BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3174—3178 (1972)

The Reaction of Troponoid with Ylide. III.[1,2] The Reaction of Tropone with Pyridinium Compounds

Yukio SUGIMURA, Nobuo SOMA, and Yukichi KISHIDA

Central Research Laboratories, Sankyo Co., Ltd., Hiromachi, Shinagawa-ku, Tokyo

(Received March 13, 1972)

Phenacylpyridinium ylide (**2**) reacted with tropone (**1**) to afford 2-hydroxy-2-phenyl-3-phenacyl-2*H*-cyclohepta[*b*]furan (**3**) which was converted into 2-(1′,2′-dibenzoylethyl)tropone (**4**). The reactions of tropone with several kinds of pyridinium bromides (**7**) yielded 2-substituted tropones in the presence of amine, and 1-azaazulene derivatives (**9, 10, 11**) in a one-step formation in the presence of ammonium acetate.

Many reactions of tropone with nucleophiles have been reported since its unique conjugated cyclic trienone system is thought to exert a contribution of the 6π cation system. We earlier reported[3] on the reaction of troponoids with sulfur ylides. In this paper we describe the reactions of tropone with pyridinium salts and pyridinium ylides under various conditions giving 2-substituted tropones and resulting in some one-step azaazulene formations. The chemistry of pyridinium salts and the corresponding ylides has been extensively studied by Krohnke and his collaborator.[4] For example, pyridinium ylide reacted with conjugated carbonyl compounds giving stable pyridinium ylides by Michael addition. The newly formed ylides were utilized to synthesize some heterocyclic systems. Since tropone generally reacts with a nucleophile at 2-position, we at first presumed that the reaction of tropone with pyridinium ylide would give an ylide having tropone moiety or, in the presence of ammonium ion, 1-azaazulene derivatives.

Results

The Reactions of Tropone with Phenacylpyridinium Ylides. When tropone (**1a**) was treated in benzene with phenacylpyridinium ylide prepared by Krohnke's method, red crystals were obtained. Recrystallization gave a pure substance of cycloheptafuran derivative (**3**), mp 134.5—135.5°C in 58.4% yield. The IR showed absorption maxima at 3450 cm^{-1} (OH stretching) and 1680 cm^{-1} (C=O stretching) and the UV exhibited $\lambda_{max}^{ethanol}$ at 240, 320, 335, and 350 nm. The patterns of the spectra closely resembled those of heptafulvene. The elemental analysis and high resolution mass spectrum agreed with the formula $C_{23}H_{18}O_3$ for **3**. **3** was converted into 2-(1′,2′-dibenzoylethyl)tropone (**4a**) on silica gel column chromatography and into a tropylium salt (**5**), $C_{46}H_{34}O_4Cl_6Pt$, by treatment with platinic chloride. The IR of **4a** showed maxima at 1690, 1635, and 1585 but lacked the OH band at 3450 cm^{-1} originally observed in **3**, while the UV highly resembled that of tropone. The elemental analysis and mass spectra agreed with

1) Studies on Seven Membered Ring Compounds XXXVIII. Part II: Y. Sugimura, N. Soma, and Y. Kishida, *Tetrahedron Lett.*, **1971**, 91.

2) A part of this work was reported at the 22nd Annual Meeting of The Chemical Society of Japan (April, 1969, Tokyo): Y. Sugimura and N. Soma, Abstract of papers, p. 1465.

3) Y. Sugimura and N. Soma, *Tetrahedron Lett.*, **1970**, 1721.

4) F. Krohnke, *Angew. Chem.*, **65**, 605 (1953). F. Krohnke and W. Zecher, *Angew. Chem. Int. Ed. Engl.*,, **1**, 626 (1962). F. Krohnke, *ibid.* **2**, 225 (1963), *ibid.* **2**, 380 (1963).

the formula for **4a** (equal to **3**). Analogously, *p*-bromophenacylpyridinium ylide reacted with tropone or 2-phenyltropone (**1b**) giving compounds of mp 195—197°C; $C_{23}H_{16}O_3Br_2$ (**4b**) in 44.5% and mp 191—193°C; $C_{29}H_{20}O_3Br_2$ (**4c**) in 54.5%, respectively. The molecular formulas were obtained by elemental analyses and mass spectra. The NMR (δ ppm, in $CDCl_3$) of **4b** exhibited ABX pattern at 3.20, 3.89, and 5.83 ($J_{AB}=18$, $J_{AX}=4$, and $J_{BX}=10$ Hz), and 6.8—7.4 (5H, protons of tropone ring), 7.5—8.0 (8H, phenyl protons). The spectroscopic data of **4c** were analogous to those of **4b**, except for the presence of one more phenyl group in the tropone system. **4c** was chosen as a representative for further hydrolysis to determine the structure; refluxing in an aqueous sodium hydroxide-methanol solution gave an oily compound (**6**), $C_{22}H_{17}O_2Br$ and *p*-bromobenzoic acid. The UV absorption maxima of **6** at 230, 255, and 330 nm in ethanol strongly suggested the presence of phenyltropone moiety in **6**. Its IR absorption maxima at 1690 (benzoyl C=O) and 1585 cm^{-1} (tropone C=O) and the NMR [in CCl_4: 2.8—3.5 (4H, A_2B_2; $-CH_2-CH_2-$), 6.8—7.0 (2H), and 7.2—7.4 (7H) ascribed to the phenyltroponyl protons, 7.48 (2H) and 7.77 (2H), ascribed to the benzoyl phenyl protons] suggested that **6** should have the structure of 2-(2′-*p*-bromobenzoylethyl)-7-phenyltropone. Mechanistic consideration together with all the evidence enabled us to assign the structure of 2-(1′,2′-di-*p*-bromobenzoylethyl)-7-phenyltropone for **4c**. Thus the structures of **4a** and **4b** were assigned to be 2-(1′,2′-dibenzoylethyl)tropone and 2-(1′,2′-di-*p*-bromobenzoylethyl)tropone, respectively. The assignments led to determination of the structures of **3** and **5** to be 2-hydroxy-2-phenyl-3-phenacyl-2*H*-cyclohepta[*b*]furan and 2-phenyl-3-phenacylcyclohepta[*b*]furanium hexachloroplatinate.[5] Analogously, tropone reacted with *p*-bromophenacylpyridinium bromide in the presence of K_2CO_3 in DMSO to give **4b** in 30% yield.

The Reactions of Pyridinium Salts with Tropone in the Presence of Amines. Application of the forementioned reactions was limited, since phenacylpyridinium ylides are so stable as to be isolated among pyridinium ylides. The use of pyridinium salts in the presence of amine was then attempted in order to extend the applicability of the reactions.

Tropone was added to a suspension of phenacylpyridinium bromide in tetrahydrofuran (THF) containing triethylamine. The reaction product obtained as a partially crystallized syrup was chromatographed to give 2-phenacyltropone (**8a**) in 61% yield. Identification was carried out by mixed melting point and spectroscopy with an authentic sample. Analogous treatments of tropone with *p*-bromophenacylpyridinium bromide (**7b**), ethoxycarbonylmethylpyridinium bromide (**7c**) and acetonylpyridinium

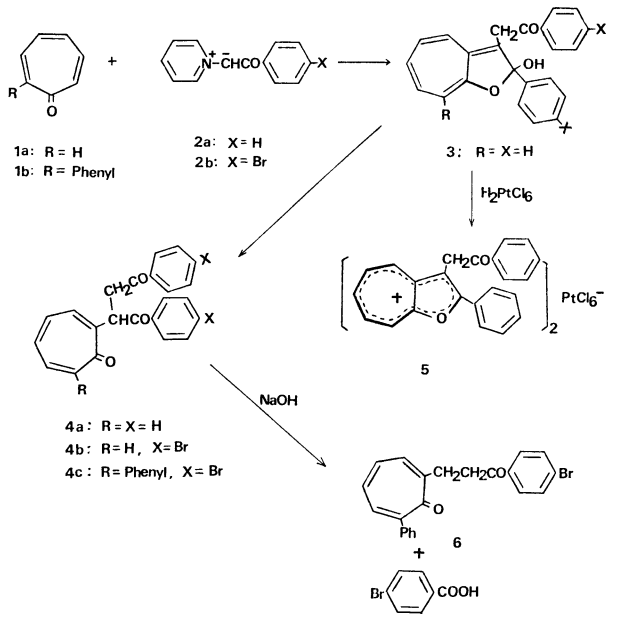


Chart 1.

bromide (**7d**) in the presence of triethylamine gave the corresponding 2-substituted tropones (**8b**, **8c**, and **8d**). Tropone did not react with *o*-cyanobenzylpyridinium bromide (**7e**) in THF–triethylamine, but reacted in ethanol–piperidine giving 2-(*o*-cyanobenzyl)tropone (**8e**) in 45.5% yield. The structure of **8e** was determined by physicochemical data (see Experimental). It is noteworthy that the reaction of tropone with *p*-bromophenacylpyridinium bromide (**7b**) gave only **8b** and not **4b** even when pyridinium bromide and amine were present in excess.

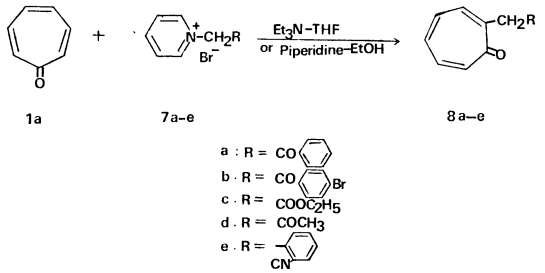


Chart 2.

Synthesis of 1-Azaazulenes. From the fact that the pyridinium ylides attack 2-position of tropone giving 2-substituted tropone, 1-azaazulene derivatives would be formed in the presence of ammonium ion. In fact 2-phenacyltropone (**8a**) was converted into 2-phenyl-1-azaazulene (**9a**) by treatment with ammonium acetate in acetic acid. **9a** was directly obtained by refluxing a mixture of tropone, phenacylpyridinium bromide (**7a**) and ammonium acetate in acetic acid. The principle of the procedure was exactly the same as in the pyridine synthesis by Krohnke.[6] Purple crystals of **9a** were obtained in 21% yield, mp 157—159°C. The structural confirmation was made by physicochemical data, especially the characteristic

5) 2-Phenylcycolhepta[*b*]furanium fluorosulfonate was isolated and the structure was determined (unpublished work). The UV absorption closely resembles that of **5** (see Experimental) and NMR suggests the hybridization of the charge in 10π system. UV: $\lambda_{max}^{ethanol}$ 255, 300, 425 nm. NMR (in DMSO): 7.94 (2H, A_2B_2), 8.25 (2H, A_2B_2), 8.33 (1H, s), 8.8—9.2 (3H. m), 9.3—9.5 (2H, m).

6) W. Zecher and F. Krohnke, *Chem. Ber.*, **94**, 690 (1961).

UV: $\lambda_{max}^{ethanol}$ 237.5 (log ε=4.20), 287.5 (4.58), 312 (4.45), 357 (4.08), and 373 (4.03) nm (the other data are given in Experimental). Analogously, tropone reacted with acetonylpyridinium bromide (**7d**) giving a blue oil of 2-methyl-1-azaazulene (**9b**), which was converted into its picrate, mp 196—198°C. A similar treatment of tropone with cyanomethylpyridinium chloride (**7f**) gave 2-imino-1,2-dihydrocyclohepta-[*b*]pyrrole (**10**), mp 177°C, in 14% yield. Identification of the structure was made by comparison of the spectroscopic data with those of an authentic sample.[7] Tropone also reacted with 2-oxo-3,4-benzocyclohexylpyridinium bromide (**7g**) in the presence of triethylenediamine (DABCO) and ammonium acetate in ethanol to give 12-aza-5,6-dihydronaphth[2,1-*a*]-azulene (**11**) as purple oil. This was dehydrogenated to 12-azanaphth[2,1-*a*]-azulene (**12**), mp 195—197°C, by refluxing with DDQ in benzene. The UV and visible light spectra of $\lambda_{max}^{ethanol}$ 337, 374, and 537 nm indicate characteristics of the structure.

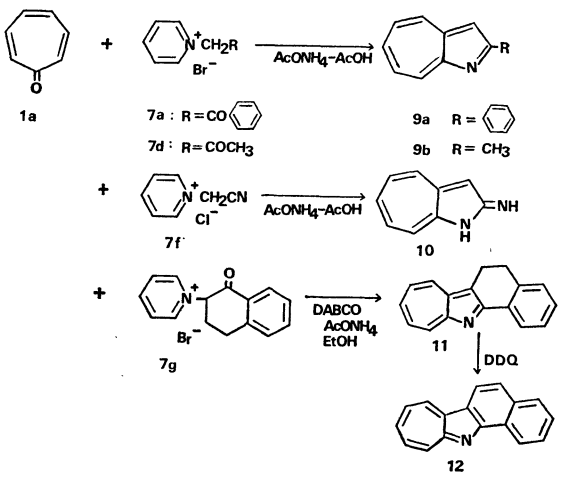
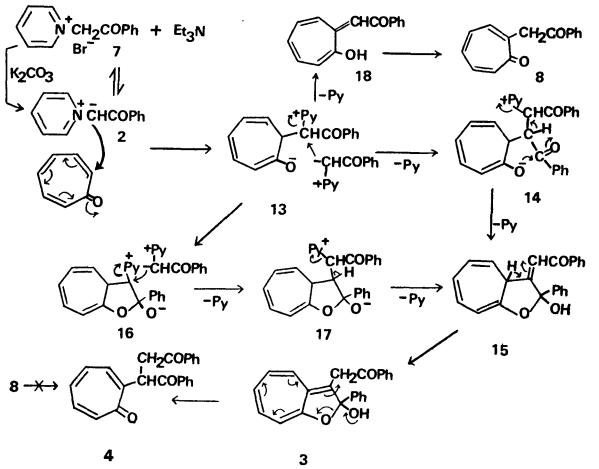


Chart 3.

Discussions

Plausible mechanisms for the formation of **3**, **4**, and **8** are shown in Fig. 1. For **3**, two moles of pyridinium ylide participate in the reaction, such a mode of reaction being very rare.[8] Pyridinium betaine (**13**) formed at first is further attacked by the second ylide to give **14** with concomitant liberation of pyridine, subsequent cyclization affording **15**. By an alternative route, betaine **13** would first cyclize to give **16** which is succeedingly attacked by the second ylide to afford **15** *via* **17**. On the other hand, for the formation of **8**, *viz.*, in the reaction of tropone with a phenacylpyridinium bromide in the presence of amine, the ylide is not present in excess so as to be able to attack **13**, since an equilibrium between the ylide (**2**) and its conjugate acid (**7**) should exist under such reaction conditions and the ylide formed is immediately consumed by tropone to give betaine (**13**). Elimination of pyridine from **13** to give heptafulvene (**18**) would be reasonable because of the stability of **18**. Phenacyltropone (**8b**) thus obtained did not give **4b** by the reaction with ylide (**2b**). Thus a proton exchange between **8** and **2** would not be feasible. Recently Sasaki *et al.*[9] reported that the reaction of tropone with ethoxycarbonylaminopyridinium ylide gave 2-ethoxycarbonylaminotropone and they obtained no 1 : 2-adduct such as **4**. It is not certain whether the difference in reaction pattern is derived from the nucleophilicity of ylide or other factors.



Py: Pyridine Ph: Phenyl

Fig. 1.

The reaction mentioned in the second paragraph is valuable for the preparation of 2-substituted tropones which have hitherto been synthesized from oxaazulanone in lower yields.

Experimental

All melting points are uncorrected. The NMR spectra were taken on Varian A-60 (60 MHz) and HA-100 (100 MHz) spectrometers, and indicated in δ ppm using TMS as an internal standard.

2-Hydroxy-2-phenyl-3-phenacyl-2H-cyclohepta[b]*furan* (*3*). Tropone (2.05 g) was added dropwise under cooling with an ice-water bath to a suspension of phenacylpyridinium ylide (**2a**) in dry benzene (80 m*l*), obtained from phenacylpyridinium bromide (7 g) and potassium carbonate (23 g) by the method of Krohnke. The reaction mixture turned red when the orange crystals of ylide were dissolved. The precipitated white crystals were separated and washed with benzene. The filtrate and washing were combined and evaporated to dryness to give reddish yellow crystals. The crystals were washed with a small amount of benzene and recrystallized from benzene-chloroform to give 1.56 g of the compound, mp 134.5—135.5°C, in 58.6% yield. The mother liquor was chromatographed and the starting tropone (1.22 g) was recovered. Found: C, 80.77; H, 5.40%. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30%. IR: ν (Nujol) 3450, 1680 cm^{-1}. UV: $\lambda_{max}^{ethanol}$ 240, 320, 335, 350 nm; $\lambda_{max}^{0.1N\,HCl}$ 250 (log ε=4.51), 292 (4.36), 423 (4.27) nm. High

7) H. Nakao, N. Soma and G. Sunagawa, *Chem. Pharm. Bull.* (Tokyo), **13**, 828 (1965).

8) For the sulfur ylide, some reactions were reported: T. Kunieda and B. Witcop, *J. Org. Chem.*, **35**, 3981 (1970).

9) T. Sasaki, K. Kanematsu, and S. Kakei, Abstract papers of The Annual Meeting of the Organic Synthetic Society of Japan (Nov. 1971, Tokyo) p. 71.

resolution mass spectrum: *m/e* M^+ 342.123. Calcd for $C_{23}H_{18}O_3$: 342.125.

*2-(1',2'-Dibenzoylethyl)tropone (**4a**).* Chromatography of **3** (1.2 g) on silica gel (100 g) with chloroform-benzene gave the compound (100 mg), mp 128—129°C. Found: C, 80.82; H, 5.40%. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30%. IR: *ν* (nujol) 1690, 1635, 1585 cm^{-1}. UV: $\lambda_{max}^{ethanol}$ 242 (log ε=4.55), 313 (3.94) nm.

2-Phenyl-3-phenacyclohepta [b] *furanium Hexachloroplatinate (**5**).* An aqueous solution of platinic chloride was added to an ethereal solution of **3** to give precipitates of yellow powder, mp above 300°C. Found: C, 51.89; H, 3.35; Cl, 19.61%. Calcd for $C_{46}H_{34}Cl_6Pt$: C, 52.28; H, 3.24; Cl, 20.1%. IR: *ν* (Nujol) 1690, 1600 cm^{-1}: UV: $\lambda_{max}^{ethanol}$ 252.5, 290, 412 nm.

*2-(1',2'-Di-*p*-bromobenzoylethyl)tropone (**4b**).* Tropone (1 g) was added under cooling with ice-water to a suspension of *p*-bromophenacylpyridinium ylide (**2b**) in dry benzene (40 m*l*) prepared from *p*-bromophenacylpyridinium bromide (5 g) in dry benzene. The reaction mixture was stirred for 2 hr at 0—10°C and the precipitated crystals were separated by filtration and washed with benzene. The filtrate and the washing were combined and evaporated to dryness to give colorless crystals. The crystals were recrystallized from benzene to give 1.87 g of the compound (**4b**), mp 195—197°C, in 44.5% yield. Found: C, 54.95; H, 3.30; Br, 31.94%. Calcd for $C_{23}H_{16}O_3Br_2$: C, 55.21; H, 3.22; Br, 31.95%. IR *ν* (Nujol) 1672, 1575 cm^{-1}. UV: $\lambda_{max}^{0.1N\,HCl}$ 258 (log ε=4.58), 314 (3.92) nm. NMR (in $CDCl_3$): 3.20 (1H, d of d, *J*=18 and 4 Hz), 3.89 (1H, d of d, *J*=18 and 10), 5.83 (1H, d of d, *J*=10 and 4), 6.8—7.4 (5H, m), 7.5—8.0 (8H, m, aromatic). Mass spectrum (*m/e*) 498 ($^{79}Br_2$, M^+), 480 ($^{79}Br_2$) 452 ($^{79}Br_2$), 315 (^{79}Br), 298 (^{79}Br), 183 (^{79}Br), 155 (^{79}Br).

*2-(1',2'-Di-*p*-bromobenzoylethyl)-7-phenyltropone (**4c**)* The compound (1.57 g) was obtained from *p*-bromophenacylpyridinium bromide (5 g) and 2-phenyltropone (910 mg) in 54.5% yield by a similar method to that for the preparation of **4b**, mp 191—193°C. Found: C, 60.34; H, 3.68; Br, 27.43%. Calcd for $C_{29}H_{20}O_3Br_2$: C, 60.44; H, 3.50; Br, 27.74%. IR $\nu_{C=O}$ (Nujol) 1685, 1585 cm^{-1}. UV: $\lambda_{max}^{ethanol}$ 259 (log ε=4.65), 312 (3.98) nm. NMR (in $CDCl_3$): 3.28 (1H, d of d, *J*=17.6 and 4 Hz), 3.93 (1H, d of d, *J*=17.6 and 9.4), 5.84 (1H, d of d, *J*=9.4 and 4), 6.75—7.05 (2H, m), 7.3—8.0 (15 H).

*2-(1',2'-Di-*p*-bromobenzoylethyl)tropone (**4b**) from the Pyridinium Salt.* A suspension of *p*-bromophenacylpyridinium bromide (3.5 g) and K_2CO_3 (0.7 g) in DMSO (30 m*l*) was stirred for 50 min at room temperature and then cooled to 0°C. Tropone (530 mg) was added to the suspension and the reaction mixture was stirred for two hours at 0°C. The reaction mixture was then poured onto ice-water and extracted with chloroform. The extract was washed with water, dried over magnesium sulfate and condensed to give oily residue (1.68 g) which partially crystallized. The crystals were collected by filtration and washed with benzene to give 120 mg of **4b**. The filtrate and washing were combined and subjected to silica gel column chromatography. The benzene-chloroform (1 : 1) eluate gave 190 mg of **4b**. Yield 30%.

*2-(2'-*p*-Bromobenzoylethyl)-7-phenyltropone (**6**).* **4c** (1 g) was added to a solution of sodium hydroxide (524 mg) in 50% aqueous methanol (50 m*l*) and the reaction mixture was refluxed for five hours. After removal of the solvents, the residual oil was extracted with chloroform. The extract was washed with water, dried over magnesium sulfate and condensed to give a partially crystallized syrup. The crystals were collected by filtration to recover the starting **4c** (350 mg). The filtrate was purified by silica gel column chromatography to afford 170 mg of compound (**6**) as syrup. Found: C, 66.70; H, 4.59; Br, 20.04%. Calcd for $C_{22}H_{17}O_2Br$: C, 67.17; H, 4.36; Br, 20.32%. IR $\nu_{C=O}$ (liquid) 1685, 1585 cm^{-1}. UV: $\lambda_{max}^{ethanol}$ 230, 255, 330 nm. NMR (in $CDCl_3$): 2.9—3.4 (4H, A_2B_2 pattern), 6.8—7.0 (2H, m), 7.2—7.4 (7H), 7.48 and 7.77 (each 2H, A_2B_2).

*2-Phenacyltropone (**8a**).* Triethylamine (1 m*l*) was added to a suspension of phenacylpyridinium bromide (**7a**, 2.78 g) in tetrahydrofuran (14 m*l*) and the reaction mixture was stirred for fifteen minutes at room temperature. To this was added a tetrahydrofuran solution of tropone (1.06 g/10 m*l*) and the whole mixture was stirred overnight at room temperature. The precipitated crystals were separated by filtration and the filtrate was condensed to give a syrup, which was purified by silica gel dry column chromatography to afford 2-phenacyltropone (**8a**, 1.43 g) in 61% yield. **8a**, mp 113—113.5°C, was identified with an authentic sample by spectrometry.

2-p-*Bromophenacyltropone (**8b**).* The compound (**8b**, 1.21 g) was obtained from *p*-bromophenacylpyridinium bromide (1.8 g), triethylamine (0.6 m*l*), and tropone (0.5 g) in 80% yield by a similar method to that for the preparation of **8a**, mp 102—104°C. Found: C, 59.45; H, 3.78; Br, 26.16%. Calcd for $C_{15}H_{11}O_2Br$: C, 59.40; H, 3.66; Br, 26.35%. IR: $\nu_{C=O}$ (nujol) 1685, 1585 cm^{-1}. NMR (in $CDCl_3$): 4.23 (2H, s), 6.9—7.3 (4H, m), 7.3—7.55 (1H, m), 7.67 (2H, A_2B_2), 8.00 (2H, A_2B_2).

*2-Ethoxycarbonylmethyltropone (**8c**).* The compound (**8c**, 0.95 g) was obtained from ethoxycarbonylmethylpyridinium bromide (**7c**, 2.46 g), triethylamine (1 m*l*), and tropone (1.0 g) in 63% yield (considering the recovery of the starting tropone, 0.42 g) by a similar method to that for the preparation of **8a**, mp 66°C (recrystallized from isopropyl ether). Found: C, 66.42; H, 6.93%. Calcd for $C_{11}H_{12}O_3$: C, 66.65; H, 6.71%. IR$\nu_{C=O}$ (Nujol) 1740, 1585 cm^{-1}. NMR (in $CDCl_3$): 1.27 (3H, t, *J*=7 Hz), 3.62 (2H, s) 4.20 (2H, q, *J*=7), 6.85—7.50 (5H, m).

*2-Acetonyltropone (**8d**).* The compound (**8d**, 1.47 g) was obtained from acetonylpyridinium bromide (**7d**, 2.16 g), triethylamine (1 m*l*), and tropone (1.06 g) in 95% yield by a similar method to that for the preparation of **8a**. **8d** was a yellow oil whose purity was checked by vpc. (PEG 10% column). Found: C, 71.54; H, 6.83%. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71%. IR: $\nu_{C=O}$ (liquid) 1715, 1585 cm^{-1}. NMR (in $CDCl_3$): 2.30 (3H, s), 3.68 (2H, s), 6.85—7.40 (5H, m).

2-o-*Cyanobenzyltropone (**8e**).* Piperidine (1 m*l*) was added to a solution of *o*-cyanotolylpyridinium bromide (**7e**, 2.77 g) in ethanol (10 m*l*) and the reaction mixture was stirred for ten minutes. Tropone (1.06 g) was then added. After being left to stand overnight at room temperature, the reaction mixture was poured onto ice-water and extracted with chloroform. The extract was washed with water, dried over magnesium sulfate, and condensed to give a syrup. The residual syrup was purified by silica gel dry column chromatography to afford 503 mg of the compound **8e** as colorless crystals which were recrystallized from chloroform-isopropyl ether, mp 110—112°C. Found: C, 81.40; H, 5.13; N, 6.18%. Calcd for $C_{15}H_{11}ON$: C, 81.43; H, 5.01; N, 6.33%. IR $\nu_{C=O}$ (Nujol) 1575, $\nu_{C\equiv N}$ 2220 cm^{-1}. NMR (in $CDCl_3$) 4.22 (2H, s), 6.9—7.8 (11H, m).

*2-Phenyl-1-azaazulene (**9a**).* Tropone (2.12 g) was added at room temperature to a solution of phenacylpyridinium bromide (**7a**, 5.6 g) and ammonium acetate (8 g) in acetic acid (40 m*l*) and the reaction mixture was stirred

and heated to refluxing. The reaction mixture turned dark red at about 80°C and black at refluxing temperature. After refluxing for two hours, the solvent was evaporated and the residual syrup was poured onto ice-water and allowed to stand overnight at room temperature. The precipitates were filtered off with the aid of celite and washed with chloroform. The filtrate and washing were combined and extracted with chloroform. The chloroform extract was washed with water, dried over magnesium sulfate and condensed to give reddish purple crystals of the compound (**9a**, 850 mg) in 21% yield, mp 157—159°C (recrystallized from benzene-cyclohexane). Found: C, 87.71; H, 5.61; N, 6.78%. Calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82%. UV: $\lambda_{max}^{ethanol}$ 237.5 (log ε=4.20), 287.5 (4.58), 312 (4.45), 357 (4.08), 373 (4.03) nm. NMR (in $CDCl_3$): 7.3—7.9 (7H, m), 8.3—8.9 (4H, m). Mass spectrum (*m/e*): 205 (M^+), 190, 178, 176, 151, 127, 102.

*2-Methyl-1-azaazulene (**9b**).* Tropone (3.18 g) was added at room temperature to a solution of acetonylpyridinium bromide (**7b**, 6.48 g) and ammonium acetate (12 g) acetic acid (60 ml). The reaction mixture was stirred and heated to refluxing. The mixture then turned dark brown. After refluxing for one hour, the solvent was evaporated and the residual syrup was poured onto ice-water. The precipitate was filtered off with the aid of celite and washed with chloroform. The combined filtrate and washing were neutralized with 10% aqueous sodium hydroxide solution and extracted with chloroform. The extract was washed with water, dried over magnesium sulfate and condensed to give a dark green syrup which was subjected to alumina column chromatography. From the benzene eluate 970 mg of the compound (**9b**) was obtained as a blue syrup (23%). **9b** was converted into its picrate of green crystal, mp 196—198°C, by treatment with an ethanol solution of picric acid. Picrate of **9b**: Found: C, 51.54; H, 3.75; N, 14.61%. Calcd for $C_{16}H_{12}N_4O_7$: C, 51.62; H, 3.25; N, 15.05%.

2-Imino-1,2-dihydrocyclohepta[b]*pyrrole (**10**).* Tropone (2.12 g) was added at room temperature to a solution of cyanomethylpyridinium chloride (**7g**, 3.09 g) and ammonium acetate (8 g) in acetic acid (30 ml) and the reaction mixture was stirred and refluxed for seven hours. After evaporation of the solvent, the residue was poured onto ice-water and allowed to stand overnight at room temperature. The precipitates were filtered off with the aid of celite, and washed with water. The combined filtrate and washing were washed with chloroform, neutralized with 10%-aqueous sodium hydroxide solution and extracted with chloroform. The chloroform extract was washed with water, dried over magnesium sulfate and condensed to give the compound as brown crystals, mp 175—177°C (recrystallized from benzene), 0.4 g (yield 14%). Found: C, 74.80; H, 5.63; N, 19.36%. Calcd for $C_9H_8N_2$: C, 74.97; H, 5.59; N, 19.43%.

12-Aza-5,6-dihydronaphth[*2,1*-a]*azulene (**11**).* 2-Oxo-3,4-benzocyclohexylpyridinium bromide (3.04 g) was added to a solution of triethylenediamine (1.12 g) and ammonium acetate (1 g) in ethanol (20 ml) and the reaction mixture was stirred at 50°C for ten minutes. Tropone (1.06 g) was added and the whole mixture was refluxed for five hours. The precipitated crystals were then filtered off and the filtrate was condensed to give a partially crystallized syrup. The crystals were filtered off and washed with benzene. The combined filtrate and washing were subjected to silica gel dry column chromatography. After development with benzene-ethyl acetate (4 : 1), each fraction of R_f 0.2 and 0.1 was collected and extracted with chloroform. The starting tropone (0.7 g) was recovered from the former the compound **11** (170 mg) as a purple syrup from the latter. Mass spectrum (*m/e*): 231 (M^+, base peak), 230, 202, 121, 93. UV: $\lambda_{max}^{ethanol}$ 244, 292, 324, 502 nm. NMR (in $CDCl_3$): 3.13 (4H, s), 6.7—7.3 (6H, m), 8.1—9.0 (3H, m).

12-Azanaphth[*2,1*-a]*azulene (**12**).* A solution of **11** (140 mg) and DDQ (300 mg) in benzene (20 ml) was refluxed for two hours. The reaction mixture was then poured onto 10%-aqueous sodium hydroxide solution and extracted with chloroform. The chloroform extract was washed with water, dried over magnesium sulfate and condensed to give violet crystals of the compound (**12**) which were recrystallized from benzene-*n*-hexane, mp 195—197°C, 60 mg. Found: C, 89.13; H, 4.76; N, 6.02%. Calcd for $C_{17}H_{11}N$: C, 89.05; H, 4.84; N, 6.11%. Mass spectrum (*m/e*): 229 (M^+, base peak), 205, 203, 202, 200, 178, 177, 176, 175, 174. UV: $\lambda_{max}^{ethanol}$ 337, 374, 537 nm. NMR (in $CDCl_3$) 7.6—8.3 (8H, m), 8.7—9.2 (3H, m).

We are grateful to Professor T. Nozoe for his helpful discussion.