(11) P. W. Jeffs, G. Ahmann, H. F. Campbell, D. S. Farrier, G. Ganguli, and R. L. Hawks, *J. Org. Chem.*, **35**, 3512 (1970).
(12) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley, New York, N. Y., 1972, Chapter 4, p 79.
(13) J. Koukel and E. E. Conn, *J. Biol. Chem.*, **236**, 2692 (1961); D. R. McCalla and A. G. Neish, *Can. J. Biochem. Physiol.*, **37**, 531 (1959).
(14) A. R. Battersby, T. A. Merbert, D. M. Foulkes, and R. B. Herbert, *J. Chem. Soc., Perkin Trans. 1*, 1730 (1972); A. R. Battersby, R. B. Herbert, E. McDonald, R. Ramage, and J. H. Clements, *ibid.*, 1741 (1972).

A Study of the Structures of Some Benzo-1,2,3-triazinium Betaines

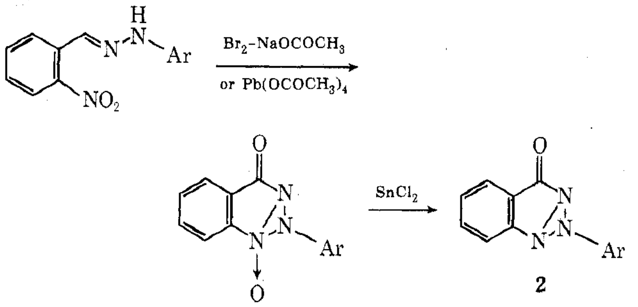
Alexander McKillop* and Ryszard J. Kobylecki

School of Chemical Sciences, University of East Anglia, Norwich, England

Received March 19, 1974

Methylation, phenylation, *p*-bromophenylation, and *p*-methylphenylation of 4(3*H*)-benzo-1,2,3-triazinone with dimethyl sulfate, diphenyl-, di-*p*-bromophenyl-, and di-*p*-tolyliodonium chloride results in formation of the N_2-substituted benzo-1,2,3-triazinium betaines **8** and **6a–c**, respectively. These latter compounds are identical with the products obtained by stannous chloride reduction of the betaines **10** and **5a–c** formed by oxidative cyclization of *o*-nitrobenzaldehyde methyl-, phenyl-, *p*-bromophenyl-, and *p*-tolylhydrazone, respectively, with lead(IV) acetate. Examination of the ir, nmr, uv, and mass spectra of the two classes of betaines **5** and **6** reveals that, while ir and nmr techniques afford little definitive evidence on structure, uv and mass spectroscopy can be used both for confirmation of structure and to distinguish between the two types of betaines.

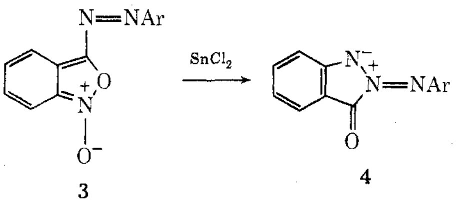
Mild oxidation of *o*-nitrobenzaldehyde arylhydrazones with either bromine–sodium acetate or lead(IV) acetate results in the overall loss of two hydrogen atoms and production of a class of *N*-aryl heterocycles, the structure of which has been the subject of uncertainty and some controversy for the past 50 years. These oxidation products were first prepared and investigated by Chattaway,[1–6] who described them as "isodiazomethanes" and formulated them as the triaziridine derivatives **1**. Structural assignment was based entirely on evidence from degradation studies; in particular, Chattaway showed that reduction of "1" with stannous chloride resulted in the loss of a single oxygen atom and formation of a second class of compounds which he represented as **2**.



1

2

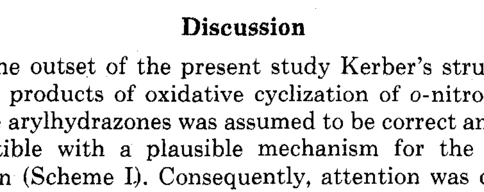
In a later reinvestigation of this work, Gibson,[7] partly on the basis of mechanistic reasoning and partly as a result of spectroscopic (uv, ir) studies, suggested that the initial oxidation products formulated by Chattaway as **1** could be better represented as the isomeric phenylazoanthranil *N*-oxides **3**, and the stannous chloride reduction products as the dipolar species **4**. More recently, however, Kerber[8] has challenged Gibson's assignments and the evidence on which they were based. Kerber pointed out that Gibson's spectroscopic data were probably not consistent with structure **4**, and that structure **3** was improbable inasmuch as anthranil *N*-oxides are a rare, if not unknown, class of heterocycle, and proposed the triazinium betaine structures **5** and **6** for the oxidation and reduction products, respectively. Kerber's assignments, like those of Gibson, were based partly on mechanistic reasoning and partly on spectroscopic (ir, uv, nmr, mass spectral) evidence.



3

4

Heterocyclic betaines have been a subject of interest in this department for some years,[9] and within this context unsuccessful attempts were made some time ago to obtain definitive evidence for the structure of the dipolar species obtained from the oxidation of *o*-nitrobenzaldehyde arylhydrazones.[10] In the present paper we report the results of a further chemical and spectroscopic investigation of these compounds and their derived reduction products which establish not only that the structures **5** and **6** proposed by Kerber for the two classes of heterocycles are correct, but that the two structural types can be clearly differentiated on the bases of their uv and mass spectra.



5

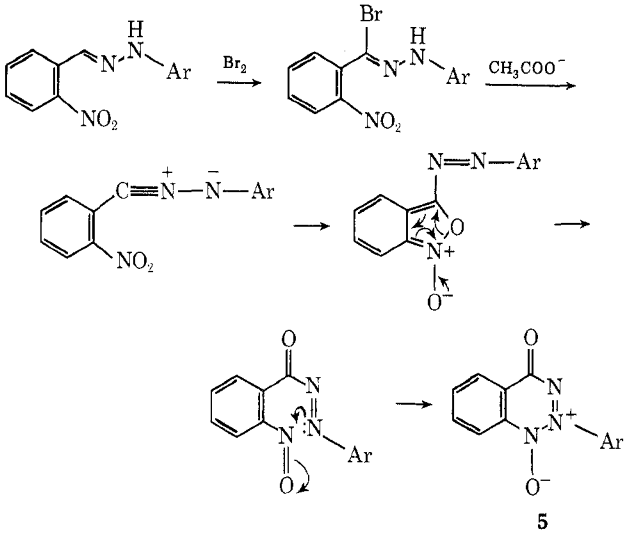
6

Discussion

At the outset of the present study Kerber's structure **5** for the products of oxidative cyclization of *o*-nitrobenzaldehyde arylhydrazones was assumed to be correct and to be compatible with a plausible mechanism for the overall reaction (Scheme I). Consequently, attention was concentrated on the development of procedures whereby compounds of the type **5** and/or **6** could be synthesized by an alternative route to that used by Chattaway. The simpler of the two series of betaines, *i.e.*, **6**, was investigated initially in the hope that, were an alternative synthesis of these compounds to be devised, it might then prove possible to effect specific N_1-oxidation to give **5**.

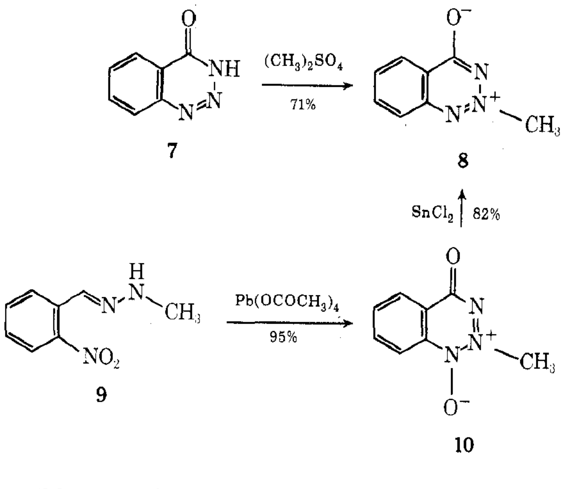
In 1968, Wagner and Gentzsch reported[11] that treatment of 4(3*H*)-benzo-1,2,3-triazinone (**7**) with dialkyl sulfates in base gave a mixture of products, namely the O- and N_3-al-

Scheme I



kylated derivatives, and a third isomer thought to be either the N_1- or N_2-alkylated compound. We have repeated this reaction and found that by using a slightly modified experimental procedure the latter compound, which is in fact the N_2 isomer, can be prepared readily in good yield. That alkylation occurs at N_2 was demonstrated in the following manner. Oxidation of *o*-nitrobenzaldehyde methylhydrazone (**9**) with lead(IV) acetate in dichloromethane gave the betaine *N*-oxide **10** (Scheme II); reduction of **10** with stannous chloride proceeded smoothly to give the betaine **8**, which was identical (melting point, mixture melting point, ir, uv, nmr, mass spectrum) with the product obtained by direct methylation of **7**.

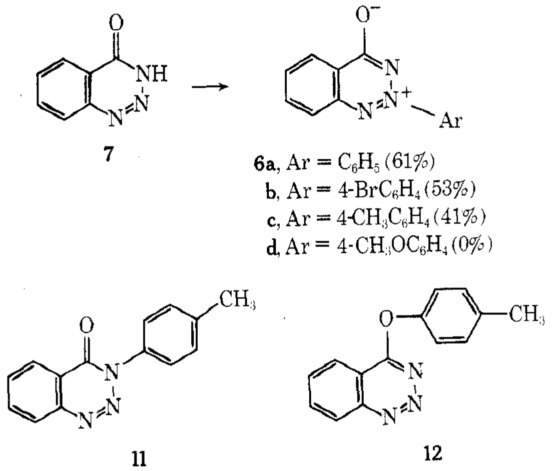
Scheme II



Possible procedures for the direct arylation of **7** were then considered, and it was concluded tha the use of diaryliodonium salts was the most promising approach. Very little work has so far been described on the reactions of these reagents with heterocyclic systems. Makarova and Nesmeyanov have reported that treatment of pyridine with diphenyliodonium fluoroborate results in formation of *N*-phenylpyridinium fluoroborate in 88% yield in an apparently straightforward nucleophilic substitution process;[12] Sandin and Brown, on the other hand, observed free-radical substitution when pyridine was treated with diphenyliodonium chloride in potassium hydroxide solution, and obtained a mixture of the isomeric 2-, 3- and 4-phenylpyridines.[13] Treatment of piperidine[14] and phthalimide[15] with diaryliodonium salts has been reported to lead only to N-arylation; with 2-quinolone, however, no N-substitution occurs, and the products are 3-phenyl-2-quinolone and 2-phenoxyquinoline.[16]

In the present study, direct phenylation of the sodium salt of 4(3*H*)-benzo-1,2,3-triazinone (**7**) proceeded smoothly to give the betaine **6a** in 61% yield (Scheme III). An exactly analogous reaction occurred with di-*p*-bromophenyliodonium chloride, and the betaine **6b** was isolated in 53% yield. In each of these cases substitution occurred solely at N_2, and no N_3- or O-arylated derivatives could be detected in the reaction mixtures. In contrast to the high regioselectivity of arylation in the above experiments, treatment of the sodium salt of **7** with di-*p*-tolyliodonium chloride gave a mixture consisting mainly of the N_2-arylated derivative **6c** together with small amounts of the N_3 (**11**) and O (**12**) isomers. The betaine **6c** was found to be thermally unstable, and after being heated at 120° (0.1 mm) for 1 hr (attempted vacuum sublimation), approximately half of it had rearranged to the *O*-aryl isomer **12**. All attempts to arylate the sodium salt of **7** with di-*p*-anisyliodonium chloride were unsuccessful; starting materials were recovered in virtually quantitative yield from each attempt. The betaines **6a–c** obtained by direct arylation were identical (melting point, mixture melting point, ir, uv, nmr, mass spectrum) with the compounds prepared by oxidative cyclization of the appropriate *o*-nitrobenzaldehyde arylhydrazones and subsequent stannous chloride reduction of the initially formed betaine *N*-oxides.

Scheme III



The results obtained in the above arylation studies can largely be explained on the basis of nucleophilic substitution of the diaryliodonium salt by the anion of 4(3*H*)-benzo-1,2,3-triazinone. Both diphenyl- and di-*p*-bromophenyliodonium chloride apparently reacted cleanly by such an SNAr mechanism; failure to observe substitution with di-*p*-anisyliodonium chloride is then not unexpected. The results with di-*p*-tolyliodonium chloride possibly indicate a changeover point in mechanism with this reagent.[16]

Independent synthesis of betaines of the types **6** and **8** having been successfully accomplished, attempts were made to N-oxidize some of these to betaines of the type **5**. Attention was concentrated on the *p*-anisyl derivative **6d** (prepared from the appropriate *o*-nitrobenzaldehyde arylhydrazone), as it was thought that this substrate should undergo N-oxidation most easily (*cf.* **6d** → **13** → **5**, Scheme IV). Compound **6d** was treated with a wide variety of oxidizing agents, *e.g.*, standard hydrogen peroxide and peracetic acid solutions, solutions of 80% hydrogen peroxide in acetic, trifluoroacetic, and concentrated sulfuric acid

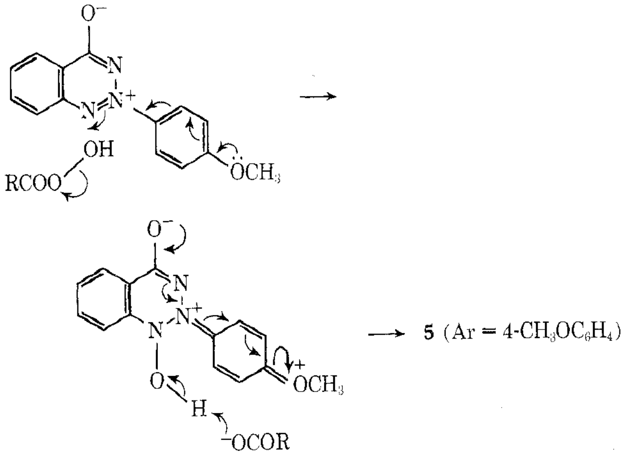
Table I
Yields and Physical Data for 2-Substituted Benzo-1,2,3-Triazinium Betaine 1-Oxides

Compd	Yield, %[a]	Mp, °C[b]	Lit. mp, °C	$\nu_{C=O}$
5a, Ar = C_6H_5	87	147–149	145[c]	1625
5b, Ar = 4-BrC_6H_4	73	144–146	144[d]	1630
5c, Ar = 4-$CH_3C_6H_4$	90	142–143	143[e]	1628
5d, Ar = 4-$CH_3OC_6H_4$	86	141	*f*	1649
5e, Ar = 4-$O_2NC_6H_4$	99	145–146	159[c]	1660
10	95	145–157	*g*	1628

[a] All compounds were prepared by oxidative cyclization of the appropriate *o*-nitrobenzaldehyde alkyl- or arylhydrazone with lead(IV) acetate (see ref *c*). [b] All compounds decomposed at or near the melting point. [c] W. A. F. Gladstone, J. B. Aylward, and R. O. C. Norman, *J. Chem. Soc. C*, 2587 (1969). [d] Reference 2. [e] Reference 3. [f] *Anal.* Calcd for $C_{14}H_{11}N_3O_3$: C, 62.45; H, 4.12; N, 15.61. Found: C, 62.03; H, 4.34; N, 15.32. [g] *Anal.* Calcd for $C_8H_7N_3O_2$: C, 54.24; H, 3.98; N, 23.72. Found: C, 54.15; H, 4.12; N, 23.87.

mixtures,[17,18] and solutions of *m*-chloroperbenzoic acid in sulfolane. Many reactions were carried out under a wide variety of conditions, but in no instance was any of the expected product **5** (Ar = 4-$CH_3OC_6H_4$) detected by tlc comparison of reaction mixtures with an authentic sample. The starting betaine **6d** was recovered in high yield in each case. Similar results were obtained with **6a–c** and with **8**.

Scheme IV



Spectroscopic Investigation. The results outlined above, in conjunction with the original degradation studies reported by Chattaway, provide conclusive evidence that the structures **5** and **6** proposed by Kerber for the two classes of betaines are correct. Concurrently with the chemical studies, we have carried out a detailed spectroscopic investigation of these betaines, the results of which are also consistent with the assigned structures. Relevant experimental data for the compounds used in this investigation are summarized in Tables I and II.

Examination of the ir and nmr spectra of all of the compounds listed in Tables I and II revealed immediately that neither of these techniques could be used with either accuracy or confidence as a basis for structural assignment with either of the two classes of betaines. The ir spectra were extremely complex and while, like the nmr spectra, they could be interpreted as being consistent with the assigned structures, they do not in our opinion offer any unambiguous proof for them. Moreover, the spectra of neither class of betaine show either significant similarities or meaningful correlations, and it is impossible to distinguish between the two classes of compounds on the basis of ir and nmr spectra.

It is possible, however, to distinguish clearly between the two classes of betaines on the basis of their uv spectra. The spectra of compounds **5a–e** and **10** are remarkably similar with respect to band shape, as are the spectra of compounds **6a–e** and **8**, but the two forms of band shapes are quite different from each other and from those of the comparison compounds **7**, **11**, **12**, and **14**. The spectra of compounds **5c**, **6c**, **11**, and **12**, for example, are shown in Figure 1, and relevant uv data for all of the compounds listed in Tables I and II are summarized in the Experimental Section.

Mass spectroscopy also provided supporting evidence on the structures of the two classes of betaines **5** and **6**, and allowed ready distinction to be made between them. The most notable contrast between the mass spectra of compounds **5a–e** and **6a–e** was the presence of a very intense parent peak for the latter compounds and the almost total absence of a parent peak for the *N*-oxides **5a–e**. All of the compounds **5a–e** underwent fragmentation to give prominent ions at *m/e* values corresponding to P − O, P − N_2 or CO, P − O − N_2 or CO, P − O − N_2 − CO, $RC_6H_4N_3^+O$, $RC_6H_4N_3^+$, $RC_6H_4N_2^+$, $RC_6H_4^+$, and $C_7H_4O^+$ or $C_6H_4N_2^+$.

Table II
Yields and Physical Data for 2-Substituted Benzo-1,2,3-triazinium Betaines and Some Comparison Compounds

Compd	Yield, %[a,b]	Mp, °C	Lit. mp, °C	$\nu_{C=O}$, cm^{-1}
6a	99	116–118.5	*c*	1650
6b	92	199–201	199–200[d]	1675
6c	67	165–167	*e*	1662
6d	88	193–194	*f*	1665
6e, Ar = 4-$O_2NC_6H_4$	78	244–245	*g*	1630
8	82	143–144	144[h]	1630
7	79	217–218	216[i]	1695
14, 3-methyl-4(3*H*)-benzo-1,2,3-triazinone		122–123	123[h]	1675
11, 3-(4-methylphenyl)-4(3*H*)-benzo-1,2,3-triazinone	69	143–144	143[d]	1687
12, 4-(4-methylphenoxy)-benzo-1,2,3-triazine	8	145–147.5	*j*	1667[k]

[a] Compounds **6a–e** and **8** were prepared by stannous chloride reduction of the corresponding betaine 1-oxides (see Table I); compounds **7**, **14**, and **11** were prepared by standard literature procedures; compound **12** was obtained as described in the Experimental Section. [b] Yields refer to isolated material. [c] *Anal.* Calcd for $C_{13}H_9N_3O$: C, 69.95; H, 4.06; N, 18.82. Found: C 70.05; H, 4.14; N, 18.68. [d] Reference 8. [e] *Anal.* Calcd for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.71. Found: C, 70.60; H, 4.72; N, 18.10. [f] *Anal.* Calcd for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.38, N, 16.59. Found: C, 66.10; H, 4 46; N, 16.97. [g] *Anal.* Calcd for $C_{13}H_8N_4O_3$: C, 58.21; H, 3.01; N, 20.89. Found: C, 57.97; H, 3.21; N, 20.93. [h] Reference 11. [i] H. Finger, *J. Prakt. Chem.*, **37**, 431 (1888). [j] *Anal.* Calcd for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.71. Found: C, 70.83; H, 4.75; N, 17.89. [k] $\nu_{C=N}$.

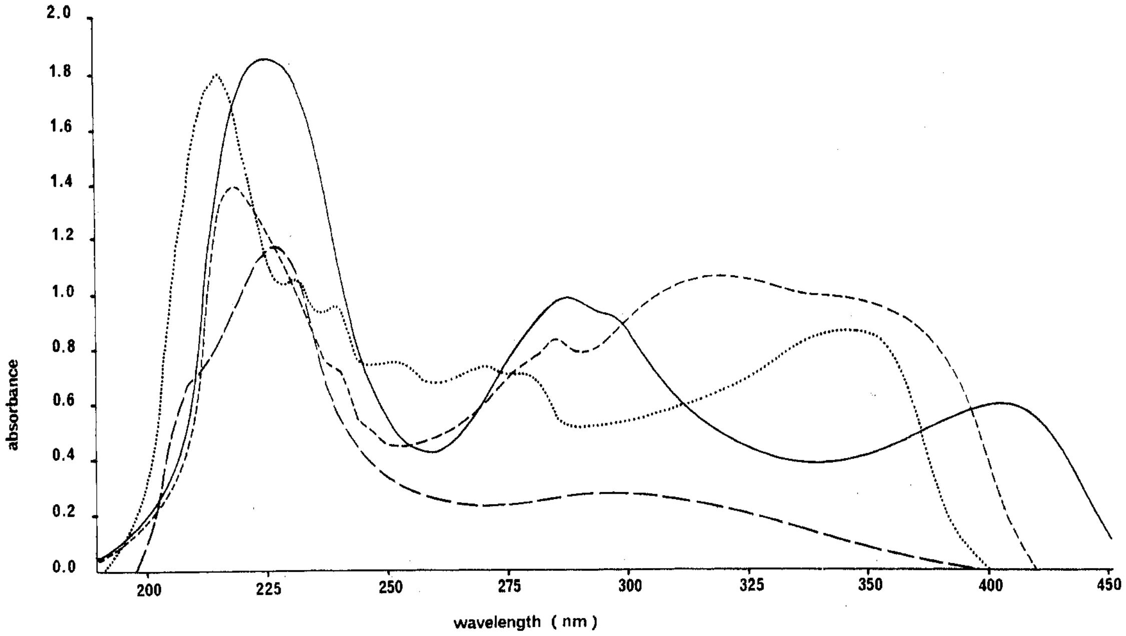


Figure 1. Uv spectra of **5c** (——), **6c** (- - - -), **11** (— — —), and **12** (·······).

In addition to a prominent parent peak, the spectra of compounds **6a–e** showed prominent ions at *m/e* values corresponding to P − N_2 or CO, P − N_2 − CO, $RC_6H_4N_2^+$, $RC_6H_4^+$, $C_7H_4O^+$ or $C_6H_4N_2^+$, and $C_6H_4^+$. The relative intensities of the various prominent ions were reasonably consistent within each group of related compounds, but they differed by a factor of 2–3 between the groups. Distinction between the betaines **10** and **8** and between compounds such as **7**, **11**, **12**, and **14** could similarly be made by the use of mass spectroscopy (see paragraph at end of paper regarding supplementary material).

From the above spectral investigation it is evident that uv and mass spectroscopic techniques can be utilized for confirmation of structure in the benzo-1,2,3-triazinium betaine field and as a means of distinguishing between the different classes of betaines **5** and **6**. It is equally evident, however, that spectroscopic data alone, as pointed out previously by Kerber,[8] are unreliable criteria on which to base the structure of complex heterocycles.

Experimental Section

Melting points were determined on a Kofler hot-stage microscope apparatus, and are uncorrected. Microanalyses were performed by Mr. A. R. Saunders of the University of East Anglia, and by the Analytical Section of I. C. I. (Pharmaceuticals Division). Infrared spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer using the standard Nujol mull technique. Nuclear magnetic resonance spectra were determined on Perkin-Elmer R-12, 60 MHz, and Varian HA-100, 100-MHz spectrometers, using tetramethylsilane as internal standard. Tlc refers to Merck preprepared silica plates, with chloroform as the eluent, unless otherwise stated. All uv spectra were recorded as solutions in ethanol on a Unicam SP-800 spectrophotometer. Solutions were made up immediately prior to recording of the spectra, as it was noticed that the betaines **5** and **6** decomposed fairly rapidly in ethanol when the solutions were exposed to light. Mass spectra were obtained at 70 eV and 300° using a Perkin-Elmer Model RMU-6E mass spectrometer.

Preparation of 2-Methylbenzo-1,2,3-triazinium Betaine 1-Oxide (10) by Oxidative Cyclization of *o*-Nitrobenzaldehyde Methylhydrazone (9). A solution of lead(IV) acetate (16.0 g, 0.036 mol) in dichloromethane (80 ml) was added in one portion to a stirred solution of **9** (6.0 g, 0.034 mol) in dichloromethane (400 ml) at room temperature. An immediate color change from orange to yellow was observed, and lead(II) acetate began to precipitate. The mixture was stirred for 15 min, after which time tlc analysis showed that no starting material remained and that a single product was present. Water (100 ml) was added, and the mixture was stirred for a further 15 min. Precipitated lead(IV) oxide was removed by vacuum filtration through Keiselguhr, and the organic layer separated; this was washed with saturated sodium bicarbonate solution until acid free and then with water (2 × 40 ml) and dried (Na_2SO_4), and the solvent was removed by evaporation under reduced pressure. The residue was recrystallized from a benzene–petroleum ether (bp 60–80°) mixture to give 5.6 g (95%) of **10** as bright yellow, needle-shaped crystals, mp slow over the range 145–157°, with extensive decomposition, softening from 140°.

Preparation of 2-Methylbenzo-1,2,3-triazinium Betaine (8) by Reduction of 2-Methylbenzo-1,2,3-triazinium Betaine 1-Oxide (10). A solution of **10** (2 g, 0.011 mol) in glacial acetic acid (10 ml) was treated with concentrated hydrochloric acid (30 ml) and cooled to 0°, when a small amount of colorless solid precipitated. A solution of stannous chloride dihydrate (2.8 g, 0.0012 mol) in concentrated hydrochloric acid (10 ml) was added dropwise over 10 min to the stirred suspension, and a colorless solid gradually precipitated. The resulting suspension was stirred at 0° for 0.5 hr, and the temperature was then allowed to rise to ambient over a further 0.5 hr. Water (100 ml) was added, the mixture was extracted with dichloromethane (3 × 40 ml), the combined extracts were washed with saturated sodium bicarbonate solution until acid free and then with water (2 × 20 ml) and dried (Na_2SO_4), and the solvent was removed by evaporation under reduced pressure. The residue was recrystallized from a chloroform–petroleum ether mixture to give 1.5 g (82%) of **8** as the hemihydrate, colorless, needle-shaped crystals, mp 122–123 (fast), 143–144° (slow) (lit.[11] mp 139–140°).

Preparation of 2-Methylbenzo-1,2,3-triazinium Betaine (8) by Direct Methylation of 7. Dimethyl sulfate (12.6 g, 0.1 mol) was added dropwise over 5 min at room temperature to a well-stirred solution of 4(3*H*)-benzo-1,2,3-triazinone (14.7 g, 0.1 mol) in sodium hydroxide solution (10% w/v, 40 ml). A transient green color was produced which gradually changed to a pale straw color, and evolution of considerable heat was noted. After being stirred for 15 min the reaction mixture appeared to be homogeneous and was cooled to room temperature in a water bath and then extracted with chloroform (4 × 30 ml). The combined extracts were washed with water (2 × 20 ml) and dried (Na_2SO_4), and the solvent was removed by evaporation under reduced pressure to give a pale tan solid. Recrystallization from a chloroform–petroleum ether mixture gave 12 g (71%) of pure **8** as pale yellow needles, mp 122–123 (fast), 143–145degr (slow) (lit.[11] mp 139–140°).

Preparation of 2-Phenylbenzo-1,2,3-triazinium Betaine (6a) by Direct Phenylation of 7. 4(3*H*)-Benzo-1,2,3-triazinone (2.94 g, 0.02 mol) was added to a solution of sodium (0.5 g, 0.022 mol) in dry, redistilled *tert*-butyl alcohol (120 ml), and the mixture was heated to reflux for 5 min to ensure complete formation of the sodium salt. Diphenyliodonium chloride[19] (6.4 g, 0.02 mol) was added and the mixture was heated to reflux for 1.25 hr. It was then cooled to room temperature, insoluble inorganic salts were removed by vacuum filtration, and the solvent was removed from the filtrate by evaporation under reduced pressure. The oily residue was triturated with warm benzene (100 ml), a further small quantity of inorganic salts was removed by vacuum filtration, and the filtrate was evaporated under reduced pressure. Trituration of the resulting oil with small quantities of petroleum ether resulted in crystallization; the solid was collected by vacuum filtration and recrystallized from a benzene–petroleum ether mixture to give 2.7 g (61%) of pure **6a** as pale yellow needles, mp 116–118°, mmp with the product prepared by the oxidative cyclization of *o*-nitrobenzaldehyde phenylhydrazone 116–117.5°.

Preparation of 2-*p*-Bromophenylbenzo-1,2,3-triazinium Betaine (6b) by Direct Arylation of 7. 4(3*H*)-Benzo-1,2,3-triazinone (2.94 g, 0.02 mol) was added to a solution of sodium (0.5 g, 0.022 mol) in dry methanol (75 ml), and the mixture was heated gently to effect solution. Di-*p*-bromophenyliodonium chloride[20] (9.5 g, 0.02 mol) was added and the mixture was then heated to reflux for 24 hr. After this time a pale yellow solid had precipitated; anhydrous methanol (40 ml) was added and the mixture was gently warmed to dissolve this precipitate. Small amounts of insoluble inorganic salts were removed by vacuum filtration of the hot reaction mixture, and cooling of the filtrate resulted in precipitation of a pale yellow solid. This was collected by vacuum filtration and identified by tlc analysis as the desired product by comparison of R_f value with that of a genuine sample. Evaporation of the filtrate gave a further crop of a pale yellow solid, extraction of which with hot petroleum ether (2 × 100 ml) removed the petroleum-soluble solid and left a pale yellow residue which was identified as the desired product by tlc comparison with a genuine sample prepared by the oxidative cyclization of *o*-nitrobenzaldehyde *p*-bromophenylhydrazone. The petroleum-soluble solid, 4.2 g (75%), was identified as *p*-iodobromobenzene.

Recrystallization of **6b** from a dichloromethane–petroleum ether mixture gave 3.2 g (53%) of pure material as pale yellow microneedles, mp 198–201° (lit.[2] mp 197°).

Preparation of 2-*p*-Tolylbenzo-1,2,3-triazinium Betaine (6c) by Direct Arylation of 7. 4(3*H*)-Benzo-1,2,3-triazinone (14.7 g, 0.1 mol) was added to a solution of sodium (2.5 g, 0.11 mol) in dry methanol (100 ml) followed by di-*p*-tolyliodonium chloride[20] (34.5 g, 0.1 mol) and the resultant mixture (pale pink solution) was heated to reflux for 24 hr. The reaction mixture was allowed to cool to room temperature, large amounts of pale brown insoluble inorganic salts were removed by vacuum filtration, and the solvent was removed by evaporation under reduced pressure. Tlc analysis of the residue showed it to consist of small amounts of polar materials, some *p*-iodotoluene, a small amount of N_3-*p*-tolyl-4(3*H*)-benzo-1,2,3-triazinone (by comparison of R_f value with that of a genuine sample[2]), and a major product corresponding in appearance and R_f value to the expected product **6c**, which had been prepared by the oxidative cyclization of *o*-nitrobenzaldehyde *p*-tolylhydrazone.

Trituration of this oily residue with small amounts of ethanol and cooling to 0° overnight resulted in crystallization of 2.0 g of a pale yellow solid which was collected and assigned structure **12** on the basis of its ir, uv, nmr, and mass spectra. Recrystallization from a chloroform–petroleum ether mixture gave 1.8 g of pure product as pale yellow, light-sensitive platelets, mp 145–7.5°.

Chromatography on silica gel of the residue left after removal of **12** gave, on elution with chloroform and evaporation of the solvent, 14 g of a pale yellow solid the R_f value of which was identical with that of the expected product **6c** which has been prepared independently by the Chattaway procedure. Examination of the nmr spectrum, however, revealed that this material was a mixture of **6c** and **12** in an approximate ratio of 4:1. Recrystallization from a chloroform-petroleum ether mixture gave 9.6 g of almost pure **6c**, mp 143–145°. Complete removal of traces of **12** from this product by either crystallization, chromatography, or sublimation was found to be impossible, and in independent experiments it was shown that when **6c** was heated above about 60° it slowly isomerized to give a 1:1 mixture of **6c** and **12**.

Uv Data. 5a: λ_{max} 227, 285, 404 nm ($\log \epsilon$ 4.28, 4.06, 3.81). **5b:** λ_{max} 222, 286, 404 nm ($\log \epsilon$ 4.31, 4.05, 3.80). **5c:** λ_{max} 226, 287, 296 (sh), 404 nm ($\log \epsilon$ 4.30, 4.03, 3.99, 3.82). **5d:** λ_{max} 230, 286, 300 (sh), 396 nm ($\log \epsilon$ 4.35, 3.91, 3.85, 3.90). **5e:** λ_{max} 230, 286, 410 nm ($\log \epsilon$ 4.38, 4.35, 3.91). **10:** λ_{max} 226, 278, 384 nm ($\log \epsilon$ 4.29, 3.89, 3.76). **6a:** λ_{max} 218, 230 (sh), 238 (sh), 276, 283, 297, 357 nm ($\log \epsilon$ 4.22, 4.09, 3.94, 4.11, 4.13, 4.07, 3.97). **6b:** λ_{max} 219, 230 (sh), 239 (sh), 278, 284, 310, 358 nm ($\log \epsilon$ 4.30, 4.17, 4.02, 4.04, 4.09, 4.15, 4.07). **6c:** λ_{max} 218, 233 (sh), 239 (sh), 247 (sh), 275 (sh), 280, 317, 350 nm ($\log \epsilon$ 4.16, 3.98, 3.88, 3.71, 3.86, 3.93, 4.04, 4.01). **6d:** λ_{max} 217, 230, 250, 276, 284, 364 nm ($\log \epsilon$ 4.23, 4.12, 3.95, 3.69, 3.69, 4.26). **6e:** λ_{max} 218, 230 (sh), 238 (sh), 277, 284, 370 nm ($\log \epsilon$ 4.26, 4.17, 4.17, 4.35, 4.34, 4.03). **8:** λ_{max} 212, 231, 238, 250 (sh), 266 (sh), 276 (sh), 335 nm ($\log \epsilon$ 4.02, 4.01, 4.00, 3.82, 3.55, 3.43, 3.86). **7:** λ_{max} 211, 224, 250, 278, 296, 307 nm ($\log \epsilon$ 4.15, 4.28, 3.71, 3.80, 3.63, 3.42). **11:** λ_{max} 212, 227, 292 nm ($\log \epsilon$ 4.30, 4.48, 3.84). **12:** λ_{max} 215, 231, 239, 251, 269, 278, 345 nm ($\log \epsilon$ 4.29, 4.13, 4.09, 3.98, 3.97, 3.96, 4.05). **14:** λ_{max} 214, 225, 252 (sh), 285, 300 (sh), 316 (sh) nm ($\log \epsilon$ 4.31, 4.35, 3.69, 3.89, 3.79, 3.61).

Acknowledgments. We should like to thank I. C. I. Pharmaceuticals Division for partial financial sulport of this project. One of us (R. J. K.) acknowledges receipt of a CAPS Studentship.

Registry No.—**5a,** 51932-42-4; **5b,** 51932-43-5; **5c,** 51932-44-6; **5d,** 51932-45-7; **5e,** 51932-46-8; **6a,** 51932-47-9; **6b,** 33986-95-7; **6c,** 51932-48-0; **6d,** 51932-49-1; **6e,** 51932-50-4; **7,** 90-16-4; **8,** 22305-46-0; **9,** 5771-05-1; **10,** 51932-51-5; **11,** 19562-37-9; **12,** 51932-52-6; **14,** 22305-44-8.

Supplementary Material Available. Line diagram mass spectra of the betaines **5a–e, 6a–e, 8,** and **10** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-2710.

References and Notes

(1) F. D. Chattaway and A. J. Walker, *J. Chem. Soc.*, 2407 (1925).
(2) F. D. Chattaway and A. J. Walker, *J. Chem. Soc.*, 232 (1927).
(3) F. D Chattaway and A. B. Adamson, *J. Chem. Soc.*, 157, 843 (1930).
(4) F. D. Chattaway and A. B. Adamson, *J. Chem. Soc.*, 2787, 2792 (1931).
(5) F. D. Chattaway and G. D. Parkes, *J. Chem. Soc.*, 1005 (1935).
(6) See also J. G. Erickson in "The Chemistry of Heterocyclic Compounds," Vol. 10, A. Weissberger, Ed., Interscience, New York, N. Y., 1956, pp 27–30.
(7) M. S. Gibson, *Tetrahedron*, **18**, 1377 (1962); *Nature (London)*, **193**, 474 (1962).
(8) R. C. Kerber, *J. Org. Chem.*, **37**, 1587 (1972).
(9) See, *e.g.*, N. Dennis, A. R. Katritzky, and Y. Takeuchi, *J. Chem. Soc., Perkin Trans. 1*, 2054 (1972).
(10) D. P. Clifford, Ph.D. Thesis, University of East Anglia, 1967.
(11) G. Wagner and H. Gentzsch, *Pharmazie*, **23**, 629 (1968).
(12) L. G. Markarova and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 617 (1945); *Chem. Abstr.*, **40**, 4686 (1946).
(13) R. B. Sandin and R. K. Brown, *J. Amer. Chem. Soc.*, **69**, 2253 (1947).
(14) F. M. Beringer, A. Brierly, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Amer. Chem. Soc.*, **75**, 2708 (1953).
(15) A. N. Nesmeyanov, L. G. Makarova, and T. P. Tolstaya, *Tetrahedron*, **1**, 145 (1957).
(16) S. Sakai, K. Nakajima, A. Ihida, I. Ishida, and M. Saito, *Yakugaku Zasshi*, **82**, 1532 (1962); *Chem. Abstr.*, **58**, 13912 (1963).
(17) G. E. Chivers and H. Suschitzky, *Chem. Commun.*, 28 (1971).
(18) G. E. Chivers and H. Suschitzky, *J. Chem. Soc. C*, 2867 (1971).
(19) F. M. Beringer, E. J. Geering, I. Kuntz, and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).
(20) F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner, and E. Sommer, *J. Amer. Chem. Soc.*, **81**, 342 (1959).