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Reaction of β-Ethoxyacrolein and *p*-Toluidine in Benzene Solution

Machiko Ono, Hinako Tanaka, and Shinzo Tamura*

School of Pharmaceutical Science, Toho University, 2-2-1, Miyama, Funabashi, 274, Japan

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1-Ethoxy-3-(*p*-methylphenylimino)-1-propene (IV) was prepared to elucidate the reaction sequence in the formation of 1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (malonaldehyde dianil of *p*-toluidine) (III) from β-ethoxyacrolein (I) and *p*-toluidine. The reaction of I and *p*-toluidine in benzene solution was followed spectrophotometrically, and evidence was obtained for the existence of IV as an intermediate in the formation of III.

Acetic acid acted as an effective catalyst for the formation of β-(*p*-toluidino)acrolein (II) from I and *p*-toluidine in benzene solution.

β-(*p*-Nitroanilino)acrolein (VIII) and β-(4-pyridylamino)acrolein 1-oxide (IX) were prepared from I and the corresponding amines under acidic conditions.

Keywords——acid-catalyzed aminolysis; 1-ethoxy-3-(*p*-methylphenylimino)-1-propene; 1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene; β-ethoxyacrolein; β-(*p*-toluidino)acrolein; β-(*p*-nitroanilino)acrolein; β-(4-pyridylamino)acrolein 1-oxide

In the previous paper[1] we reported a kinetic study of the formation of β-arylaminoacrolein derivatives from β-ethoxyacrolein (I) and aromatic primary amines. Neither triethylamine nor acetic acid acted as an effective catalyst for the formation of β-(*p*-toluidino)-acrolein (II) from I and *p*-toluidine in ethanolic solution. In the presence of acetic acid a large amount of 1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (malonaldehyde dianil of *p*-toluidine) (III) was formed as a by-product.

Since the rate of formation of III from II and *p*-toluidine in the presence of acetic acid was much slower than that of formation of III in the reaction solution of I and *p*-toluidine, it was concluded that the formation of the major part of III in the reaction of I and *p*-toluidine proceeds not *via* the reaction of II and *p*-toluidine but possibly *via* an intermediate, 1-ethoxy-3-(*p*-methylphenylimino)-1-propene (IV) (Chart I). This phenomenon could not be pursued then, because IV was unknown at that time.

In this paper we wish to report the preparation of IV and to present evidence for the presence of IV as an intemediate of the formation of III in the reaction of I and *p*-toluidine in benzene solution.

The preparation of IV was achieved as follows: II was added gradually to thionyl chloride under ice cooling. The precipitated crude 1-chloro-3-(*p*-methylphenylimno)-1-propene hydrochloride (V) was added, without purification, to an ethanolic solution of sodium ethoxide. Distillation of the product under reduced pressure followed by recrystallization from petroleum ether afforded IV as colorless crystals melting at 61°C. The results of elemental anal-

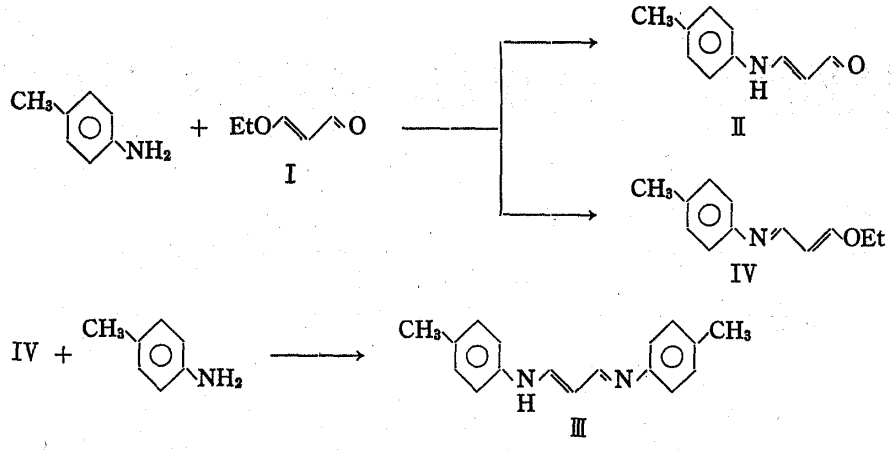


Chart 1

ysis and the ^{1}H nuclear magnetic resonance (^{1}H-NMR) spectrum of the sample were consistent with the structure IV. The signals of the ^{1}H-NMR spectrum of IV (about 0.2 M in chloroform-*d*) disappeared immediately after addition of an equimolar amount of *p*-toluidine to the solution, and signals attributable to III were observed, suggesting that IV reacts readily with *p*-toluidine to form III, and this was confirmed by a preparative experiment.

In the previous paper[1] we reported that the reaction of I and *p*-toluidine proceeded much more slowly in benzene than in ethanol, and that the molar ratio II to III was nearly

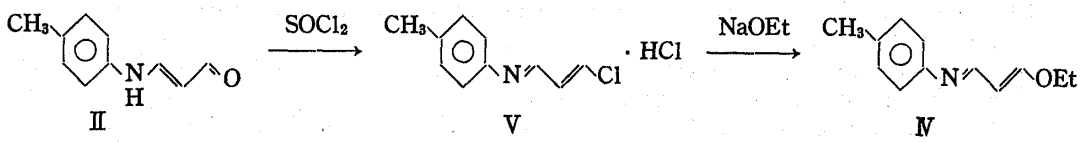


Chart 2

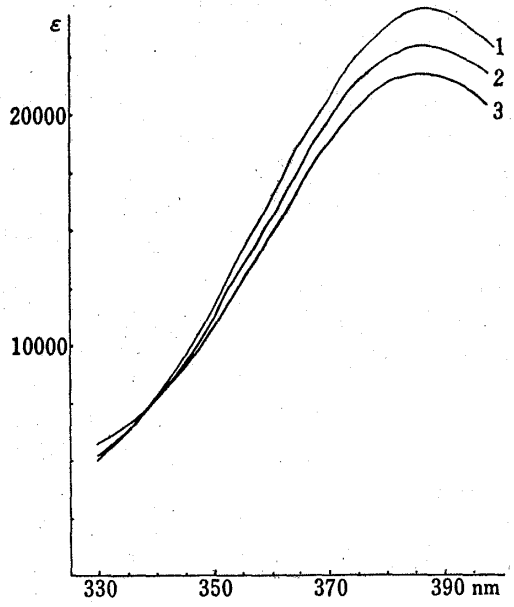


Fig. 1. Change of the UV Spectrum of III (3×10^{-2} M) in Benzene in the Presence of *p*-Toluidine (1.2 M)

1: immediately after dissolution.
2: at 325 min after dissolution.
3: at 1440 min after dissolution.

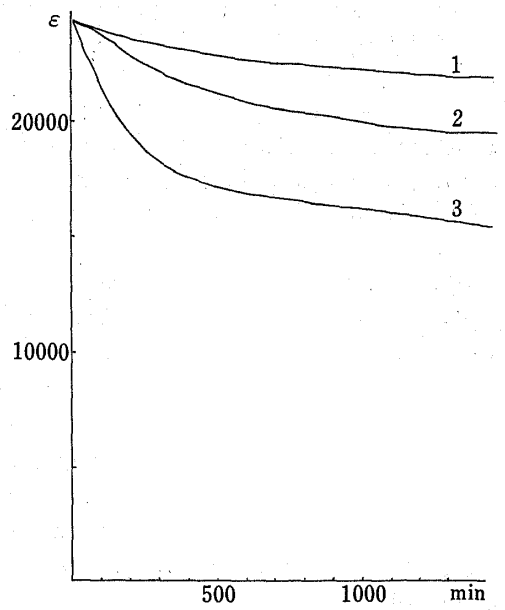


Fig. 2. Decrease of Optical Density at 385 nm of Benzene Solutions of III in the Presence of *p*-Toluidine

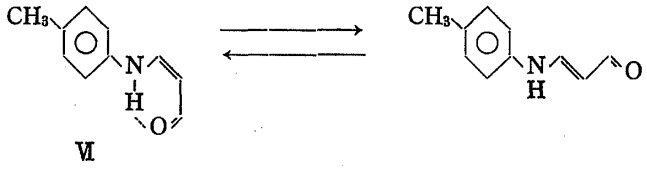
1: III 3×10^{-2} M *p*-toluidine 1.2 M.
2: III 1.5×10^{-2} M *p*-toluidine 1.2 M.
3: III 4.5×10^{-3} M *p*-toluidine 1.2 M.

unity in benzene solution. The results were based on measurement of the ultraviolet absorption (UV) spectra of the reaction solution, but the calculated concentrations of II and III were inexact because we overlooked abnormal UV spectral behavior of III and II. First, the UV spectrum of III changed gradually on standing in the presence of excess *p*-toluidine, *i.e.*, the optical density at 385 nm (λ_{max} of III) of 3×10^{-2} M benzene solution decreased to 83% of the initial value after 24 h at 30°C in the presence of 1.2 M *p*-toluidine (Fig. 1). The decrease of the optical density was greater at higher concentrations of *p*-toluidine and lower concentrations of III (Fig. 2). The UV spectra of 2×10^{-2} M and 4.5×10^{-3} M benzene solutions of III showed no change on standing in the presence of an equimolar concentration of *p*-toluidine in each case, and the change of that of a 2×10^{-5} M benzene solution of III was negligible for 24 h in the presence of 2×10^{-2} M *p*-toluidine.

In the previous work[1] the kinetic study of the reaction of I and *p*-toluidine in benzene was made at 2×10^{-2} M initial concentration of I in the presence of excess *p*-toluidine (1 M). The optical densities at around 385 nm should therefore have been corrected for the above effect. The kinetic examination of the formation of III, therefore, must be carried out under conditions avoiding the presence of excess *p*-toluidine.

Second, the UV spectrum of II in benzene solution changed on standing at room temperature, *i.e.*, the absorption maximum appeared at 317 nm immediately after dissolution, but this shifted to 353 nm after 24 h, and an isosbestic point was observed at 333 nm (Fig. 3). In the previous work,[1] the concentrations of II and III in the reaction solution were evaluated spectrophotometrically using the extinction coefficients of each compound at the given wavelengths. However, the values of the extinction coefficients of II used for evaluation were determined before the solution reached the equilibrium state.

In the previous paper[2] we reported that II consists of both *s-cis* (VI) and *s-trans* forms in chloroform-*d* (Chart 3). The ^{1}H–NMR spectrum of II in chloroform-*d* showed double



VI

Chart 3

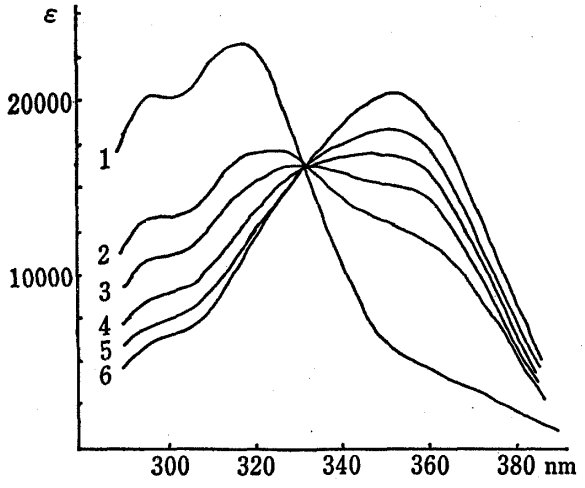


Fig. 3. Change of the UV Spectrum of II in Benzene (4×10^{-3} M)

1: initial pattern. 2: 1 h after dissolution.
3: 2 h after dissolution. 4: 3 h after dissolution.
5: 5 h after dissolution. 6: 24 h after dissolution.

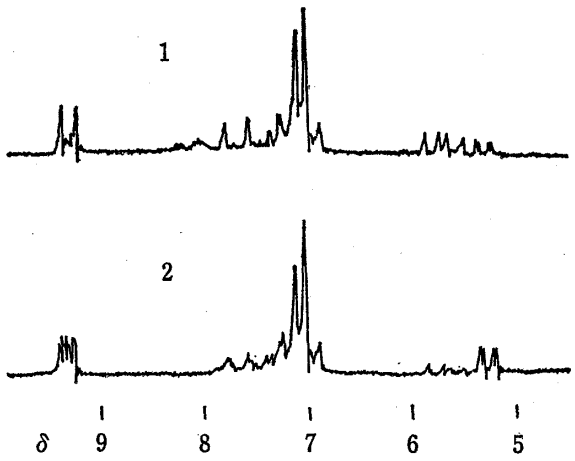


Fig. 4. ^{1}H-NMR Spectra of II in $CDCl_3$

1: immediately after dissolution.
2: 30 min after dissolution.

doublet signals due to the α-position of *s-cis* and *s-trans* forms at δ 5.28 (J=2, 7.5 Hz) and 5.70 (J=8.5, 13 Hz), respectively. The latter signal was of higher intensity than the former when the spectrum was recorded immediately after dissolution. The relation was, however, reversed after 30 min at 25°C, and the relation was unchanged after 24 h standing of the solution at the same temperature (Fig. 4). This means that II exists as the *s-trans* form in the crystalline state, and that the *s-cis* form is more stable than the *s-trans* form in chloroform-*d* solution. The ^{1}H-NMR spectrum of II in benzene-d_6 could not be recorded by the continuous wave approach owing to the low solubility of II in benzene-d_6. It was recorded by the pulse Fourier transform approach. The accumulation was started immediately after dissolution, and the spectrum obtained after accumulation for 17 min at 35°C showed double doublet signals due to α-position of *s-cis* and *s-trans* forms at δ 4.89 (J=2, 7 Hz) and 5.41 (J=8, 13 Hz), respectively. The former was of higher intensity than the latter, and the pattern was unchanged after 24 h standing of the solution at room temperature, suggesting that the conformational isomerization of II in benzene-d_6 is practically completed within 17 min. The conformational isomerization of II in benzene is not, therefore, responsible for the abnormal UV spectral behavior of II.

The reason for the abnormal UV spectral behavior of II and of III is not yet known. The kinetic examination of the reaction of *p*-tolui dneand I or IV in benzene solution was carried out under conditions avoiding high concentrations of *p*-toluidine in the reaction solution, and the values of extinction coefficients of II measured at 24 h after dissolution were used for evaluation of II the concentration of each component in the reaction solution (Fig. 3).

The UV spectra of III, IV and *p*-toluidine in benzene are shown in Fig. 5. The kinetic examination of the formation of III from equimolar amounts of IV and *p*-toluidine was carried out in benzene at 30°C. The concentration of each component was evaluated by the least-squares method using the optical densities at 290, 295, 320, 345, 385, and 390 nm of the reaction solution. The sum of the evaluated concentrations of III and IV was in good agree-

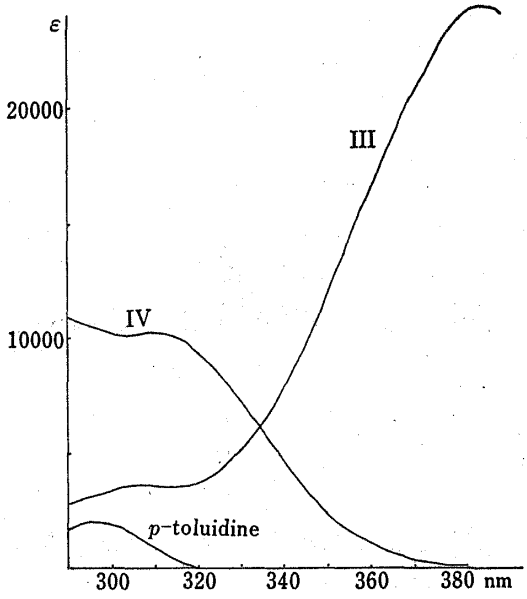


Fig. 5. UV Spectra of III, IV and *p*-Toluidine in Benzene

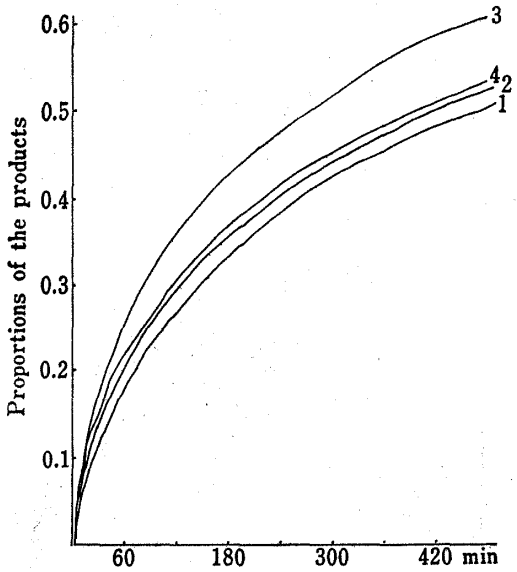


Fig. 6. The Formation of III from Equimolar Initial Concentrations of IV and *p*-Toluidine at 30°C

1,2: Initial concentration 5×10^{-3}
3,4: Initial concentration 7.5×10^{-3} M
1,3: The reaction was started immediately after the dissolution of IV in benzene.
2,4: The reaction was started 24 h after the dissolution of IV in benzene.

ment with the initial concentration of IV, and the optical densities at 290, 295, 300, 305, 310, 315, 320, 325, 330, 335, 340, 345, 350, 355, 360, 365, 370, 375, 380, 385, and 390 nm of the reaction solution were in good agreement with the values calculated from the concentrations of III, IV and *p*-toluidine for each measurement. An isosbestic point was observed at 333nm. The results were, however, not reproducible in repeated experiments and were affected by the time lag of the dissolution of IV in benzene and the initiation of the reaction. The results of typical runs are shown in Fig. 6, and they were not consistent with a rate equation of second order or third order.

The kinetic examination of the reaction of I (0.4 M) and *p*-toluidine (2×10^{-2} M initial concentration) was carried out in benzene at 30°C. The reaction was followed by measurement of the UV spectrum of the reaction solution. The absorption by I could not be neglected and was subtracted from the optical density of the reaction solution at each wavelength. The experimental data were treated in two ways. Procedure A: The concentrations of *p*-toluidine, II and III were evaluated by the least-squares method using the optical densities at 300, 305, 351, 353, 387 and 389 nm of the reaction solution for each measurement assuming that no product other than II and III was formed in the reaction solution. Procedure B: The concentrations of *p*-toluidine, II, III and IV were evaluated by the least-squares method using the optical densities at 300, 305, 310, 315, 320, 325, 351, 353, 387 and 389 nm of the reaction solution, for each measurement, assuming that IV was formed in a detectable amount in the solution. As a preliminary experiment, the UV spectrum of a standard solution containing II, III, IV and *p*-toluidine of known concentrations was subjected to procedures A and B, and satisfactory results were obtained. Procedure A seemed to be invalid, *i.e.*, the sum of the concentrations of *p*-toluidine, II and twice the concentration of III evaluated by procedure A was inconsistent with the initial concentration of *p*-toluidine for each measurement (Table I), and the calculated value of extinction coefficient of the reaction solution (based on the extinction coefficient and evaluated concentration of each component) was incosistent with the experimental value at each wavelength (Fig. 7). On the other hand, procedure B gave satisfactory results on comparison of the sum of the calculated concentrations of the components with the initial concentration of *p*-toluidine, and also on comparison of the calculated and experimental extinction coefficient at each wavelength of the reaction solution (Tables I and II).

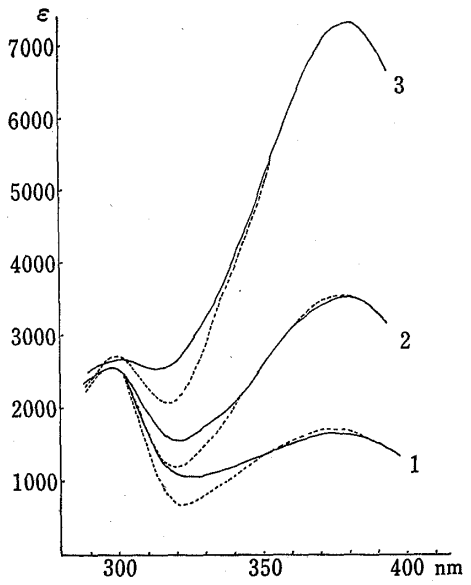


Fig. 7. UV Spectra of the Reaction Solution of I and *p*-Toluidine in Benzene at 30°C

——: experimental curve.
——: calculated curve (procedure A).
1: at 40 min after initiation of the reaction.
2: at 80 min after initiation of the reaction.
3: at 240 min after initiation of the reaction.

This result suggests that IV was formed in detectable amount in the reaction solution, and the proposed sequence of formation of III (Chart I) was supported by the observation that the formation of III from II was negligible on standing for 24 h at 30°C in the presence of 2×10^{-2} M *p*-toluidine in benzene solution. The progress of the reaction of I and *p*-toluidine in benzene is shown in Fig. 8A. The reaction of I and *p*-toluidine was also followed in the presence of 5×10^{-3} M acetic acid at 30°C. The result is shown in Fig. 8B.

Clearly acetic acid accelerates not only the formation of III but also the formation of II in the reaction of I and *p*-toluidine. In the previous paper[1] we reported that acetic acid

did not act as an effective catalyst for the formation of II from I and *p*-toluidine in ethanolic solution. The formation of II is much faster in ethanol (the second-order rate constant is 5.66×10^{-3} M^{-1} s^{-1}, ref.1) than in benzene, *i.e.*, the half-life of *p*-toluidine is calculated to be 5 min in ethanol in the presence of 0.4 M I while that in benzene was about 120 min in the presence of the same concentration of I (Fig. 8 A, Table II). Presumably the catalytic effect of acetic acid is masked by more effective solvent catalysis in ethanolic solution. In a kinetic study on oxime and semicarbazone formation, Jencks[3] pointed out that the addition of semicarbazide to the carbonyl group is subject to both general and specific acid catalysis, while acid catalysis is of minor importance for the addition of the stronger base, hydroxylamine. In the formation of β-arylaminoacrolein from I and a weak base, such as *p*-nitroaniline, acids would be expected to act as effective catalysts, while acids will promote the formation of malonaldehyde dianil.[2] In a study on the hydrolysis of malonaldehyde dianil[4] we found that the equilibrium of the formation of maolnaldehyde dianil from β-arylaminoacrolein and amine was affected by the acidity of the medium, and the weaker the basicity of the amine, the higher the acidity of the medium favorable for dianil formation. Compound III was formed when II and *p*-toluidine were reacted in aqueous ethanol in the presence of equimolar amounts

Table I. Calculated Proportions of Reaction Products and Starting Material in the Reaction Solution of I and *p*-Toluidine in Benzene at 30°C

Calculated by Procedure A

min	II	III	*p*-Toluidine	Total[a]
30	0.028	0.040	1.109	1.149
40	0.034	0.059	1.089	1.241
50	0.040	0.081	1.047	1.248
60	0.043	0.100	1.006	1.250
80	0.053	0.133	0.911	1.229
120	0.064	0.175	0.813	1.226
160	0.078	0.218	0.726	1.240
200	0.083	0.253	0.676	1.265
240	0.091	0.278	0.650	1.297
280	0.094	0.293	0.592	1.271
400	0.109	0.325	0.510	1.269
1880	0.151	0.256	0.432	1.294

Calculated by Procedure B

min	II	IV	III	*p*-Toluidine	Total[b]
30	0.022	0.047	0.041	0.834	0.986
40	0.027	0.052	0.060	0.793	0.991
50	0.033	0.053	0.081	0.741	0.990
60	0.036	0.054	0.101	0.697	0.989
80	0.046	0.051	0.133	0.622	0.985
120	0.057	0.059	0.175	0.475	0.941
160	0.071	0.057	0.219	0.397	0.963
200	0.075	0.063	0.254	0.313	0.959
240	0.083	0.067	0.279	0.263	0.970
280	0.085	0.064	0.294	0.233	0.969
400	0.101	0.064	0.326	0.137	0.954
1880	0.142	0.066	0.357	0.046	0.968

a) Sum of the proportions of II and *p*-toluidine and twice that of III.
b) Sum of the proportions of II, IV and *p*-toluidine and twice that of III.

TABLE II. Experimental and Calculated Values of the Extinction Coefficient of the Reaction Solution of I and *p*-Toluidine in Benzene at 30°C

Calculated by Procedure B

min / nm	40		80		160		240	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
290	2410	2300	2370	2280	2470	2310	2520	2410
295	2550	2500	2520	2470	2600	2500	2630	2580
300	2470	2460	2480	2480	2570	2550	2690	2670
305	2170	2170	2270	2270	2440	2450	2640	2630
310	1750	1750	1980	1980	2310	2320	2560	2590
315	1340	1340	1690	1690	2200	2200	2550	2570
320	1110	1110	1570	1570	2190	2200	2640	2640
325	1090	1080	1640	1630	2400	2370	2910	2870
330	1100	1100	1760	1760	2580	2620	3200	3190
335	1160	1140	1920	1920	2870	2910	3580	3550
340	1210	1200	2110	2120	3230	3270	4050	4000
345	1270	1270	2360	2350	3600	3670	4550	4520
350	1370	1360	2610	2600	4040	4110	5100	5080
355	1460	1460	2870	2880	4490	4590	5690	5700
360	1530	1530	3100	3180	4910	4940	6210	6160
365	1580	1590	3280	3270	5260	5270	6640	6590
370	1620	1630	3420	3420	5480	5540	6980	6950
375	1640	1660	3500	3520	5670	5720	7190	7200
380	1620	1640	3520	3540	5750	5760	7280	7280
385	1590	1590	3460	3470	5660	5660	7160	7170
390	1500	1510	3340	3330	5460	5460	6960	6930

Extinction coefficients are based on the initial concentration of *p*-toluidine.

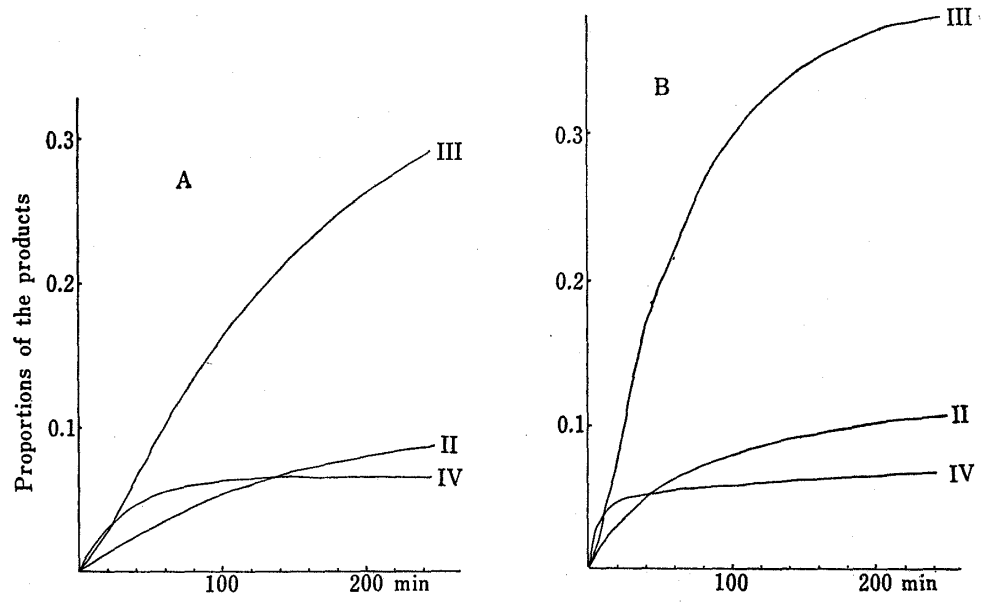


Fig. 8. The Reaction of I and *p*-Toluidine in Benzene at 30°C

A: initial concentration of *p*-toluidine, 2×10^{-2} M; I, 0.4 M.
B: initial concentration of *p*-toluidine, 2×10^{-2} M; I, 0.4 M; AcOH, 5×10^{-3} M.

of acetic acid and sodium acetate.[4] The formation of malonaldehyde dianil of *p*-nitroaniline, a weak base, should require more acidic conditions. As expected, *β*-(*p*-nitroanilino)acrolein (VII), which could not be obtained by the reaction of *p*-nitroaniline and I in methanol,[4] was obtained when *p*-nitroanililne and I were reacted in aqueous acetic acid. *β*-(4-Pyridylamino)-acrolein 1-oxide (VIII) was also obtained when 4-aminopyridine 1-oxide and I were reacted in ethanolic solution in the presence of acetic acid (Chart 4).

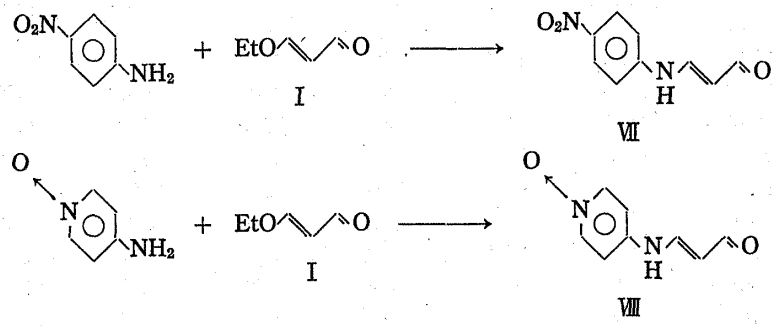


Chart 4

Experimental

All melting points are uncorrected. The UV spectra were measured on a Hitachi spectrophotometer model 139 and the ^{1}H-NMR spectra were recorded on JNM-PMX 60 and Hitachi R 900 NMR spectrometers with tetramethylsilane as an internal or external (capillary) standard. The following abbreviations are used: singlet (s), doublet (d), double doublet (dd), triplet (t) and quartet (q).

1-Chloro-3-(*p*-methylphenylimino)-1-propene Hydrochloride (V)——*β*-(*p*-Toluidino)acrolein (II) (0.5 g) was added in portions to 4.5 g of $SOCl_2$ under ice cooling. The precipitate was collected and washed with anhydrous benzene to give 0.56 g (84%) of crude V. mp 111°C. ^{1}H-NMR (CD_3OD) δ: 2.38 (3H, CH_3, s), 6.47 (1H, 2-position, t, J=12 Hz), 8.37 (1H, 1-position, d, J=12 Hz) and 9.20 (1H, 3-position, d, J=12 Hz).

1-Ethoxy-3-(*p*-methylphenylimino)-1-propene (IV)——A solution of 1.12 g of V in 3 ml of anhydrous EtOH was added to a solution of EtONa prepared from 0.47 g of Na and 10 ml of anhydrous EtOH. A piece of dry ice was added to the mixture and the precipitate was filtered off. The filtrate was concentrated under reduced pressure, and the residue was dissolved in anhydrous ether. The ether solution was concentrated under reduced pressure and the residue was distilled under reduced pressure (0.02 mmHg) on an oil bath (115°C). The distillate (0.20 g) was recrystallized from petroleum ether to give 0.13 g of pure IV. mp 61°C. *Anal.* Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.44; H 7.89; N, 7.97. ^{1}H-NMR ($CDCl_3$) δ: 1.36 (3H, Me of EtO, t, J=7 Hz), 2.16 (3H, Me, s), 3.97 (2H, CH_2 of EtO, q, J=7 Hz) 5.92 (1H, 2-position, dd, J=10, 13 Hz), 7.11 (1H, 1-position, d, J=13 Hz) and 8.03 (1H, 3-position, d, J=10 Hz). These signals disappeared immediately after the addition of an equimolar amount of *p*-toluidine to the solution, and signals of III were observed at δ 2.32 (6H, 2Me, s), 5.13 (1H, 2-position, t, J=7 Hz) and 7.68 (2H, 1- and 3-position, d, J=7 Hz), as well as signals of EtOH at δ 1.21 (3H, Me, t, J=7 Hz) and 3.70 (2H, CH_2, q, J=7 Hz), suggesting that IV reacts readily with *p*-toluidine to form III and EtOH.

Reaction of IV and *p*-Toluidine in Benzene——Compound IV (60.3 mg) was added to a solution of 35.5 mg of *p*-toluidine in 5 ml of benzene, and the solution was concentrated under reduced pressure to give 62 mg (78%) of crude III. Recrystallization from benzene afforded 42 mg (53%) of pure III. mp 164°C. It was identical with an authentic sample[2] on the basis of mixed melting point measurement and comparison of their IR spectra.

Reaction of IV and *p*-Toluidine in EtOH——Compound IV (60.5 mg) was added to a solution of 35.5 mg of *p*-toluidine in 5 ml of EtOH, and the reaction mixture was concentrated under reduced pressure to give 75 mg (94%) of crude III. Recrystallization from benzene afforded 60 mg (72%) of pure III. mp 164°C. It was identical with an authentic sample[2] on the basis of mixed melting point measurement and comparison of their IR spectra.

***β*-(*p*-Nitroanilino)acrolein (VII)**——*p*-Nitroaniline (1.38 g) was dissolved in 17 ml of hot AcOH (60°C), and 13 ml of H_2O was added to the solution. The solution was stirred, and 1.20 g of *β*-ethoxyacrolein (I) was added dropwise. The reaction mixture was allowed to stand overnight. The resulting precipitate was collected and washed with ether to give 1.60 g (83%) of crude VII. Recrystallization from CH_3COCH_3 gave 1.43 g (75%) of pure VII. mp 199°C (dec.). *Anal.* Calcd for $C_9H_8N_2O_3$: C, 56.25; H, 4.20; N, 14.58. Found: C, 56.41; H, 4.11; N, 14.26. ^{1}H-NMR (CD_3SOCD_3) δ: 5.68 (1H, *α*-position, dd, J=9, 13 Hz), 7.39 (2H, *o*-position, d, J=9 Hz) 8.26 (2H, *m*-position, d, J=9 Hz), 8.26 (1H, *β*-position, t, J=13 Hz), 9.42 (1H, CHO, d, J=9 Hz) and 10.62 (1H, NH, d, J=13 Hz).

Reaction of β-Ethoxyacrolein (I) and *p*-Nitroaniline in EtOH——*p*-Nitroaniline (1.38 g) was dissolved in 25 ml of EtOH containing 0.1 g of AcOH, and 1.20 g of I was added to the solution. The reaction mixture was heated at 60°C for 4 h. The precipitate was collected (1.06 g) and recrystallized from CH_3SOCH_3. The deposited crystals were filtered with suction, and washed with EtOH to give 0.84 g of 1-(*p*-nitrophenylamino)-3-(*p*-nitrophenylimino)-1-propene (malonaldehyde dianil of *p*-nitroaniline). mp 204°C (dec.). *Anal.* Calcd for $C_{15}H_{12}N_4O_4$: C, 57.69; H, 3.87; N, 17.94. Found: C, 57.72; H 3.72; N, 18.20. ^{1}H-NMR (CD_3SOCD_3) δ: 6.08 (1H, 2-position t, J=13 Hz), 7.28 (4H, *o*-position, d, J=9 Hz) and 10.38 (1H, NH, s). The signal of the *m*-position was observed at δ 8.27 as a doublet (J=9 Hz) and the signals of the 1- and 3-positions overlapped with it.

The filtrate was concentrated under reduced pressure, and the residue was recrystallized from CH_3COCH_3 to give 0.25 g of VII. mp 199°C (dec.).

β-(4-Pyridylamino)acrolein 1-Oxide (VIII)——β-Ethoxyacrolein (I) (2.40 g) was added to a solution of 2.20 g of 4-aminopyridine 1-oxide in 35 ml of EtOH containing 0.1 g of AcOH. The solution was heated at 60°C for 14 h, and concentrated under reduced pressure. The residue was washed with ether, and recrystallized from H_2O to give 1.63 g (45%) of VIII. mp 145°C. *Anal.* Calcd for $C_8H_8N_2O_2 \cdot H_2O$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.51; H, 5.41; N, 15.28. ^{1}H-NMR (D_2O) δ: 6.23 (1H, α-position, dd, J=9, 13 Hz), 7.72 (2H, 3- and 5-position, d, J=8 Hz), 8.50 (1H, β-position, d, J=13 Hz) 8.67 (2H, 2- and 6-position, d, J=8 Hz) and 9.67 (1H, CHO, d, J=9 Hz).

Preliminary Experiment on Procedures A and B——A standard solution of a mixture of II, III, IV and *p*-toluidine in benzene was prepared as follows: one ml of a solution of III (2.08×10^{-5} M), 1 ml of a solution of IV (1.96×10^{-5} M), 1 ml of a solution of *p*-toluidine (4.74×10^{-5} M) and 1 ml of a solution of II (1.01×10^{-5} M), which had been prepared from a 5.006×10^{-3} M solution (prepared 24 h before this experiment) immediately before this experiment, were added to benzene in a 10 ml volumetric flask and the mixture was diluted to the mark with benzene. The molar ratio of II, III, IV and *p*-toluidine in the solution was 0.103: 0.212: 0.200: 0.484. The mixture was subjected to procedure B, which gave a molar ratio of II: III: IV: *p*-toluidine= 0.102: 0.224: 0.191: 0.469. Another standard solution of a mixture of II, III and *p*-toluidine (molar ratio of II: III: *p*-toluidine=0.129: 0.265: 0.605) was similarly prepared, and was subjected to procedures A and B, which gave molar ratios of II: III: *p*-toluidine=0.121: 0.277: 0.617 and of II: III: IV: *p*-toluidine=0.121: 0.277: 0.007: 0.579, respectively.

References

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