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PHOTOACETYLATION OF SUBSTITUTED ADAMANTANES. EXCLUSIVE BRIDGEHEAD SUBSTITUTION AND A LARGE ρ* VALUE[1]

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Ionic substitution of adamantane gives a bridgehead product,[2] while radical substitution gives a bridge as well as a bridgehead product[3] depending on polar and steric factors.[4] Now we wish to report that photoacetylation[5] of adamantane (or a bridgehead substituted adamantane Ia-If) with biacetyl afforded the corresponding bridgehead acetyl derivative exclusively and in excellent or good yield. The procedure has a remarkable advantage in preparing acetyladamantanes directly under mild condition. It is especially useful in a case where the hydrocarbon has a substituent sensitive to acid.[6] The second interesting point to note is that the ρ* value obtained from relative reactivities of substituted adamantanes, Ia-f, (Table 1) was more negative than the ρ*'s observed for typical free radical substitutions or excited benzophenone (Table 2). The hydrogen abstracting species in the photoacetylation was concluded to be n, π* triplet of biacetyl on the basis of the observation that the acetylation was completely quenched by addition of pyrene as shown in Table 3. Thus the conclusion may be drawn that a hydrogen abstracting species,[9] oxygen atom of n, π* triplet of biacetyl, is of considerable bulkiness[10] and is considerably electrophilic, more electrophilic than n, π* triplet of benzophenone (see Table 2).

Thus, a solution of adamantane (5.0 g) and biacetyl (30 ml) in methylene chloride (80 ml) was irradiated in a pyrex vessel by a high pressure 100 w mercury lamp with water cooling and

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Table 1. Relative Rates of Bridgehead Hydrogen Abstraction from $Ad^{(1)}X$ by the Photoexcited Biacetyl

X	H	CH_3	OCH_3	CO_2CH_3	Br	CH_3, CH_3
σ^{*a}	0.00	-0.10	0.52	0.71	1.00	-0.20
$\frac{k_X}{k_H}$	1.00 ± 0.028	0.879 ± 0.008	0.403^b	0.220 ± 0.0036	0.0528 ± 0.0004	1.016 ± 0.012

a. inductive effects estimated from Taft's σ^* values for a series of CH_2X were adopted elsewhere. see ref. 14

b. taken as a standard, k was statistically corrected

Table 2. ρ Value of Homolytic H-Abstraction

substrate	abstracting species	kind of σ employed	reference
$1\text{-}X\text{-}C_{10}H_{14}\text{-}3\text{-}H^a$	$\cdot Br$	σ^*	-0.59^c
$1\text{-}X\text{-}C_{10}H_{14}\text{-}3\text{-}H$	$\cdot CCl_3$	σ^*	-0.40^d
$1\text{-}X\text{-}C_{10}H_{14}\text{-}3\text{-}H$	$CH_3(CH_3CO)\underset{\cdot}{C}-\underset{\cdot}{O}$	σ^*	-0.71
$(1\text{-}X\text{-}C_{10}H_{14}\text{-}3\text{-}H$	$(C_6H_5)_2\underset{\cdot}{C}-\underset{\cdot}{O}$	σ^*	$-0.32)^b$
$(1\text{-}X\text{-}C_{10}H_{14}\text{-}3\text{-}H$	$(CH_3)_3C-O\cdot$	σ^*	$-0.10)^b$

a. 1-substituted adamantanes.

b. extrapolated from ρ values of radical attack on substituted toluenes to that on substituted adamantanes.

c. G. J. Gleicher, J. L. Jackson, P. H. Owens, J. D. Unruh, Tetrahedron Lett., 833 (1969).

d. ref. 14

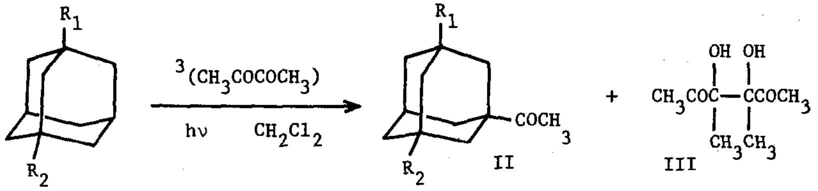
under nitrogen for 8.5 hours. Together with 3.9 g of unreacted adamantane, 1.33 g of practically pure 1-acetyladamantane, mp 53-54° (lit. 53-54°[11]) was obtained (92 % based on consumed adamantane). Similarly, substituted acetyladamantanes IIa-f were obtained, which showed satisfactory spectra and elemental analyses. IR absorption at 1700 cm^{-1}, (M-43) fragment

Table 3. Effect of Pyrene or Oxygen on the Photoacetylation of Adamantane

(2.0 g of adamantane, 10.0 g of biacetyl in 70 ml of methylene chloride)

condition	1-acetyladamantane (%)	1-adamantanol (%)
N_2, 2.0 hr	13.8	——
N_2, 235 mg of pyrene added,[7] 2.0 hr	0.0	——
O_2, 1.5 hr[8]	40.0	8.3

peak as well as molecular peak in massspectroscopy were found characteristic of II. A coupling product of acetylacetohydryl radical, III, was also obtained in an approximately equimolar amount to II, mp 96-97° (lit 95-96°,[12a] 96-97°[12b]).



I. a. R_1=R_2=H; b. R_1=CH_3, R_2=H; c. R_1=OCH_3, R_2=H*; d. R_1=CO_2CH_3, R_2=H;
e. R_1=Br, R_2=H; f. R_1=R_2=CH_3
* 1-adamantyloxyacetone was also obtained

The utillization of substituted adamantanes for the mechanistic study of the photosubstitution (or other photo reactions) seems to have a wide applicability, since adamantane skeleton is known as an ideal transmission media of polar effect[13, 14] and it has no absorption at common n, π* or π, π* absorption region.

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