Selective Catalytic Hydrogenation of Aromatic Nitro Groups in the Presence of Acetylenes. Synthesis of (3-Aminophenyl)acetylene via Hydrogenation of Dimethylcarbinol Substituted (3-Nitrophenyl)acetylene over Heterogeneous Metallic Ruthenium Catalyst

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Received September 18, 1978

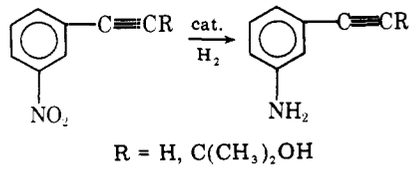
Heterogeneous metallic ruthenium catalyst was found to be selective for preferential hydrogenation of aromatic nitro groups in the presence of acetylenes. Thus, 2-methyl-4-(3-nitrophenyl)-3-butyn-2-ol was hydrogenated to 2-methyl-4-(3-aminophenyl)-3-butyn-2-ol in essentially quantitative yields. Removal of the dimethylcarbinol blocking group to afford (3-aminophenyl)acetylene was achieved by simple heating in the presence of a catalytic amount of caustic. (3-Nitrophenyl)acetylene itself was initially hydrogenated to (3-aminophenyl)acetylene, but the catalyst was poisoned through strong adsorption.

Recent interest in (aminophenyl)acetylenes as end-capping agents in the synthesis of high performance polyimide resins[1,2] prompts us to report on the selective catalytic hydrogenation of 2-methyl-4-(3-nitrophenyl)-3-butyn-2-ol to the corresponding amine over a heterogeneous metallic ruthenium catalyst.

The literature indicates that only chemical reducing agents such as ferrous sulfate,[1] sodium hydrosulfite,[2] and zinc in ammonia[3] have been used to reduce aromatic nitro groups in phenylacetylenes. While the yields range from poor to excellent, most of the reductions with these reagents operate in high dilution, require a large excess of reagents, involve filtration of colloidal precipitates, and in general are too tedious for a large-scale production. Catalytic hydrogenation with molecular hydrogen would eliminate many of the above difficulties, but no satisfactory method for the selective hydrogenation of nitro groups in the presence of an acetylenic triple bond has been reported as yet. The hydrogenation of nitro groups in olefins, less reactive than acetylenes, is already problematic, except for cases involving special structures.[4] Kuzembaev et al. studied the competitive hydrogenation of phenylacetylene and nitrobenzene over nickel and platinum on alumina catalysts and found the addition of hydrogen to the acetylene to be nonselective.[5] Hydrogenation of phenylacetylene over palladium on alumina occurred 2–3 times faster in the presence of nitrobenzene than in its absence.[6] Hennion and Barrett hydrogenated propargyl esters of *p*-nitrobenzoic acid over palladium on barium sulfate and converted the ethynyl group to a vinyl group, without affecting the nitro group.[7] Grob and Jenny hydrogenated 2-nitrooctadec-4-yn-1,3-diol over Lindlar catalyst and obtained 2-nitrooctadec-4-en-1,3-diol selectively.[8] The nitro group and the acetylene bond are the two most reactive species known toward catalytic hydrogenation. Therefore, a wide spectrum of products could be expected from the hydrogenation of (3-nitrophenyl)acetylene, since the nitro group, the ring, and the acetylene bond can all be hydrogenated.

Results and Discussion

A screening investigation was conducted in which noble metal and nickel catalysts were tested for hydrogenation of (3-nitrophenyl)-acetylene (Table I). The results showed ruthenium to be very selective toward (3-aminophenyl)acetylene formation. Ruthenium on charcoal was active at room temperature, while ruthenium on alumina, or unsupported ruthenium dioxide, required temperatures of 50 °C or higher. Rhodium on alumina and Raney nickel were nonselective at room temperature but showed a substantial improvement in selectivity to (3-aminophenyl)acetylene at −30 °C, conditions under which rates were impractical. Osmium showed promise at low conversions but was selective at high conversions. In each case a very high catalyst to substrate ratio was used.



(1)

R = H, $C(CH_3)_2OH$

To determine catalyst life, recycle runs were carried out with 5% ruthenium on charcoal (Table II). The catalyst became completely inactive after only three cycles. Initially it was assumed that the (aminophenyl)acetylene being produced probably trimerized to give a triphenylbenzene structure (as in the case of phenylacetylene hydrogenation)[9] and led to catalyst deactivation through coating of the surface. Analysis of the residue, however, identified the byproducts largely as a mixture of 3,3′-diethynylazo- and 3,3′-diethynylazoxybenzenes, and none of the speculated trimer. It appears then that deactivation results from an overly strong adsorption of terminal acetylene on the catalyst, since nitrobenzene and *p*-nitrotoluene were quantitatively converted to the corresponding amines over the same ruthenium catalysts,[10] without any evidence of poisoning. The spent catalysts were fully restored to their initial activity by reactivation in water (200 °C, 1000 psig H_2, 1 h), but such a procedure failed to restore their selectivity.

The relative reactivities for several model compounds were determined by a competitive method in order to establish structure–reactivity relationships (Table III). The results with acetylenic compounds showed the reactivity sequence RC≡CH > ArC≡CH > ArC≡CR. Nitrobenzene was more reactive than nitrocyclohexane. The overall sequence, on a hydrogen uptake basis, is RC≡CH > ArC≡CH ~ $ArNO_2$ > ArC≡CR ~ RNO_2. The lower reactivity of the disubstituted acetylene compared to that of phenylacetylene was assumed to be due to the more pronounced steric crowding, which hinders the contact between the functional group and the catalyst surface. If this assumption is correct, then by placing a blocking group on the acetylene portion of (3-nitrophenyl)acetylene, one could hope to maintain the high rate of nitro group hydrogenation, while at the same time protecting the catalyst from deactivation. A reasonable blocking group which could readily be added to and removed from (3-nitrophenyl)acetylene is the dimethylcarbinol group.[11] To test our postulate, 2-methyl-4-(3-nitrophenyl)-3-butyn-2-ol was prepared in a 40% yield by reacting (3-nitrophenyl)acetylene with acetone in liquid ammonia (eq 2). The same product is more elegantly obtained in a 90%

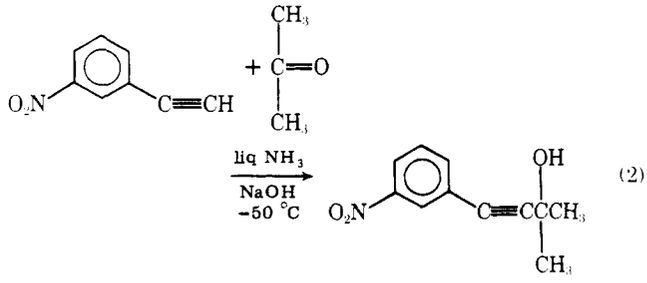


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Table I. Catalytic Hydrogenation of (3-Nitrophenyl)acetylene (NPA) Catalyst Screening[a]

expt no.	reaction conditions: temp, °C	pressure, psig H_2	time, min	catalyst	NPA,[h] % conversion	% selectivity (GLC): APA[c]	AS[d]	NS[e]	NEB[f]	EA[g]
1	100	1000	45	none	0	no reaction (blank run)				
2	100	1000	12	5% $Os/BaSO_4$	3	100	rxn stopped after low conversion			
3	120	1000	25	5% $Os/BaSO_4$	4	85	15	(continuation of run 2)		
4	100	1000	30	5% Os/C	73	22	18	42	13	5
5	25	50	120	5% Ru/C	92	96	3		1	
6	60	50	130	5% Ru/alumina	90	90	5	3	1	1
7	50	50	110	0.15 g RuO_2[b]	43	96	3		1	
8	26	50	8	5% $Pd/BaSO_4$	100			58	38	4
9	26	50	11	5% Pd/C	100			2	81	15
10	25	50	6	5% Pd/asbestos	85			66	34	
11	25	50	1	5% $Pd/CaCO_3$	100			30	60	10
12	24	50	4	Raney Ni	96	38	18	26	7	11
13	−30	50	147	Raney Ni	10	47	3	41		9
14	24	50	10	5% Rh/alumina	78	13	10	53		24
15	−30	50	190	5% Rh/alumina	37	53	1	33	13	
16	25	50	3	0.15 g PtO_2	81	1	6	67	24	2
17	−40	50	124	0.15 g PtO_2	14			83	17	

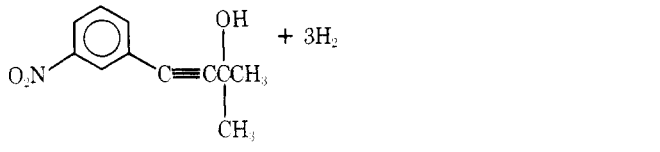
[a] Reactants: 1.0 g of catalyst, 2.0 g of NPA, 130 mL of isopropyl alcohol. [b] Methanol. [c] APA = (3-aminophenyl)acetylene; registry no. 54060-30-9. [d] AS = 3-aminostyrene; registry no. 15411-43-5. [e] NS = 3-nitrostyrene; registry no. 586-39-0. [f] NEB = 3-nitroethylbenzene; registry no. 7369-50-8. [g] EA = 3-ethylaniline; registry no. 587-02-0. [h] Registry no. 3034-94-4.

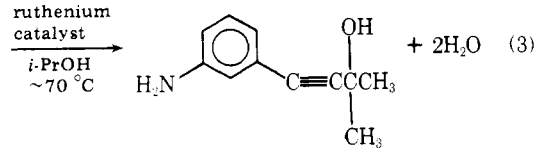
Table II. Catalytic Hydrogenation of (3-Nitrophenyl)acetylene (NPA) Catalyst Recycle Study[a]

expt no.	induction time, min	pressure drop, psig	reaction time, min	catalyst cycle no.	NPA, % conversion	% selectivity[b]: APA	AS	others	residue, % (GLC)[c]
18	23	35	126	1	100[d]	82	16	2	13.6
19	7	30	140	2	92	95	4	1	26.0
20	8	20	135	3	47	90	8	2	25.4
21[e]	1	10	21	1	100	91	8	1	7.7

[a] Reactants: 1.0 g 5% Ru/C (RIC), 2.0 g NPA, 130 mL isopropyl alcohol; 25 °C, 50 psig H_2. [b] Visible portion of product only (GLC). [c] By difference, internal standard method (GLC). [d] Overhydrogenated. Similar run with 50% NPA conversion gave 94% APA selectivity and 2.1% of residue. [e] 5% Ru/alumina (RIC), 50 °C, 50 psig H_2.

yield from palladium-catalyzed, copper-promoted condensation of *m*-bromonitrobenzene with 3-methyl-1-butyn-3-ol.[12] Hydrogenations of the blocked phenylacetylene (eq 3) are shown in Table IV. Results indicate that ruthenium is an excellent catalyst for selectively hydrogenating 2-methyl-4-(3-nitrophenyl)-3-butyn-2-ol to the corresponding amine. In some runs the reaction stopped after taking up a stoichiometric amount of hydrogen, but in most cases the reactions had to be terminated. Successful reuse of catalyst has been demonstrated, with no loss in activity and selectivity. The final reaction step (eq 4), removal of the protecting group, was easily achieved by heating





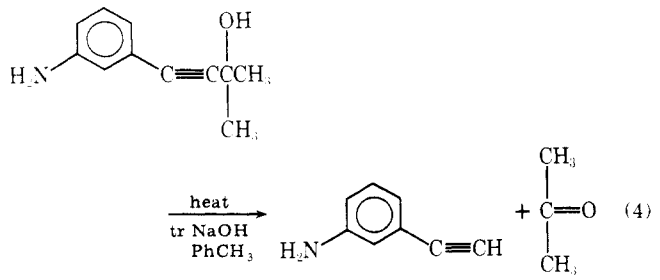


Table III. Competitive Hydrogenation of Model Compounds over Ruthenium on Charcoal Catalyst (25 °C, 50 psig H_2)

substrate	registry no.	rel reactivity per molecule	rel reactivity on H_2 uptake basis[b]
3-nitrostyrene		34.5	11.5
(3-nitrophenyl)acetylene		23.8	7.9
3-nitroacetophenone	121-89-1	16.2	5.4
3-bromonitrobenzene	585-79-5	11.8	3.9
3-chloronitrobenzene	121-73-3	7.0	2.3
p-nitrotoluene	99-99-0	3.0	1.0
1-octyne	629-05-0	2.3	2.3
nitrobenzene	98-95-3	2.1	0.7
phenylacetylene	536-74-3	1.00[a]	1.00[a]
nitrocyclohexane	1122-60-7	0.3	0.1
1-phenyl-1-butyne	622-76-4	0.2	0.2

[a] Assumed standard. [b] One mole to reduce acetylene; three moles to reduce NO_2. Reactivities were related to phenylacetylene using the expression $k_a/k_b = \log([A]_f/[A]_i)/\log([B]_f/[B]_i)$, where A and B refer to concentrations of the two substrates before and after the reaction. Chlorobenzene served as the internal standard. Conversion level: 1–3%.

under reflux in the presence of a catalytic amount of caustic. This reaction is an equilibrium reaction, and acetone formed must be removed from the system to drive reaction to completion.

An unsuccessful attempt was made to reduce (3-nitrophenyl)-acetylene using a homogeneous dichlorotris(triphenylphosphine)-ruthenium(II) catalyst[13] in isopropyl alcohol–benzene solvent (1/1,

Table IV. Hydrogenation of 2-Methyl-4-(3-nitrophenyl)-3-butyn-2-ol

expt no.	RH, g	solvent (mL)	catalyst type	catalyst g	reaction conditions: temp, °C	pressure, psig H_2	time, h	% RH conv	% selectivity to amine	remarks
22	2.1	toluene (150)	5% Ru/alumina	1	70	50–60	2.3	0	0	as RuO_2, no activation
23	2.1	toluene (150)	5% Ru/alumina	1	70	50–60	0.6	100	100	activated (200 °C, 1000 psig H_2, 1 h, water)
24	2.1	toluene (150)	5% Ru/alumina	1	70	50–60	0.2	79	100	activated (350 °C, H_2 flow, 3 h)
24	2.1	*i*-PrOH (150)	5% Ru/alumina	1	50	50–60	3.5[a]	100	100	
26	2.1	*i*-PrOH (100)	5% Ru/alumina	1	50	50–60	2.5	95	95[b]	1st cycle; ROC/RIC
27	2.1	*i*-PrOH (150)	5% Ru/alumina	1	50	50–60	5.0[a]	100	100	2nd cycle
28	2.1	*i*-PrOH (150)	5% Ru/alumina	1	50	50–60	4.3[a]	100	100	3rd cycle
29	2.1	*i*-PrOH (150)	5% Ru/alumina	1	50	50–60	3.5	99	98	4th cycle
30	20.5	*i*-PrOH (200)	5% Ru/alumina	1	70	40–60	24[a]	100	100	5th cycle
31	2.1	*i*-PrOH (150)	5% Ru/charcoal	0.5	20	35–60	21	99	95[b]	ROC/RIC
32	4.1	none	5% Ru/alumina	1	70	50–60	4.5	90	100	
33	2.1	*i*-PrOH (150)	5% Ru/alumina	1	50	50–60	4.3	100	58[c]	rnx allowed to proceed beyond stoich.
34	4.1	*i*-PrOH (150)	Raney Ni	3	20	50–60	0.3	100	0	2-methyl-4-(3-aminophenyl)butan-2-ol only; mp 65–66 °C
35	2.0	*i*-PrOH (150)	5% $BaRuO_3$/alumina[d]	1	50	50–60	1.8	85	90	

[a] Reaction stopped after stoichiometric pressure drop. [b] Traces of azo and azoxy reduction intermediates present (GLC). [c] Also present: 2-methyl-4-(3-aminophenyl)-3-buten-2-ol (22%) and 2-methyl-4-(3-aminophenyl)-butan-2-ol (14%). [d] This catalyst was prepared by T. P. Kobylinski and B. W. Taylor, U.S. Patent 3 097 968.

25 °C, 50 psig H_2, 16 h). The product was a mixture of 3-nitrostyrene (94%) and 3-nitroethylbenzene (6%) at 42% conversion. The active hydride species ($RuClH(Ph_3P)_3$) is therefore highly specific for the reduction of unsaturated C–C bonds and is not suited for (aminophenyl)acetylene preparation.

Experimental Section

All hydrogenations were carried our in a Parr low-pressure shaker or in a 1-L, 316-stainless steel, magnetically stirred autoclave (Autoclave Engineers, Inc., Erie, PA). Catalysts used in this work were purchased from Research Organic/Inorganic Chemical Corp. (ROC/RIC) or prepared in this laboratory. RuO_2 was purchased from K&K Laboratories. NMR spectra were obtained on a Varian T-60 spectrometer. Shifts are quoted in δ units, parts per million, relative to Me_4Si.

A typical procedure involved placing a substrate, solvent, and catalyst into a reactor and hydrogenating until the theoretical amount of hydrogen had been absorbed. After depressuring, the reaction mixture is filtered to recover the catalyst, and then solvent is removed on a rotary evaporator to give the product as the residue.

Preparation of Ruthenium Oxide Catalyst. γ-Alumina was ground to a powder, passed through a 100-mesh screen, and calcined (540 °C., 10 h). The calcined alumina was then impregnated by the incipient wetness technique using an aqueous solution of ruthenium chloride hydrate to result in 5% by weight ruthenium (calculated as the metal). The material was oven dried at 120 °C for 24 h and calcined (540 °C, 10 h). This catalyst exhibited no catalytic activity and required activation. Activation was achieved by simply passing a stream of hydrogen upward through a tube containing the catalyst (350 °C, 3 h) or by activation in water in an autoclave (200 °C, 1000 psig H_2, 1 h). Both modes of activation produced comparable results.

Preparation of 2-Methyl-4-(3-nitrophenyl)-3-butyn-2-ol. A mixture containing 7.4 g (0.05 mol) of (3-nitrophenyl)acetylene and 7.9 g (0.136 mol) of acetone was added over 20 min, while stirring, to 100 mL of liquid ammonia containing 2 g of crushed sodium hydroxide pellets at −50 °C. After 30 min, the reaction was allowed to warm up and the ammonia was allowed to evaporate off. The residue was treated with 50 mL of water and extracted with ether. After drying ($MgSO_4$) and evaporation of ether, 6.8 g of crude product was obtained. Distillation afforded 4.1 g (40%) of product, bp 162–4 °C, at 2 mm of Hg: NMR (acetone-d_6, Me_4Si) 1.6 (s, 6, CH_3), 4.63 (s, 1, OH), 7.6–8.3 (m, 4, ring); mp (flakes, from C_6H_{12}) 47.5–49.5 °C.

Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.37; H, 5.55; N, 6.75.

Removal of the Dimethylcarbinol Group. About 1.4 g of 2-methyl-4-(3-nitrophenyl)-3-butyn-2-ol was heated under reflux for 1 h in the presence of one pellet of sodium hydroxide in 15 mL of toluene. Analysis by GLC showed (3-nitrophenyl)acetylene to be formed in 98% yield: $n^{20}D$, 1.5887; NMR (CCl_4, Me_4Si) δ 3.2 (s, 1, C≡CH), 7.2–8.3 (m, 4, ring).

Hydrogenation of 2-Methyl-4-(3-nitrophenyl)-3-butyn-2-ol. A total of 20.5 g of nitro compound was hydrogenated in 200 mL of isopropyl alcohol over ruthenium catalyst (5% Ru/alumina, 1.0 g) in a standard Parr shaker (70 °C, 40–60 psig H_2) until the theoretical amount of hydrogen was consumed (monitored by pressure drop). Reaction mixture was cooled and filtered and isopropyl alcohol stripped off on a rotary evaporator to give 18 g of tan solid, mp 114–6 °C. Recrystallization from toluene gave cream colored needles: mp 117–8 °C; NMR ($CDCl_3$, Me_4Si) δ 1.56 (s, 6, CH_3), 3.8–4.6 (s, 3, NH_2, OH, exchanges with D_2O), and 6.6–7.2 (m, 4, ring); MS (*m/e*) 157 ($M - H_2O$)$^+$, 117 (M − acetone)$^+$, but no parent ion.

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.63; H, 7.38; N, 7.48.

Preparation of (3-Aminophenyl)acetylene from 2-Methyl-4-(3-aminophenyl)-3-butyn-2-ol. About 2 g of 2-methyl-4-(3-aminophenyl)-3-butyn-2-ol was dissolved in 15 mL of toluene containing one pellet (0.1 g) of sodium hydroxide which had been crushed

to a powder. The mixture was charged to a 100 mL, round-bottom flask equipped with a Dean-Stark trap and condenser. The mixture was refluxed for 1 h, and the acetone byproduct was removed periodically through the Dean-Stark trap. The reaction product was then cooled, and the mixture was filtered to remove particles of caustic. After the solvent was stripped, a quantitative yield of 3-aminophenylacetylene (1.4 g) of greater than 98% purity as analyzed by gas chromatography was obtained: $n^{20}D$, 1.6186; NMR (CCl_4, Me_4Si) δ 3.0 (s, 1, C≡CH), 3.6 (s, 2, NH_2, exchanges with D_2O), and 6.3–7.2 (m, 4, ring).

Hydrogenation of (3-Nitrophenyl)acetylene Using a Homogeneous Catalyst. One gram of (3-nitrophenyl)acetylene in 130 mL of isopropyl alcohol–benzene (1/1) was hydrogenated in the Parr shaker in the presence of 0.15 g of dichlorotris(triphenylphosphine)-ruthenium(II) and one drop of triethylamine. After reacting for 16 h (25 °C, 50 psig H_2), the amber solution was analyzed by GLC. The products formed were identified as 3-nitrostyrene (94%) and 3-nitroethylbenzene (6%) at 42% substrate conversion.

Registry No.—2-Methyl-4-(3-nitrophenyl)-3-butyn-2-ol, 33432-52-9; ruthenium oxide, 12036-10-1; 2-methyl-4-(3-aminophenyl)-3-butyn-2-ol, 69088-96-6; acetone, 67-64-1; alumina, 1344-28-1; ruthenium chloride, 10049-08-8.

References and Notes

(1) N. Bilow, A. L. Landis, and L. J. Miller, U.S. Patent 3 845 018 (1974).
(2) R. F. Kovar and F. E. Arnold, U.S. Patent 3 975 444 (1976).
(3) A. Burawoy and J. P. Critchley, *Tetrahedron*, 340 (1959).
(4) P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals", Academic Press, New York, 1976, p 178.
(5) K. K. Kuzembaev, K. A. Zhubanov, and D. V. Sokol'skii, *Dokl. Vses. Konf. Khim. Atsetilena, 4th*, **3**, 235 (1972); *Chem. Abstr.*, **79**, 77771r (1963).
(6) K. A. Zhubanov, D. V. Sokol'skii, E. P. Mazin, and N. G. Krupenya, *Zh. Prikl. Khim. (Leningrad)*, **47**, 1885 (1974); *Chem. Abstr.*, **81**, 151684z (1974).
(7) G. F. Hennion and S. O. Barrett, *J. Am. Chem. Soc.*, **79**, 2146 (1957).
(8) C. Grob and E. Jenny, U.S. Patent 3 118 946 (1964).
(9) D. V. Sokol'skii, G. N. Sharifkanova, and N. F. Noskova, *Dokl. Akad. Nauk SSSR*, **194**, 599 (1970).
(10) Nitrobenzene and *p*-nitrotoluene were routinely used by us to test the activity of ruthenium catalysts.
(11) L. Fieser and M. Fieser, "Advanced Organic Chemistry", Reinhold, New York, 1961, p 235.
(12) E. T. Sabourin and C. M. Selwitz, U.S. Patent Application 840 553 (1978).
(13) D. Evans, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Nature (London)*, **208**, 1203 (1965).

Exploitation of Intramolecular Photochemical Arylation of N-Substituted Enaminones. Efficient, General Synthesis of Heterocyclic Compounds

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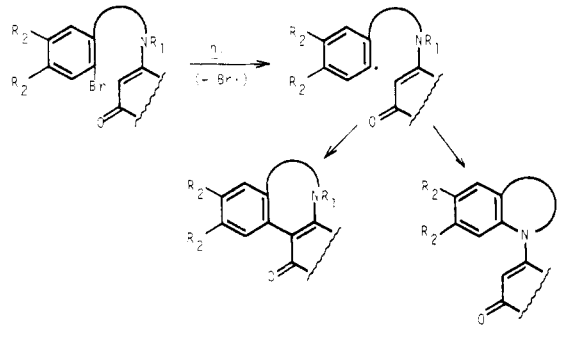
Received October 17, 1978

A general and facile photochemical method for the introduction of aryl groups into the enaminone system and its use in preparing heterocyclic compounds of varying ring sizes have been developed. Upon the photolysis of the *N*-phenyl (**3a, 3b,** and **5**), *N*-benzyl (**3c** and **7**), and *N*-phenethyl (**3d** and **9**) enaminones, intramolecular C-arylation proceeds to give the carbazoles (**4a, 4b,** and **6**), the phenanthridines (**9** and **10**), and the benzazepines (**12** and **13**), respectively. On the other hand, upon the photolysis of the *N*-phenethyl enaminone **15**, N-arylation occurs to give the indoline **18**. When the *N*-phenylpropyl enaminone **3e** is photolyzed, the benzazocine **22** and the tetrahydroquinoline **23** are obtained via competing process between C–C and C–N coupling, respectively. The applicability of this method to the synthesis of the naturally derived compound **28**, which is related to the lycorine alkaloids, is demonstrated.

Conjugated enamines such as enaminones are of current interest because of their unique characteristics different from those of both enamines and ketones with respect to physical properties and chemical behavior. The enaminone system, N—C=C—C=O, consists of three conjugated functional groups, i.e., amino, double bond, and carbonyl, and thus possesses five reaction sites. Despite the rather abundant literature on alkylation and acylation at these reaction sites, there appear to have been remarkably few reports of arylation, although such a process would be potentially useful.[1] We would like to report a photochemical method for the direct introduction of aryl groups into the enaminone system which provides a new, general synthesis of heterocyclic compounds with a variety of ring sizes. The reaction proceeds by a homolytic mechanism involving aryl radicals.



The required halo enaminones **3a–e** for photolysis were readily prepared by condensation of cyclic β-diketones **1** with appropriate primary amines **2** in fair to excellent yields (Table I). The structures of these products were determined by their analytical and spectral data (Table II).

Initial studies of photolysis of the halo enaminones so obtained were conducted with the *N*-phenyl derivatives **3a** and **3b** in dioxane–acetonitrile to afford the carbazoles **4a** and **4b** in 80 and 86% yield, respectively. Similar photolysis of the tertiary enaminone **5**, prepared by selective N-alkylation[2] with ethyl iodide and sodium hydride in toluene, gave the carbazole **6** in 64% yield.

The *N*-benzyl enaminone **3c** was next irradiated in dioxane–acetonitrile to give the phenanthridone **9** in 25% yield. When the tertiary enaminone **7**, prepared from **3c** by similar treatment with ethyl iodide described above for the preparation of **5**, was irradiated in dioxane, the diketo phenan-

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