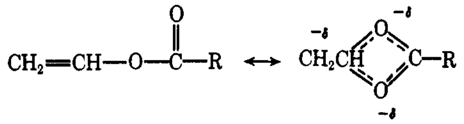
The formation of [A] adducts exclusively during the addition to vinyl esters could be explained by the following resonance structure:



The high electron density is at the terminal carbon. Regardless of the mechanism, it is obvious that here is another case where modern analytical methods show reactions to be more complicated than previously realized.

EXPERIMENTAL

General procedure: 0.2 mole of the olefin and 0.1 mole of the thiol were mixed in a 250-cc borosilicate glass round-bottomed flask and exposed at room temperature to a uv lamp for 4–6 hr. The examination by gas-liquid chromatography (glc) of the reaction mixture indicated the absence of free thiol. The unreacted volatile olefin was evaporated at reduced pressure, and the resulting adducts were examined again by glc and by nmr to determine the presence and the ratio of products type [A] to [B]. The latter, when present, showed the characteristic methyl doublet in the nmr spectrum. The relative amount of [A] and [B] formed was estimated from the area of the glc peaks (column SE 52, 10% silicone). In many cases, [A] was isolated by distillation at reduced pressure, and the physical properties of the distillates are listed in Tables I and II. The structure of these compounds was confirmed by nmr. Their glc showed single peaks. The same amount of [B] was formed when thiophenyl was reacted with allyl alcohol in presence of AIBN at 72°C for 6 hr. The addition to freshly distilled vinyl acetate and isopropenyl acetate was conducted at 0–5°C.

Identification of [B] adducts: The early distillates of the reaction mixtures were rich in [B] and 2-phenylthiopropanol, *p*-chlorophenylthio-2-propanol, 1-phenyl-2-phenylthiopropane, phenylthio-2-propylpropionate and 1,1-dimethyl-2-phenylthiopropane were identified by nmr and glc in these fractions. 1-Phenyl-2-phenylthiopropane and 2-benzylthio-1-propanol were isolated by glc from their respective reaction mixtures and their structures identified by ir. 2-Phenylthio-1-propanol and *p*-chlorophenylthio-2-propanol-1 were prepared independently by reacting allyl alcohol with thiophenol and *p*-chlorothiophenol, respectively, in presence of elementary sulfur (*3*, *8*). These adducts were found, by glc, to be identical to the Markovnikov-type adduct resulting from the free-radical catalyzed reaction of the respective mercaptans and allyl alcohol. 2-Methylthio-1-propanol was isolated by distillation and its structure confirmed previously by nmr, ir, and glc (*3*). Elemental analyses (sulfur) in agreement with theoretical values have been obtained and were submitted for review.

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Received for review January 13, 1971. Accepted August 19, 1971.

Gamma-Bromo- and Gamma-Iodoacetoacetanilides

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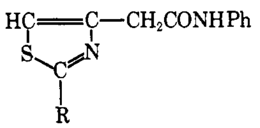
Gamma-bromoacetoacetanilides (I) (Table I) were prepared by the action of bromine on acetoacetanilides in acetic acid [or in chloroform (*3*)]:

$$\mathrm{CH_3COCH_2CONH{-}Ar} \xrightarrow[\mathrm{AcOH}]{\mathrm{Br_2}} \underset{\mathrm{I}}{\mathrm{BrCH_2COCH_2CONH{-}Ar}}$$

The infrared spectrum of Ia (KBr) showed bands at 3290 (NH), 1725 (CO), 1655 (CONH), 1600, 1550, 1500, 750, 690 cm^{-1} (monosubstituted phenyl). The nmr spectrum of Ia showed two singlets at δ 3.80 and 4.05 ppm assigned to the methylene groups of —COCH$_2$CO— and BrCH$_2$CO—, respectively.

Ia reacted with thiourea and with thioacetamide to give IIa, b, respectively.



IIa, R = NH$_2$
b, R = CH$_3$

When I was treated with sodium iodide in acetone or in methanol, γ-iodoacetoacetanilides (III) were obtained (Table II).

$$\underset{\mathrm{I}}{\mathrm{BrCH_2COCH_2CONH{-}Ar}} \xrightarrow{\mathrm{NaI}} \underset{\mathrm{III}}{\mathrm{ICH_2COCH_2CONH{-}Ar}}$$

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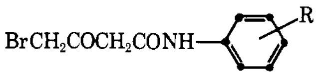
γ-Bromoacetoacetanilides were prepared by the action of bromine on acetoacetanilides in acetic acid; then they were transformed into the γ-iodo derivatives. Both classes of compounds were coupled with diazonium salts to give the corresponding α-arylazo derivatives. 2-Amino- and 2-methylthiazole-4-acetic acid anilides were obtained by reaction by γ-bromoacetoacetanilide with thiourea and thioacetamide, respectively. γ-Iodoacetoacetanilide was cyclized to 4-iodomethyl-2-quinolone. The ir and nmr spectra of these derivatives are discussed.

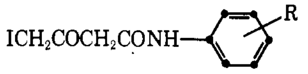
Table I. γ-Bromoacetoacetanilides[a]



	R	Yield, %	Mp, °C[b]	Formula	
Ib	*o*-CH_3[c]	68	142 dec	$C_{11}H_{12}BrNO_2$	(270.1)
c	*p*-CH_3[c]	71	147 dec	$C_{11}H_{12}BrNO_2$	(270.1)
d	*p*-OCH_3[c]	62	135 dec	$C_{11}H_{12}BrNO_3$	(286.1)
e	*p*-OC_2H_5[c]	62	146 dec	$C_{12}H_{14}BrNO_3$	(300.1)
f	*p*-Cl[d]	67	125–6	$C_{10}H_9ClBrNO_2$	(290.6)
g	*p*-Br[d]	64	123–5	$C_{10}H_9Br_2NO_2$	(335.0)

[a] Elemental analyses (C, H, N, Br) in agreement with theoretical values have been obtained and were submitted for review. [b] Melting points are not corrected. [c] Crystallized from ethanol. [d] Crystallized from chloroform.

Table II. γ-Iodoacetoacetanilides[a]

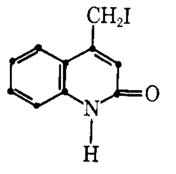


	R	Yield, %	Mp, °C[b]	Formula	
IIIa	H[c]	53	127 dec	$C_{10}H_{10}INO_2$	(303.1)
b	*o*-CH_3[c]	58	143 dec	$C_{11}H_{12}INO_2$	(317.1)
c	*p*-CH_3[c]	50	143 dec	$C_{11}H_{12}INO_2$	(317.1)
d	*p*-OCH_3[c]	46	124–5	$C_{11}H_{12}INO_3$	(333.1)
e	*p*-OC_2H_5[d]	43	137 dec	$C_{12}H_{14}INO_3$	(347.1)
f	*p*-Cl[c]	45	113–4	$C_{10}H_9ClINO_2$	(337.6)
g	*p*-Br[d]	48	122 dec	$C_{10}H_9BrINO_2$	(382.0)

[a] Elemental analyses (C, H, N, I) in agreement with theoretical values have been obtained and were submitted for review. [b] Melting points are not corrected. [c] Crystallized from ethanol. [d] Crystallized from chloroform–petroleum ether (bp 60–80°).

The γ- and α-iodoacetoacetanilides behaved differently toward ethanolic ferric chloride. While the γ-iodo derivatives gave an immediate violet color with ferric chloride, the α-iodo compounds (*1*) became greenish-brown which developed slowly.

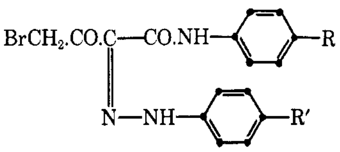
Cyclization of IIIa by concentrated sulfuric acid led to the formation of 4-iodomethyl-2-quinolone (IV).



IV

Acetoacetanilides have been known to couple with diazonium salts to give α-arylazo derivatives (*4*). Now we report that γ-bromo- (I) and γ-iodoacetoacetanilides (III) coupled with diazotized anilines produced the α-arylazo derivatives, V (Table III) and VI, (Table IV), respectively (4-halogeno-2,3-dioxobutananilides 2-arylhydrazones). (For the sake of convenience, these compounds are referred to here as arylazo derivatives, irrespective of their actual structures.)

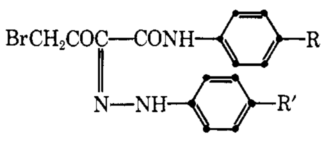
Table III. α-Arylazo–γ-Bromoacetoacetanilides[a]



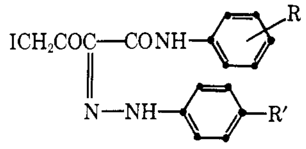
	R	R′	Yield, %	Mp, °C	Solvent	Formula	
Va	H	H	55	152	AcOH	$C_{16}H_{14}BrN_3O_2$	(360.2)
b	H	NO_2	48	198	Benzene-benzine	$C_{16}H_{13}BrN_4O_4$	(405.2)
c	CH_3	H	48	135	AcOH	$C_{17}H_{16}BrN_3O_2$	(374.2)
d	CH_3	Br	60	182	AcOH	$C_{17}H_{15}Br_2N_3O_2$	(453.1)
e	OCH_3	Br	45	179	Benzene	$C_{17}H_{15}Br_2N_3O_3$	(469.1)
f	OCH_3	NO_2	56	205	AcOH	$C_{17}H_{15}BrN_4O_5$	(435.2)
g	Br	Br	45	184	AcOH	$C_{16}H_{12}Br_3N_3O_2$	(518.0)
h	Br	NO_2	65	209	AcOH	$C_{16}H_{12}Br_2N_4O_4$	(484.1)
i	Cl	Br	40	191	AcOH	$C_{16}H_{12}Br_2ClN_3O_2$	(473.6)
j	Cl	NO_2	60	210	AcOH	$C_{16}H_{12}BrClN_4O_4$	(439.7)

[a] Elemental analyses (C, H, Br) in agreement with theoretical values have been obtained and were submitted for review.

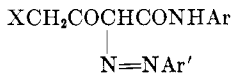
The spectra of Va indicated that these compounds existed in the hydrazone form rather than the azo structure, VII. Thus, the nmr spectrum of VIa showed no signal corresponding to the C—H hydrogen which would be present in the azo structure, VII. Also, the ir spectrum of Va pointed to a hydrazone structure; the carbonyl stretching vibration in γ-bromoacetoacetanilide (Ia) was shifted to a lower frequency in the case of the azo derivative, Va; this was attributed to the effect of conjugation of C=O with a C=N group and hydrogen bonding (*5*, *6*).



V



VI



$$XCH_2COCHCONHAr$$
$$N{=}NAr'$$

VII

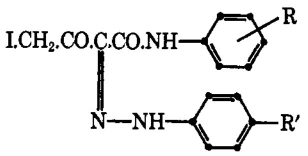
EXPERIMENTAL

Melting points were not corrected. Ir spectra were recorded on a Perkin-Elmer 457 grating Infrared Spectrophotometer (KBr pellets). Nmr spectra were recorded on a Varian A-60A spectrophotometer, with TMS as internal reference.

Acetoacetanilides. Acetoacetanilide, acetoaceto-*o*- and *p*-toluidide, and acetoaceto-*p*-anisidide were commercial products. The others were prepared according to the method of Frisch and Bogert (*2*).

Bromination of Acetoacetanilides—General Procedure. Acetoacetanilide (0.05 mole) dissolved in acetic acid (ca. 40 ml) was treated with bromine (0.05 mole) in acetic acid (20 ml),

Table IV. α-Arylazo–γ-Iodoacetoacetanilides[a]



	R	R′	Yield, %	Mp,[b] °C	Formula	
VIa	H	H	48	160	$C_{16}H_{14}IN_3O_2$	(407.2)
b	*o*-CH_3	CH_3	55	150	$C_{18}H_{18}IN_3O_2$	(435.2)
c	*p*-CH_3	H	56	169	$C_{17}H_{16}IN_3O_2$	(421.2)
d	*p*-CH_3	CH_3	45	167	$C_{18}H_{18}IN_3O_2$	(435.2)
e	*p*-OCH_3	H	60	185	$C_{17}H_{16}IN_3O_3$	(437.2)
f	*p*-OCH_3	CH_3	55	181	$C_{18}H_{18}IN_3O_3$	(451.2)
g	*p*-Cl	CH_3	50	164	$C_{17}H_{15}ClIN_3O_2$	(455.7)

[a] Elemental analyses (C, H, I) in agreement with theoretical values have been obtained and were submitted for review. [b] Crystallized from acetic acid.

and left overnight. The product that separated was collected and recrystallized from ethanol (9.5 grams), mp 137° dec (see Table I).

2-Aminothiazole–4-Acetic Acid Anilide (IIa). Compound Ia (2.6 grams) and thiourea (0.8 gram; 1 mole) were refluxed in ethanol (ca. 40 ml) for 3 hr. The solution was concentrated, made alkaline with ammonium hydroxide, and evaporated. The residue was collected and crystallized from aqueous methanol (charcoal) to give 1.2 grams (50%) of IIIa, mp 152–4°. Nmr (TFA): δ 4.03 (s, 2, CH_2). Found: C, 56.80; H, 4.99; N, 17.73; S, 13.59%. $C_{11}H_{11}N_3OS$ (233.3) required: C, 56.63; H, 4.75; N, 18.01; S, 13.74%.

2-Methylthiazole–4-Acetic Acid Anilide (IIb). Compound Ia (2.6 grams) and thioacetamide (0.8 gram) were refluxed in ethanol (30 ml) for 3 hr, then poured into cold water. The precipitate (1.6 grams; 65%) was collected and crystallized from water, mp 126–7°C. Found: C, 62.03; H, 5.14; N, 11.98; S, 13.69%. $C_{12}H_{12}N_2OS$ (232.3) required C, 62.04; H, 5.20; N, 12.06; S, 13.80%.

Action of Sodium Iodide on γ-Bromoacetoacetanilide—General Procedure. The bromo compound (4 grams) was dissolved in 50 ml of a 10% solution of anhydrous sodium iodide in acetone (or both constituents were separately dissolved in acetone, then mixed) at room temperature. After 1–2 hr, the brown solution was filtered (from sodium bromide) and evaporated. The residue was triturated with water and crystallized from ethanol, mp 127°C (depressed when mixed with α-iodoacetoacetanilide). When its ethanolic solution was treated with ferric chloride, a deep violet color appeared immediately. The γ-iodoacetoacetanilides obtained are listed in Table II.

The ir spectrum of IIIa (KBr) was similar to that of Ia; showing bands at 3290 (NH), 1720 (CO), and 1650 cm^{-1} (CONH). It was different from that of α-iodoacetoacetanilide, which showed absorption at 1360 (CH_3CO), and 875 cm^{-1} (CH_3) (bands which were absent from the spectra of Ia and IIIa).

The nmr spectrum of IIIa ($CDCl_3$) showed 2-methylene groups at δ 3.85 and 4.02 ppm. In contrast, the nmr spectrum ($CDCl_3$) of α-iodoacetoacetanilide showed a methyl group at δ 2.50 ppm.

Cyclization of γ-Iodoacetoacetanilide (IV). Two grams of IIIa were dissolved in ca. 5 ml of cold concentrated sulfuric acid and left at room temperature for 2–3 hr (heating on the water bath caused decomposition as evidenced by the evolution of violet vapors). The solution was then poured onto ice and the product was collected, washed with water, and crystallized from ethanol as colorless crystals, mp 240°C. Nmr spectrum (TFA): shows a methylene group at δ 4.90 ppm similar to that of 4-bromomethyl-2-quinolone at δ 4.92; and different from 4-methyl-2-quinolone which shows a methyl group at δ 2.97 ppm. Found: C, 42.41; H, 2.87; I, 44.25; N, 4.72%. $C_{10}H_8INO$ (285.1) required: C, 42.13; H, 2.83; I, 44.51; N, 4.91%.

α-Arylazo–γ-Halogenoacetoacetanilides—General Procedure. A cold solution of the appropriate diazonium salt (prepared from 0.01 mole of the aromatic amine dissolved in 5 ml of concentrated HCl and 10 ml of water, and treated with 2 grams of sodium nitrite in 5 ml of water) was added gradually with stirring to 0.01 mole of the γ-halogenoacetoacetanilide in ca. 20 ml of ethanol containing 3 grams of sodium acetate. After complete addition, the mixture was left for 1 hr in the ice bath. The yellow to orange solid that separated was collected, washed thoroughly with water and crystallized from acetic acid (cf. Tables IV).

The nmr spectrum of Va (TFA) showed a methylene group at δ 4.72 ppm in contrast with α-phenylazo-acetoacetanilide which showed ($CDCl_3$), a methyl group at δ 2.55 ppm.

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RECEIVED for review March 1, 1971. Accepted September 22, 1971.

Synthesis of Cyclobutanone

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Several procedures are available for the preparation of cyclobutanone (*1*, *5*), but all suffer from one or more drawbacks when large quantities (100 grams) of cyclobutanone are desired. Explosive materials (e.g., diazomethane), rigorously dry conditions, large quantities of solvents, expensive reagents, low yields, and lengthy procedures are some of these drawbacks. We describe here the preparation of large quantities of IV relatively free of such limitations.

During the course of other work (*6*), we developed a synthesis which easily produced large quantities (500 grams/run) of

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