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Reaction of 3,4,4-Trichloro-1-(4-methylphenyl)-3-buten-1-one with Amines

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Abstract—Reaction of 3,4,4-trichloro-1-(4-methylphenyl)-3-buten-1-one with amines results in replacement of the internal chlorine atom and is accompanied by prototropic allyl rearrangement leading to formation of the corresponding 3-amino-4,4-dichloro-1-(4-methylphenyl)-2-buten-1-ones. The reaction of the title compound with 2,4-dinitrophenylhydrazine yields 3,4,4-trichloro-1-(4-methylphenyl)-3-buten-1-one 2,4-dinitrophenylhydrazone and is not accompanied by allyl rearrangement.

Chlorine-containing unsaturated ketones are convenient synthons which are used for the preparation of biologically active compounds with various kinds of activity [1, 2]. These compounds can react with amines both with replacement of chlorine atoms and at the carbonyl group [3, 4], depending on the number and position of chlorine atoms and structure of the molecule. Reactions of chlorinated ketones with amines having several nucleophilic centers underlie a known method for building up heterocyclic systems [4–7]. We recently described a convenient procedure for synthesizing aryl trichloroallyl ketones starting from accessible trichlorovinylacetic acid [8]. The goal of the present study was to examine reactions of one of the ketones thus prepared, namely 3,4,4-trichloro-1-(4-methylphenyl)-3-buten-1-one (**I**), with primary (aniline, *tert*-butylamine) and secondary amines (piperidine, morpholine, diethylamine) and also with difunctional nucleophiles, such as 2-aminoethanol, ethylenediamine, and 2,4-dinitrophenylhydrazine.

We have found that the reaction of ketone **I** with aniline, 2-aminoethanol, ethylenediamine, and secondary amines involves replacement of the internal chlorine atom and is accompanied by prototropic allyl rearrangement. As a result, the corresponding 3-amino-4,4-dichloro-1-(4-methylphenyl)-2-buten-1-ones **II**–**VII** were obtained (Scheme 1). The reaction of ketone **I** with *tert*-butylamine was not selective, and it resulted in complete tarring of the reaction mixture despite variation of the conditions (temperature, solvent, and reactant ratio). The reaction of **I** with aniline was also accompanied by strong tarring, and the yield of product **II** did not exceed 20%. On the other hand, ketone **I** reacted with secondary amines and difunctional nucleophiles (ethylenediamine and 2-aminoethanol) in a fairly selective fashion, and the yield of amino ketones **III**–**VII** was 52–94%. In the reaction with ethylenediamine both amino groups of the nucleophile and two molecules of ketone **I** were involved, and the product was *N*,*N*′-bis-[1-dichloromethyl-3-(4-methylphenyl)-3-oxo-1-propenyl]ethylenediamine (**III**). 2-Aminoethanol reacted with **I** only at the amino group, while the hydroxy group remained unchanged.

The occurrence of allyl rearrangement during the reaction of ketone **I** with amines was additionally confirmed by independent synthesis of 4,4-dichloro-1-(4-methylphenyl)-3-morpholino-2-buten-1-one by treatment with morpholine of specially synthesized 3,4,4-trichloro-1-(4-methylphenyl)-2-buten-1-one (**Ia**), which is isomeric to **I**. Ketone **Ia** was prepared by acylation of toluene with 3,4,4-trichlorocrotonoyl chloride (Scheme 2). The amino ketones synthesized by the two methods were fully identical.

Ketone **I** reacted with 2,4-dinitrophenylhydrazine, following a classical pattern, i.e., at the carbonyl group with formation of 3,4,4-trichloro-1-(4-methylphenyl)-3-buten-1-one 2,4-dinitrophenylhydrazone (**VIII**, yield 95%). No allyl rearrangement occurred in this case.

The structure of products **II**–**VIII** was established on the basis of their elemental compositions and IR,

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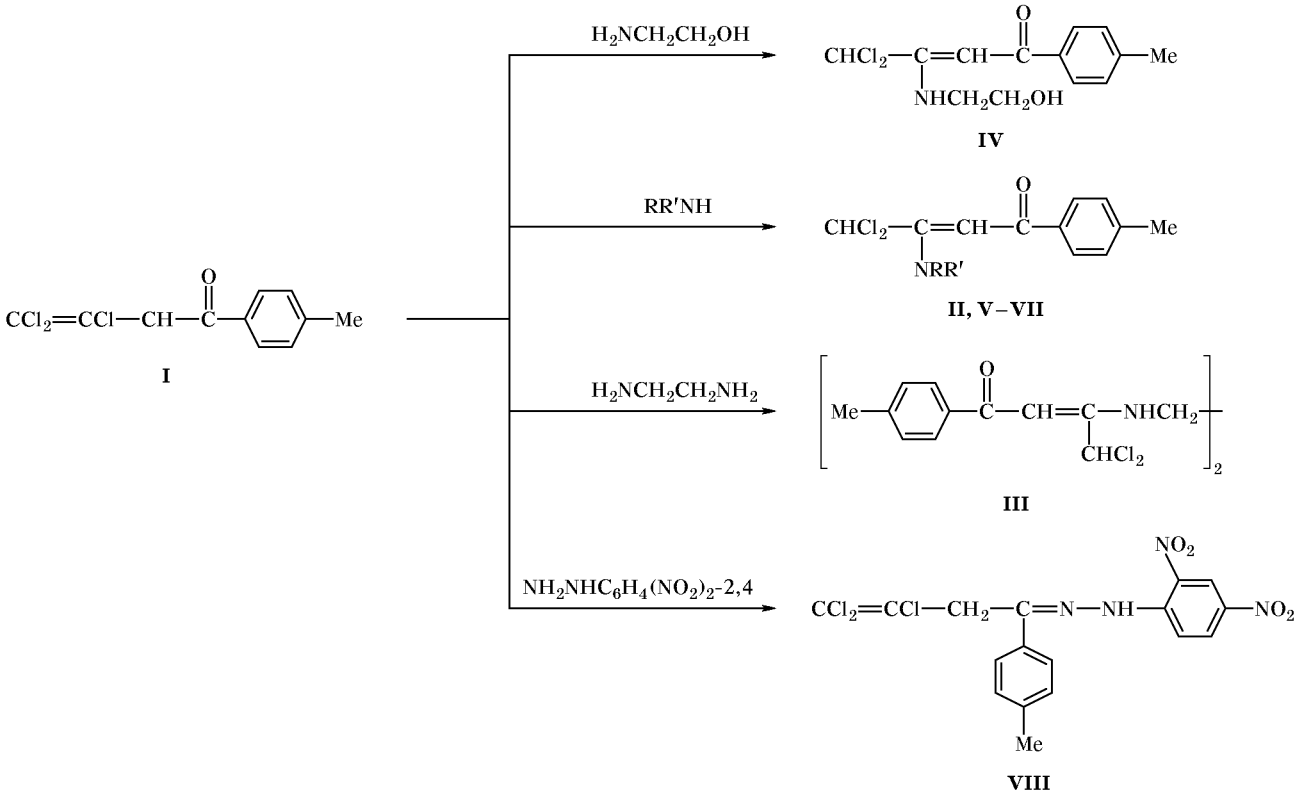
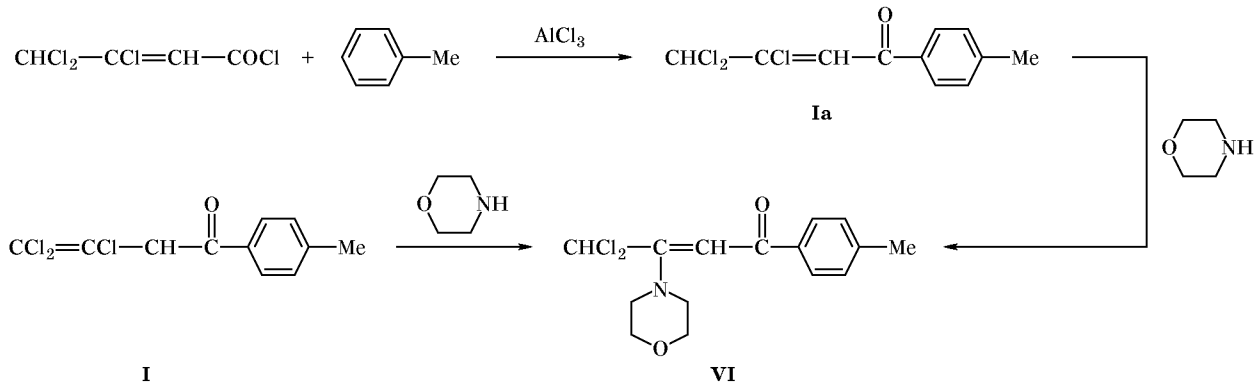
Scheme 1.



II, R = H, R′ = Ph; **V**, RR′ = $CH_2(CH_2)_2CH_2$; **VI**, RR′ = $(CH_2)_2O(CH_2)_2$; **VII**, R = R′ = Et.

Scheme 2.



^{1}H and ^{13}C NMR, and mass spectra (see table). In the IR spectra of **II**–**VII** stretching vibrations of the carbonyl group appeared as a strong absorption band in the region 1540–1606 cm^{-1}. The reduced carbonyl frequency is typical of α,β-unsaturated β-aminoketones [9]. A medium-intensity band at 1504–1660 cm^{-1} belongs to stretching vibrations of the double C=C bond. The N–H group in compounds **II**–**IV** and **VIII** gives rise to absorption at 3225–3281 cm^{-1}, and the hydroxy group in **IV** is characterized by absorption at 3457 cm^{-1}. A strong absorption band at 1612 cm^{-1} in the spectrum of hydrazone **VIII** corresponds to the C=N bond.

The ^{1}H NMR spectra of compounds **II**–**VII** lack characteristic signal from CH_2 group at δ 4.25 ppm, which is present in the spectra of initial ketone **I**, but two singlets in the region δ 5.65–9.14 ppm are present, which belong to protons of the =CH– and

Yields, melting points, IR and ^{1}H NMR spectra, and elemental analyses of amino ketones **II**–**VII** and dinitrophenylhydrazone **VIII**

Comp. no.	Yield, %	mp, °C	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm
II	20	185–186 (decomp.)	1596 (C=O); 1574, 1607, 1660 (C=C); 749, 781 (C−Cl); 3275 (NH)	2.41 s (3H, CH_3), 6.48 s (1H, =CH), 6.75 s (1H, $CHCl_2$), 7.50 m (9H, H_{arom}), 12.05 br.s (1H, NH)
III	52	142–144 (decomp.)	1606 (C=O); 1551, 1583 (C=C); 737, 776 (C−Cl); 3225 (NH)	2.38 s (6H, CH_3), 3.96 m (4H, $2CH_2$), 6.02 s (2H, =CH), 6.23 s (2H, $CHCl_2$), 7.21 d (4H, H_{arom}), 7.76 d (4H, H_{arom}), 11.02 br.s (2H, NH)
IV	80	78–80	1606 (C=O); 1544, 1580 (C=C); 748, 777 (C−Cl); 3272 (NH); 3457 (OH)	1.90 br.s (1H, OH), 2.38 s (3H, CH_3), 3.84 m (4H, CH_2), 6.07 s (1H, =CH), 6.34 s (1H, $CHCl_2$), 7.21 d (2H, H_{arom}), 7.77 d (2H, H_{arom}), 11.15 br.s (1H, NH)
V	87	107–109	1548 (C=O); 1574, 1604, 1620 (C=C); 760, 796 (C−Cl)	1.74 m (6H, CH_2C), 2.39 s (3H, CH_3), 3.62 m (4H, CH_2N), 5.77 s (1H, $CHCl_2$), 7.20 d (2H, H_{arom}), 7.76 d (2H, H_{arom}), 8.99 s (1H, =CH)
VI	94	108–110	1543 (C=O); 1564, 1599, 1620 (C=C); 754, 799 (C−Cl)	2.38 s (3H, CH_3), 3.59 m (4H, CH_2N), 3.70 m (4H, CH_2O), 5.79 s (1H, $CHCl_2$), 7.20 d (2H, H_{arom}), 7.75 d (2H, H_{arom}), 8.86 s (1H, =CH)
VII	80	78–80	1540 (C=O); 1568, 1601 (C=C); 769, 795 (C−Cl)	1.31 t (6H, CH_3), 2.39 s (3H, CH_3), 3.59 q (4H, CH_2), 5.65 s (1H, $CHCl_2$), 7.21 d (2H, H_{arom}), 7.75 d (2H, H_{arom}), 9.14 s (1H, =CH)
VIII	95	151–152	1612 (C=N); 1537, 1590 (C=C); 1340, 1500 (NO_2); 744, 837 (C−Cl), 3281 (NH)	2.43 s (3H, CH_3), 4.18 s (2H, CH_2), 7.28 d (2H, H_{arom}), 7.72 d (2H, H_{arom}), 8.10 d (1H, H_{arom}), 8.39 d.d (1H, H_{arom}), 9.15 d (1H, $H_{arom.}$), 11.44 br.s (1H, NH)

Comp. no.	Found, %				Formula	Calculated, %				*M*	
	C	H	Cl	N		C	H	Cl	N	found[a]	calcd.
II	63.98	4.45	22.50	4.52	$C_{17}H_{15}Cl_2NO$	63.77	4.72	22.14	4.37	319	320.21
III	56.38	5.11	27.33	5.55	$C_{24}H_{24}Cl_4N_2O_2$	56.05	4.70	27.57	5.45	256	514.28
IV	54.38	5.45	24.51	4.71	$C_{13}H_{15}Cl_2NO_2$	54.18	5.25	24.61	4.86	287	288.17
V	61.67	6.01	23.08	4.58	$C_{16}H_{19}Cl_2NO$	61.55	6.13	22.71	4.49	311	312.24
VI	57.02	5.80	23.00	4.32	$C_{15}H_{17}Cl_2NO_2$	57.34	5.45	22.57	4.46	313	314.21
VII	60.33	6.80	24.05	4.33	$C_{15}H_{19}Cl_2NO$	60.01	6.38	23.62	4.67	299	300.23
VIII	46.45	3.31	23.65	12.55	$C_{17}H_{13}Cl_3N_4O_4$	46.02	2.95	23.98	12.63	442	443.67

[a] The molecular weights were determined by mass spectrometry (the M^+ values are given for the ^{35}Cl isotope); the mass spectrum of compound **III** contained no molecular ion, and the observed $M^+/2$ value is given).

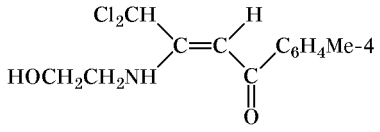
$CHCl_2$ groups. These data indicate that the process is accompanied by allyl rearrangement. Unlike products **II**–**VII**, the ^{1}H NMR spectrum of dinitrophenylhydrazone **VIII** contains a singlet at δ 4.18 ppm, which belongs to methylene protons. This means that the formation of hydrazone **VIII** is not accompanied by allyl rearrangement. In the ^{1}H NMR spectra of **II**–**IV** and **VIII** we also observed broadened singlets from the NH protons at δ 11.02–12.05 ppm. The hydroxy proton in **IV** appears at δ 1.90 ppm. The above signal assignments are confirmed by the ^{13}C NMR spectra of compounds **III**, **IV**, and **VIII**. The spectra of amino ketones **III** and **IV**, recorded with complete decoupling from protons and in the DEPT mode,

contain a signal at δ_C 68.46 and 68.55 ppm, respectively, due to carbon atom of the dichloromethyl group. The aliphatic =CH group gives a signal at δ_C 90.81 (**III**) and 89.90 ppm (**IV**). Compound **VIII** shows in the ^{13}C NMR spectrum no signals in the region δ_C 60–100 ppm, but a signal at δ_C 34.60 ppm is present, which is typical of an aliphatic methylene group [10].

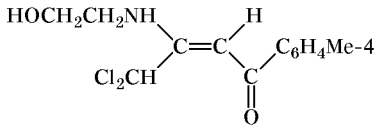
The assignments made on the basis of the ^{13}C NMR spectra are fairly reliable and are consistent with published data for structurally related compounds [10, 11]; these results were also used to interpret the ^1H NMR spectra of **II**–**IV** in the region of =CH and $CHCl_2$ signals. There were no difficulties in the identification of signals from these groups in the spectra of amino ketones **V**–**VII**: the singlet at δ 8.86–9.14 ppm corresponds to the olefinic =CH proton, and that at δ 5.65–5.77 ppm, to the $CHCl_2$ group. The ^1H NMR spectra of **II**–**IV** were interpreted using H–D exchange technique with ketone **IV** as an example. The =CH and $CHCl_2$ groups in **IV** give rise to two singlets at δ 6.07 and 6.34 ppm. When a solution of **IV** in CD_3OD was kept for 24 h at 20°C, no signal at δ 6.07 ppm was observed in the ^1H NMR spectrum. In the ^{13}C NMR spectrum of the same sample, the =CH signal appeared at δ_C 89.9 ppm as a triplet due to exchange with deuterium. Hence the ^1H signal at δ 6.07 ppm belongs to the olefinic =CH proton, and the signal at δ 6.34 ppm, to the $CHCl_2$ group. Likewise, in the ^1H NMR spectra of amino ketones **II** and **III**, the signals at δ 6.48 and 6.02 ppm, respectively, correspond to the =CH proton, whereas those located at δ 6.75 and 6.23 ppm belong to the $CHCl_2$ moiety.

The electron-impact mass spectra of compounds **II** and **IV**–**VIII** contain the molecular ion peaks and fragment ion peaks arising from elimination of chlorine and hydrogen atoms and aryl groups from the molecular ion. The isotope ratio in the molecular ion clusters is equal to 100 : 65 for compounds **II** and **IV**–**VII** and 100 : 98 : 32 for **VIII**, indicating the presence of, respectively, two and three chlorine atoms in the molecule [12, 13]. Compound **III** gives no molecular ion peak in the mass spectrum, but a low-abundand isotope cluster corresponding to $M^+/2$ is observed.

Amino ketones **II**–**VII** can exist as *cis* and *trans* isomers with respect to the C=C bond. According to the TLC and NMR data, they were isolated as single isomers. Their configuration was established by ^1H NMR spectroscopy using NOE technique with compound **IV** as an example. It is known that intramolecular NOE becomes appreciable when the distance between the corresponding hydrogen atoms does not exceed 3 Å [14, 15]. The results of MNDO–PM3 semiempirical quantum-chemical calculations [16, 17] of optimal geometry of both isomeric forms of amino ketone **IV** (**IVa** and **IVb**) showed that the distance between the hydrogen atoms in the $CHCl_2-C=CH-$ fragment of **IVa** is 2.25 Å; the corresponding distance in structure **IVb** is 3.77 Å:



IVa

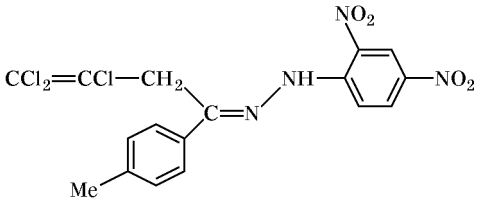


IVb

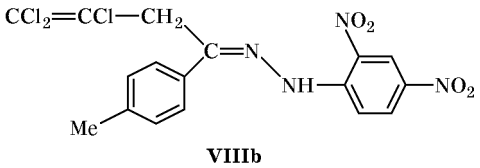
Selective irradiation of a sample of ketone **IV** at a frequency corresponding to the =CH resonance (δ 6.07 ppm) gave a response at δ 6.34 ppm, corresponding to the $CHCl_2$ group. Therefore, amino ketone **IV** should be assigned structure **IVa** with *cis* arrangement of the $CHCl_2$ group and olefinic proton. This conformation could give rise to intramolecular hydrogen bond N–H···O=C which stabilizes the molecule and is typical of β-aminovinyl ketones [18]. The presence of intramolecular hydrogen bond is confirmed by the reduced stretching vibration frequencies of the amino groups in the IR spectra of compounds **II**–**IV** (3225–3275 cm^{-1}).

Theoretically, dinitrophenylhydrazone **VIII** can exist as two isomers with *cis* (**VIIIa**) and *trans* (**VIIIb**) arrangement of the dinitrophenyl and trichloroallyl fragments with respect to the C=N bond. According to our results, hydrazone **VIII** is formed (methanol, 20–25°C, 3 h) as a single isomer. However, when a solution of this isomer in methanol was heated under reflux or the reaction of **I** with 2,4-dinitrophenylhydrazine was carried out in boiling methanol, a mixture of two isomers at a ratio of 2 : 5 was obtained. The isomers were separated by column chromatography on silica gel and were identified on the basis of the ^1H NMR spectra using the aromatic solvent-induced shift technique (ASIS). This method implies that replacement of an aliphatic solvent by aromatic induces shifts of ^1H signals, the maximal shift being observed for a group located *cis* with respect to the dinitrophenylhydrazone moiety [19]. In the case of isomers **VIIIa**/**VIIIb** it is most convenient and reliable to examine variation in the position of

the CH_2 group singlet, for signals from aromatic protons overlap. On replacement of $CDCl_3$ by C_6D_6, the strongest shift ($\Delta\delta$ 36 Hz) was observed for the isomer formed at room temperature. Therefore, it should be assigned structure **VIIIa** with *cis* arrangement of the trichloroallyl and dinitrophenyl groups. The other isomer ($\Delta\delta$ 10 Hz), which is obtained at elevated temperature or is formed from the first one on heating in boiling methanol, is likely to have structure **VIIIb**. According to the results of MNDO–PM3 semiempirical quantum-chemical calculations [15, 16] performed with complete gradient optimization of geometric parameters, the heat of formation of isomer **VIIIa** is greater by 2.96 kcal/mol than that of **VIIIb**. Thus structure **VIIIb** is thermodynamically more favorable, and isomer **VIIIa** is converted into **VIIIb** on heating.



VIIIa



VIIIb

EXPERIMENTAL

The IR spectra were recorded on a Protege-460 Fourier spectrometer from samples pelleted with KBr. The NMR spectra were obtained on a Tesla-567A instrument operating at 100 MHz (for ^1H); $CDCl_3$ was used as solvent, and the chemical shifts were measured relative to TMS. The mass spectra (50 eV) were run on an MKh-1320 mass spectrometer.

3,4,4-Trichloro-1-(4-methylphenyl)-3-buten-1-one (I) was synthesized from 3,4,4-trichloro-3-butenoyl chloride and toluene according to the procedure reported in [8].

3,4,4-Trichloro-1-(4-methylphenyl)-2-buten-1-one (Ia) was obtained as described in [8], by condensation of 3,4,4-trichloro-2-butenoyl chloride [20] and toluene in the presence of $AlCl_3$. Yield 61%, mp 68–69°C. IR spectrum, ν, cm^{-1}: 1661 (C=O); 1599 (C=C); 757, 821 (C–Cl). ^1H NMR spectrum, δ, ppm: 2.43 s (3H, CH_3), 6.34 s (1H, $CHCl_2$), 7.27 s (1H, $=CH_{aliph}$), 7.29 d (2H, H_{arom}), 7.83 d (2H, H_{arom}). Found, %: C 50.16; H 3.47; Cl 40.30. $[M]^+$ 262 (for ^{35}Cl). $C_{11}H_9Cl_3O$. Calculated, %: C 50.13; H 3.44; Cl 40.36. *M* 263.55.

3-Anilino-4,4-dichloro-1-(4-methylphenyl)-2-buten-1-one (II). A mixture of 2 g (7.6 mmol) of 3,4,4-trichloro-(4-methylphenyl)-3-buten-1-one (**I**) and 1.42 g (15.2 mmol) of aniline in 20 ml of dry benzene was refluxed for 25 h. The solvent was removed under reduced pressure, 50 ml of hexane was added with stirring to the oily residue, and the precipitate was filtered off, washed with water, hexane, and ether, and dried under reduced pressure. Yield 0.49 g (20%), mp 185–186°C (decomp.).

***N*,*N*′-Bis[1-dichloromethyl-3-(4-methylphenyl)-3-oxo-1-propenyl]ethylenediamine (III).** Ketone **I**, 1 g (3.8 mmol), was dissolved in 10 ml of ether, 0.5 g (8.3 mmol) of ethylenediamine in 5 ml of ether was added dropwise, and the mixture was stirred for 4 h at 20°C. The precipitate was filtered off, washed with water and ether, and dried under reduced pressure. Yield 0.51 g (52%). mp 142–144°C (decomp.). ^{13}C NMR spectrum, δ_C, ppm: 21.83 (CH_3); 44.70 (CH_2N); 68.46 ($CHCl_2$); 90.81 ($=CH_{aliph}$); 128.13, 129.97 (CH_{arom}); 137.82, 142.89, 159.96, 190.80 (C_{quat}).

4,4-Dichloro-3-(2-hydroxyethylamino)-1-(4-methylphenyl)-2-buten-1-one (IV). A solution of 0.51 g (8.3 mmol) of 2-aminoethanol in 5 ml of ethanol was added dropwise to a mixture of 1 g (3.8 mmol) of ketone **I** and 10 ml of ethanol, and the mixture was stirred at 20°C until it became homogeneous. It was then stirred for 5 h at 70°C, evaporated under reduced pressure to 1/3 of the initial volume, and poured onto ice. The residue was filtered off, washed with water, hexane, and ether, and dried under reduced pressure. Yield 0.87 g (80%). mp 80–82°C. ^{13}C NMR spectrum, δ_C, ppm: 21.81 (CH_3); 46.81 (CH_2N); 62.04 (CH_2O); 68.55 ($CHCl_2$); 89.90 ($=CH_{aliph}$); 121.01, 129.92 (CH_{arom}); 138.07, 142.56, 160.28, 189.76 (C_{quat}).

Amino ketones V–VII were synthesized as described above for compound **III**, from ketone **I** and the corresponding secondary amines. Their yields, melting points, spectral parameters, and analytical data are given in table. The same procedure was used to obtain 4,4-dichloro-1-(4-methylphenyl)-3-morpholino-2-buten-1-one (**VI**) from ketone **Ia** and morpholine (yield 80%).

3,4,4-Trichloro-1-(4-methylphenyl)-3-buten-1-one 2,4-dinitrophenylhydrazone (VIII). 2,4-Dinitrophenylhydrazine, 1.59 g (8 mmol), was dissolved in 15 ml of concentrated sulfuric acid, and the solution was added with stirring to a mixture of 20 ml of water

and 70 ml of methanol. The resulting solution was added dropwise to 2.12 g (8 mmol) of ketone **I** in 40 ml of methanol. The mixture was stirred for 3 h at 20–25°C, and the precipitate was filtered off, washed with water and ether, and dried under reduced pressure. Yield 3.39 g (95%). mp 150–151°C.

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