

bis(triphenylacetic)carbonic anhydride, trifluoroacetic anhydride, and trichloroacetic acid.

**Registry No.**—IV, 670-54-2; XI, 76-02-8; hydrogen peroxide, 7722-84-1; bis(triphenylacetic) carbonic anhydride, 10075-58-8; triphenylacetic anhydride, 10075-59-9; V, 3189-43-3; VII, 1115-12-4;  $\text{Cl}_3\text{CCOCCl}_3$ , 116-16-5;  $\text{Cl}_3\text{CCOOCH}_2\text{CH}_3$ , 515-84-4.

**Acknowledgment.**—Research reported in this publication was supported by the Advanced Projects Agency and under contract to the Office of Naval Research.

### A Convenient Synthesis of Dimethyl 4-Phenylacridinates<sup>1,2</sup>

EDWARD C. TAYLOR AND NED D. HEINDEL

Department of Chemistry, Princeton University,  
Princeton, New Jersey

Received November 10, 1965

The reaction of  $\alpha$ -amino ketones and dimethyl acetylenedicarboxylate to give an initial Michael adduct which then underwent dehydrative cyclization to pyrrole carboxylates has been described in the recent literature.<sup>3,4</sup> Mention was made<sup>3</sup> of the synthesis of a quinoline, 2,3-dicarbomethoxy-4-methylquinoline (dimethyl 4-methylacridinate) from 2-aminoacetophenone, but no experimental conditions or physical properties were given.

We have examined the analogous reaction of dimethyl acetylenedicarboxylate with a number of 2-aminobenzophenones and have found that dimethyl 4-phenylacridinates are formed directly without isolation of the intermediate Michael adducts. (See Table I.) Under the same reaction conditions, 2-aminoacetophenone yielded only the intermediate enamine adduct which, however, displayed *two* modes of cyclization. Upon heating under reflux in methanolic sodium methoxide it underwent dehydrative cyclization to the expected dimethyl 4-methylacridinate. On the other hand, pyrolysis generated the Conrad Limpach cyclization product, 8-acetyl-2-carbomethoxy-4(1H)-quinolone.

The observation that the Michael adduct of 2-aminoacetophenone required basic conditions for dehydrative cyclization, while the reaction of 2-aminobenzophenones and dimethyl acetylenedicarboxylate yielded the acridinates directly, undoubtedly reflects the greater electron deficiency at the ketone carbonyl in the Michael adducts formed from the benzophenones.

Dimethyl 6-nitro-4-phenylacridinate was obtained in low yield from dimethyl acetylenedicarboxylate and 5-nitro-2-aminobenzophenone. In this instance it seems probable that the diminished basicity of the aromatic amine decreases the facility with which the initial

Michael addition takes place. Efforts to effect an analogous cyclization with other acetylenic precursors such as diphenylacetylene, phenylacetylene, methyl propiolate, and ethyl phenylpropiolate were unsuccessful. Only starting materials were recovered in these cases.

In an attempt to prepare derivatives of 4-hydroxy-4-phenyl-1,2,3,4-tetrahydroacridinic acid, the possible photoenolization of several 2-aminobenzophenones was investigated. Yang and Rivas<sup>5</sup> have reported that 2-methylbenzophenone is inert to photopinacol formation in alcohol solution because it undergoes an internal hydrogen transfer to a transient dienic system which can be trapped by reaction with a suitable dienophile. 2-Aminobenzophenones are also inert to photoreduction, and the possibility that photoenolization occurs here as well has been suggested as a possible explanation.<sup>6</sup> We have examined the photolysis of a mixture of 5-chloro-2-aminobenzophenone and diethyl maleate in dry benzene but were unable to obtain any evidence for the formation of the photoenol.<sup>7</sup> Since the reaction of dimethyl acetylenedicarboxylate ("dark reaction") with 5-nitro-2-aminobenzophenone is very sluggish, as mentioned above, the possible reaction of these two components under photolysis conditions was also examined. There was no detectable formation of a quinoline product, and we thus conclude that no trapable photoenol is produced from 2-aminobenzophenones.

### Experimental Section<sup>8</sup>

**General Procedure for the Preparation of Dimethyl 4-Phenylacridinates.**—A solution of 0.02 mole of the 2-aminobenzophenone<sup>9</sup> and 0.02 mole of dimethyl acetylenedicarboxylate in 100 ml of benzene was heated under reflux for 24 hr and evaporated to dryness under reduced pressure, and the residue was recrystallized from methanol. The analytical samples were conveniently prepared by sublimation at 100° (0.05 mm).

**Dimethyl 4-Methylacridinate.**—Treatment of 0.02 mole of 2-aminoacetophenone with 0.02 mole of dimethyl acetylenedicarboxylate under the conditions described above gave the intermediate enamine adduct, mp 95.5–97°, in 74% yield.

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{16}\text{NO}_3$ : C, 60.65; H, 5.46; N, 5.06. Found: C, 60.45; H, 5.38; N, 5.09.

The nmr spectrum ( $\text{DCCl}_3$ ) of this enamine adduct showed the acetyl methyl protons as a singlet at 2.62, the two ester methyl protons as singlets at 3.72 and 3.78, the single vinyl proton signal at 5.62,<sup>10</sup> an aromatic multiplet at 6.6–7.9, and the N–H proton as a singlet at 11.90 ppm (ratio 3:3:3:1:4:1).

A solution of 1.5 g of this enamine adduct in 50 ml of anhydrous methanol containing 0.08 g of sodium methoxide was heated under reflux for 4 hr, the methanol was removed under reduced pressure, the residual oil was taken up in hot benzene, and the

(5) N. C. Yang and C. Rivas, *J. Am. Chem. Soc.*, **83**, 2213 (1961).

(6) J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

(7) Even if a nonphotolytic Michael addition of 5-chloro-2-aminobenzophenone to diethyl maleate had taken place, the product would have been saturated and thus unable to undergo enamine addition to the carbonyl group. Thus the isolation of a 4-hydroxy-1,2,3,4-tetrahydroacridinic acid would have been direct evidence for photoenolization. Dimethyl acetylenedicarboxylate (as employed by Yang<sup>5</sup>) could not be used as a trapping dienophile, since the "dark reaction" gives rise to the same dimethyl 4-arylacridinate as Diels–Alder addition to the photoenol.

(8) We are indebted for the microanalyses to Dr. George I. Robertson, Florham Park, N. J.

(9) We are indebted to Dr. L. H. Sternbach of the Hoffmann-La Roche Research Laboratories, Nutley, N. J., for generous gifts of *o*-aminobenzophenone, 2-amino-5-chlorobenzophenone, and 2-amino-5-nitrobenzophenone.

(10) A single resonance signal in the vinyl region can be interpreted as evidence for the formation of a single geometric isomer from the amine-to-acetylene addition; see, for example, J. E. Dolfini, *J. Org. Chem.*, **30**, 1298 (1965); R. Huisgen, K. Herbig, A. Siegl, and H. Huber, *Chem. Ber.*, **99**, 2526 (1966), and references cited therein.

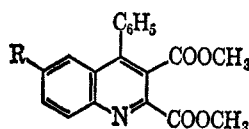
(1) Presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, Abstracts, p 8M.

(2) This investigation was supported in part by a National Science Postdoctoral Fellowship to N. D. H., and in part by a grant (CA-02551) to Princeton University from the National Cancer Institute, National Institutes of Health.

(3) J. B. Hendrickson, R. Rees, and J. F. Templeton, *J. Am. Chem. Soc.*, **86**, 107 (1964).

(4) D. S. James and P. E. Fanta, *J. Org. Chem.*, **27**, 3346 (1962).

TABLE I  
DIMETHYL 4-PHENYLACRIDINATES



R	Registry no.	Yield, %	Mp, °C	Formula	Anal., %					
					Calcd			Found		
					C	H	N	C	H	N
H	10039-67-5	76	129-130	C <sub>19</sub> H <sub>15</sub> NO <sub>4</sub>	71.02	4.71	4.36	70.76	4.86	4.40
Cl	10037-28-2	78	162.5-163	C <sub>19</sub> H <sub>14</sub> NO <sub>4</sub> Cl	64.14	3.97	3.94	64.17	4.32	3.77
Br	10037-29-3	70	169.5-170.5	C <sub>19</sub> H <sub>14</sub> NO <sub>4</sub> Br	57.01	3.53	3.50	56.79	3.09	3.58
NO <sub>2</sub>	10037-30-6	14	149-150	C <sub>19</sub> H <sub>14</sub> N <sub>2</sub> O <sub>6</sub>	62.30	3.86	7.64	61.79	3.90	7.25

solution was filtered hot. Addition of cold hexane to the filtrate resulted in precipitation of 1.1 g (77%) of white flakes. The analytical sample, mp 97.5-99°, was prepared by recrystallization from benzene-hexane (1:1).

Anal. Calcd for C<sub>14</sub>H<sub>13</sub>NO<sub>4</sub>: C, 64.86; H, 5.06; N, 5.40. Found: C, 64.60; H, 5.13; N, 5.29.

The nmr spectrum (CCl<sub>4</sub>) showed the 4-methyl protons as a singlet at 2.67, the two ester methyl groups as singlets at 3.92 and 3.98, and the aromatic protons as a multiplet at 7.4-8.2 ppm (ratio 3:3:3:4).

8-Acetyl-2-carbomethoxy-4(1H)-quinolone was prepared from the above enamine adduct by fusion of 2.78 g in a test tube, followed by boiling of the melt for 5 min. The residual red oil was cooled, taken up in a minimum of hot methanol, and cooled to give 1.27 g of pink crystals. These were sublimed *in vacuo* to give 1.21 g (49%) of yellow crystals, mp 176-177°.

Anal. Calcd for C<sub>13</sub>H<sub>11</sub>NO<sub>4</sub>: C, 63.66; H, 4.52; N, 5.71. Found: C, 63.75; H, 4.33; N, 5.62.

The nmr spectrum (DCCl<sub>3</sub>) showed the acetyl methyl protons as a singlet at 2.80, the ester methyl protons as a singlet at 4.08, an aromatic multiplet at 7.2-8.6, the C-3 aromatic proton as a doublet (*J* = 2 cps, split by the N-H proton) at 6.92, and the N-H proton as a broad signal at 12.86 ppm (ratio 3:3:3:1:1).

2-Amino-5-bromobenzophenone was prepared from 5-bromo-isatoic anhydride,<sup>11</sup> benzene, and aluminum chloride according to the method described for the preparation of 2-aminobenzophenone.<sup>12</sup> Recrystallization of the crude product first from ethanol and then from petroleum ether (bp 30-60°)-benzene (1:1) gave the desired product in 21% yield, mp 109-110° (lit.<sup>13</sup> mp 110°).

**Registry No.**—Dimethyl 4-methylacridinate, 10037-31-7; 8-acetyl-2-carbomethoxy-4(1H)-quinolone, 10037-32-8; enamine adduct, 10037-33-9.

(11) R. Adams and H. R. Snyder, *J. Am. Chem. Soc.*, **60**, 1411 (1938).

(12) F. S. Statham, *J. Chem. Soc.*, 213 (1951).

(13) J. F. J. Dippy and V. Moss, *ibid.*, 2205 (1952).

### Butadiene from Vinyl Chloride. The Platinum(II)-Catalyzed Coupling of Vinyl Halides

FRANK N. JONES

Contribution No. 1178 from the Central Research Department,  
Experimental Station, E. I. du Pont de Nemours and Company,  
Wilmington, Delaware

Received December 30, 1966

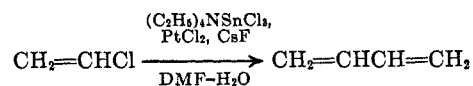
Vinyl halides having  $\beta$  hydrogens generally undergo  $\beta$  elimination to acetylenes in preference to coupling to conjugated dienes under Wurtz reaction conditions.<sup>1,2</sup>

(1) A. Kirmann and C. Moureu, *Compt. rend.*, **181**, 671 (1925).

(2) C. Prevost and C. Moureu, *ibid.*, **184**, 1460 (1927).

No method of converting vinyl halides to butadiene has been described.

We have found that reductive coupling of vinyl chloride to butadiene is effected at 25° by Sn(II) in solutions containing catalytic amounts of PtCl<sub>2</sub>. The reaction is cocatalyzed by cesium fluoride. Under the best conditions, conversion to butadiene is nearly quantitative.



The coupling reaction is best performed by stirring a mixture of 2 molar equiv of (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NSnCl<sub>2</sub>, 1 equiv of PtCl<sub>2</sub>, and CsF in dimethylformamide (DMF) containing 2% water under an atmosphere of vinyl chloride. When (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NSnCl<sub>2</sub> is used in excess, the yield is 97% based on vinyl chloride in 40 hr at 25°. When water is omitted from the solvent, the reaction is slightly faster, but side reactions limit the yield of 85-90%. When CsF is omitted, the reaction is slow, being only 8% complete in 18 hr and 40% complete in 600 hr.

Besides DMF, the reaction can also be performed in acetonitrile or dimethyl sulfoxide (DMSO). The reaction is about as fast in acetonitrile as in DMF, but the latter is convenient because of its lower volatility. The reaction is slower in DMSO. Little or no coupling occurs when the solvent is ethanol, acetone, pyridine, or water. When tin(II) is introduced as stannous chloride dihydrate or as lithium trichlorostannite, yields are inferior.

A series of experiments was performed in which the Sn:Pt ratio was varied by changing the amount of PtCl<sub>2</sub> used. Cesium fluoride but not water was added to the reaction mixtures; the reactions were stopped after 18 hr at 25°. The conversions and yields are given in Table I. It is seen that the conversion to butadiene falls rapidly as the Sn:Pt ratio is increased above 5:1.

Mixtures of Pt(II) and Sn(II) chlorides in non-aqueous media are known to form intensely colored, labile coordination compounds in which the SnCl<sub>3</sub><sup>-</sup> anion acts as a donor ligand. Salts of the [(SnCl<sub>3</sub>)<sub>2</sub>-PtCl<sub>2</sub>]<sup>2-</sup> and [(SnCl<sub>3</sub>)<sub>5</sub>Pt]<sup>3-</sup> anions have been isolated from such solutions.<sup>3-5</sup> The intensely red solutions in which the reductive coupling reaction occurs almost certainly contain substantial amounts of these species. The data in Table I indicate that conversion of most of

(3) R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1691 (1963).

(4) A. G. Davies, G. Wilkinson, and J. F. Young, *ibid.*, **85**, 1692 (1963).

(5) R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *ibid.*, **87**, 658 (1965).