtOH (60%) furnished white needles: mp 152–154°; ir (KBr) 3400 (NH), 3300–3180, 1634 cm^{-1}; nmr ($CDCl_3$) τ 2.50–2.90 (m, 10 H) and 5.47 (NH_2, exchangeable with D_2O); mass spectrum m/e (per cent) 236 (41, $M^{\cdot +}$), 208 (27, $M^{\cdot +} - CO$, m* at m/e 183.3), 105 (100, $PhCO^+$).

Anal. (determined by high-resolution exact mass measurement). Calcd for $C_{15}H_{12}N_2O$: 236.09495. Found: 236.09391.

Another procedure for the preparation of **11** consisted in allowing equimolar amounts (0.04 mol) of **10** and $NH_2OH \cdot HCl$ in EtOH (75 ml) to react at reflux temperature for 2 hr. Then the solution was partially evaporated and cooled to give **11** in 58% yield.

Compound **11** (1.2 g) was dissolved in acetic anhydride (15 ml) and allowed to stand at room temperature for 28 days. After cooling of the reaction mixture, **5a** crystallized out in 70% yield, mp 154–157° (benzene).

Note: When **11** was heated in acetic anhydride or in boiling m-xylene containing acetyl chloride, the N,N-diacetylated derivative (mp 145–146.5°) was obtained in high yield (67–84%).

Synthesis of 15a by the Schmidt Reaction. To a magnetically stirred solution of **14a** (0.5 g) in chloroform (15 ml) was added slowly concentrated sulfuric acid (15 ml) and then NaN_3 (1 g). The mixture was stirred for 24 hr at room temperature before being quenched into ice. The yellow precipitate was filtered and crystallized from MeOH (20 ml) to give pure **15a** in 61% yield: mp 196–198°; ir (KBr) 3320 (NH), 1662, 1628, 1530 cm^{-1}; nmr ($CDCl_3$) τ 2.75 (s, 10 H), 3.32 (br, NH, exchangeable with D_2O), and 7.20 (d, 3 H, J = 5 Hz); mass spectrum m/e (per cent) 278 (35, $M^{\cdot +}$), 220 (100, $M^{\cdot +} - CH_3NHCO\cdot$, m* at m/e 174.1), 192 (30, 220 − CO, m* at m/e 167.5).

Anal. Calcd for $C_{17}H_{14}N_2O_2$ (278): C, 73.37; H, 5.03; N, 10.07. Found: C, 73.40; H, 5.05; N, 10.00.

Kinetic Measurements. Decalin solutions of **4a** (*ca.* 1.25 g in 50 ml) were allowed to decompose at the appropriate temperature and the rates of decomposition were followed by recording the decrease of the azide absorption band at about 2130 cm^{-1} in the ir as a function of time. Details concerning the procedure have been described elsewhere.[10]

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Registry No.—**4a**, 51002-99-4; **4b**, 51003-00-0; **5a**, 52392-71-9; **5b**, 52392-72-0; **10**, 5415-07-6; **11**, 52392-73-1; **11** N,N-diacetylated derivative, 52470-18-5; **14a**, 1631-96-5; **15a**, 52438-82-1; $NH_2OH \cdot HCl$, 5470-11-1.

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Convenient Synthesis of the Tricarbonyliron Complex of Cyclobutadienecarboxylic Acid[1]

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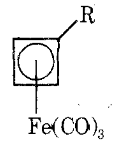
Recently, in connection with another synthetic program, we needed a convenient source of synthetically useful amounts of the tricarbonyliron complex of cyclobutadienecarboxylic acid (**1b**). Earlier preparations of this compound require parent complex **1a** and involve either formylation–oxidation in <1% overall yield[2] or methylthioformylation–hydrolysis in 34% yield.[2b] Because existent methods for preparing **1a** are either expensive or inefficient, we sought a more direct route to **1b** and have found that application of the photopyrone route of Rosenblum and Gatsonis[3] to the readily prepared 3-carbomethoxy-2-pyrone (**2**)[4] provides a convenient entry to monocarboxyl derivatives of **1a** and, by implication, to other types of monosubstituted derivatives.

Experimentally, a solution of **2** in THF is irradiated until disappearance of the pyrone, and the presumed photopyrone **3** is irradiated for 1 hr in the presence of a 100% excess of iron pentacarbonyl. Although the immediate product, methyl ester **1c**, is isolable, it is a liquid and is sensitive to light. Consequently, the product was most conveniently isolated as crystalline **1b** after a saponification step. Qualitative analysis of the effect of varying irradiation time (during complexation) and relative amount of iron pentacarbonyl indicated that the maximum yield (21%) of **1b** is obtained under the specified conditions.



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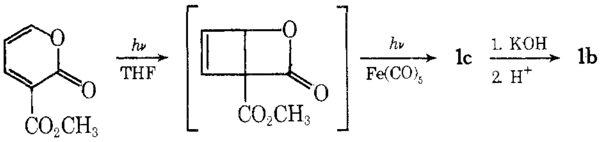

2 3

a, R = H
b, R = CO_2H
c, R = CO_2CH_3

Experimental Section

Melting points and boiling points are uncorrected. Ir spectra were recorded on a Perkin-Elmer 521 spectrophotometer. Nmr spectra were recorded on a Varian Associates A60-A spectrophotometer using TMS as internal standard. Microanalysis was performed by Galbraith Laboratories, Knoxville, Tenn.

Tricarbonyl[1,2,3,4-η-1,3-cyclobutadienecarboxylic acid]-iron (1b). A solution of 1.00 g (6.50 mmol) of 3-carbomethoxy-2-

pyrone[4] in 180 ml of dry THF was placed in a photochemical reaction vessel immersed in an ice bath and irradiated for 22 hr under nitrogen with a Hanovia 450-W high-pressure mercury lamp fitted with a Pyrex filter. By this time, the pyrone had disappeared as indicated by ir spectroscopy. Iron pentacarbonyl (2.55 g, 13.0 mmol) was then added, and irradiation was continued for 1 hr. The reaction mixture was concentrated on a rotary evaporator at reduced pressure at room temperature,[5] and the residue was washed through a 4.5-in. × 1.5-in. wet-packed column of alumina with methylene chloride (400–500-ml total volume). Crude ester **1c** was obtained by collection and evaporation of the first colored band eluted. This material was immediately mixed with a solution of 0.80 g of 85% potassium hydroxide in 1 ml of water and 5 ml of methanol and stirred for 2 hr. The resulting mixture was combined with 50 ml of water, washed with 50 ml of methylene chloride, acidified with concentrated hydrochloric acid, and extracted with 2 × 50 ml of ether. The ether extracts were dried over magnesium sulfate and evaporated, and the residue was recrystallized from carbon tetrachloride to give 325 mg (21%) of **1b**, mp 147–149° (lit[2b] mp 151–152°), the ir and nmr spectra of which were identical with those reported by Fitzpatrick.[2b]

Tricarbonyl[methyl 1,2,3,4-η-1,3-cyclobutadienecarboxylate]iron (1c). The crude ester obtained in the preceding experiment was purified by preparative tlc (20 cm × 20 cm silica gel plate, development with $CHCl_3$) followed by evaporative distillation [bath temperature 34–38° (1.2 mm)] to give **1c** as a yellow oil: ir ($CHCl_3$) 2068, 1988, and 1709 cm^{-1}; nmr ($CDCl_3$) δ 3.67 (s, 3 H, OCH_3), 4.28 (s, 1 H, para proton), and 4.51 (s, 2 H, ortho protons).

Anal. Calcd for $C_9H_6FeO_5$: C, 43.24; H, 2.42; Fe, 22.34. Found: C, 43.11; H, 2.47; Fe, 22.10.

Registry No.—**1b**, 52571-39-8; **1c**, 52571-40-1; **2**, 25991-27-9; iron pentacarbonyl, 13463-40-6.

References and Notes

[1] This work was supported by Public Health Service Research Grant No. CA-12008 from the National Cancer Institute.

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[5] Because **1c** is sensitive to prolonged exposure to light, it was kept in the dark as much as possible during this and subsequent manipulations.

Tetrahydrofuran-Promoted Aryl–Alkyl Coupling Involving Organolithium Reagents

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The reaction of aryl halides with organolithium compounds in diethyl ether or other less polar solvents is dominated by the halogen–metal interconversion[1] (eq 1). The coupling of the aryl and alkyl groups in these solvents generally takes place very slowly.[1] We have noted that the coupling reaction (eq 2) is markedly promoted by tetrahydrofuran (THF),[2] producing cleanly the cross-coupled products in many cases.[2]

$$\text{ArBr} + \text{RLi} \xrightarrow[25°]{\text{ether}} \text{ArLi} + \text{RBr} \qquad (1)$$

$$\text{ArBr} + \text{RLi} \xrightarrow[25°]{\text{THF}} \text{ArR} + \text{LiBr} \qquad (2)$$

For example, the reaction of 1-bromonaphthalene with n-butyllithium in a 1:5 mixture of hexane and THF produces 1-n-butylnaphthalene (**1**) in 72% yield within 1 hr at room temperature, whereas the corresponding reaction in a

Table I
Tetrahydrofuran-Promoted Aryl–Alkyl Coupling

Aryl reagent	Registry no.	(ArX)	Alkyl reagent	Registry no.	(RY)	Procedure[a]	Product[b]	Registry no.	Yield, %[c]
o-Tolyl	95-46-2	Br	*n*-Butyl	109-72-8	Li	I	*o*-*n*-Butyltoluene[d]	1595-11-5	65
m-Tolyl	591-17-3	Br	*n*-Butyl		Li	I	*m*-*n*-Butyltoluene[e]	1595-04-6	63
p-Tolyl	106-38-7	Br	*n*-Butyl		Li	I	*p*-*n*-Butyltoluene[f]	1595-05-7	69
1-Naphthyl	90-11-9	Br	*n*-Butyl		Li	I	1-*n*-Butylnaphthalene[g]	1634-09-9	66 (72)
1-Naphthyl		Br	*sec*-Butyl	598-30-1	Li	I	1-*sec*-Butylnaphthalene	1680-58-6	(<1)
1-Naphthyl		Br	*t*-Butyl	594-19-4	Li	I	1-*tert*-Butylnaphthalene	17085-91-5	(<1)
4-Methyl-1-naphthyl	6627-78-7	Br	*n*-Butyl		Li	I	1-*n*-Butyl-4-methylnaphthalene[h]	52718-76-0	52
4-Methyl-1-naphthyl		Br	Ethyl	811-49-4	Li	I	1-Ethyl-4-methylnaphthalene[i]	27424-87-9	60
2-Methyl-1-naphthyl	2586-62-1	Br	Ethyl		Li	I	1-Ethyl-2-methylnaphthalene[j]	17057-93-1	66
Phenyl	591-51-5	Li	*n*-Octyl	111-83-1	Br	II	*n*-Octylbenzene[g]	2189-60-8	82 (87)
Phenyl	108-86-1	Br	*n*-Octyl		Br	III	*n*-Octylbenzene		70 (76)
1-Naphthyl		Br	*n*-Octyl		Br	III	1-*n*-Octylnaphthalene[g]	2876-51-9	60 (74)

[a] For definition of procedures I, II, and III, see the Experimental Section. [b] All isolated products yielded satisfactory pmr and ir data, and 1-*n*-butyl-4-methylnaphthalene gave the correct analytical data. [c] By isolation. The numbers in parentheses are yields by glpc (SE-30). [d] n^{25}D 1.4933 (lit.[7] n^{20}D 1.4960). [e] $n^{25.5}$D 1.4892 (lit.[7] n^{20}D 1.4910). [f] $n^{25.5}$D 1.4886 (lit.[7] n^{20}D 1.4916). [g] For physical constants, see the Experimental Section. [h] Bp 91–94° (0.04 mm); n^{25}D 1.5729. [i] Bp 83–86° (0.25 mm); n^{25}D 1.5976 [lit.[6] bp 122° (40 mm)]. [j] Bp 76–79° (0.15 mm); n^{25}D 1.5974 [lit. bp 133–134° (15 mm) from R. B. Carlin and K. P. Sivaramakrishnan, *J. Org. Chem.*, 35, 3368 (1970)].