Dyes and Pigments 9 (1988) 459–466

Diphenylmethane and Triphenylmethane Dye Ethynovinylogues with Absorption Bands in the Near-Infrared*

Shuzo Akiyama, Shin'ichi Nakatsuji, Kenichiro Nakashima
& Seiko Yamasaki

Faculty of Pharmaceutical Sciences, Nagasaki University,
1–14 Bunkyo-machi, Nagasaki 852, Japan

(Received 20 November 1987; accepted 4 January 1988)

ABSTRACT

Diphenylmethane and triphenylmethane dye ethynovinylogues (i.e., substituted (ethynyl) (vinyl) carbenium ions), light-absorbing in the near-infrared (up to 814 nm in CH_2Cl_2*), have been synthesized by treatment of 1,3,5-trisubstituted 1-penten-4-yn-3-ols with acids. The light absorption behaviour of the bis(*p*-dimethylaminophenylethynyl)phenyl carbenium ion and related dyes in acidic medium is described.*

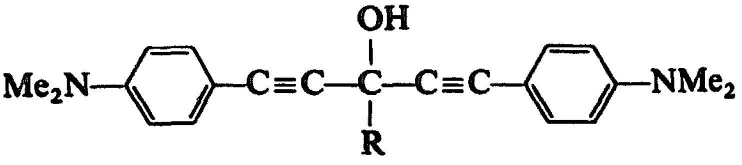
1 INTRODUCTION

Near-infrared (near IR) dyes are of interest for applications in optical and laser data technology[1] and in recent communications[2,3] we reported the first examples of triphenylmethane dye ethynologues (i.e., *p*-dimethylaminophenylethynylxanthenylium, thioxanthenylium, and selenoxanthenylium perchlorates) absorbing in the near-IR. We further planned to extend the conjugated system by introducing a vinyl group into the diphenylmethane or triphenylmethane dye ethynologue system (Scheme 1); moreover, we were interested in comparing an acidic medium reaction of the 1,3,5-trisubstituted 1-penten-4-yn-3-ols (3) with that of the corresponding dehydro compounds (5) which readily gave pyrylium salts instead of the anticipated ethy-

---

* Ethynologues of Triphenylmethane Dyes V: Part IV.[2,3]

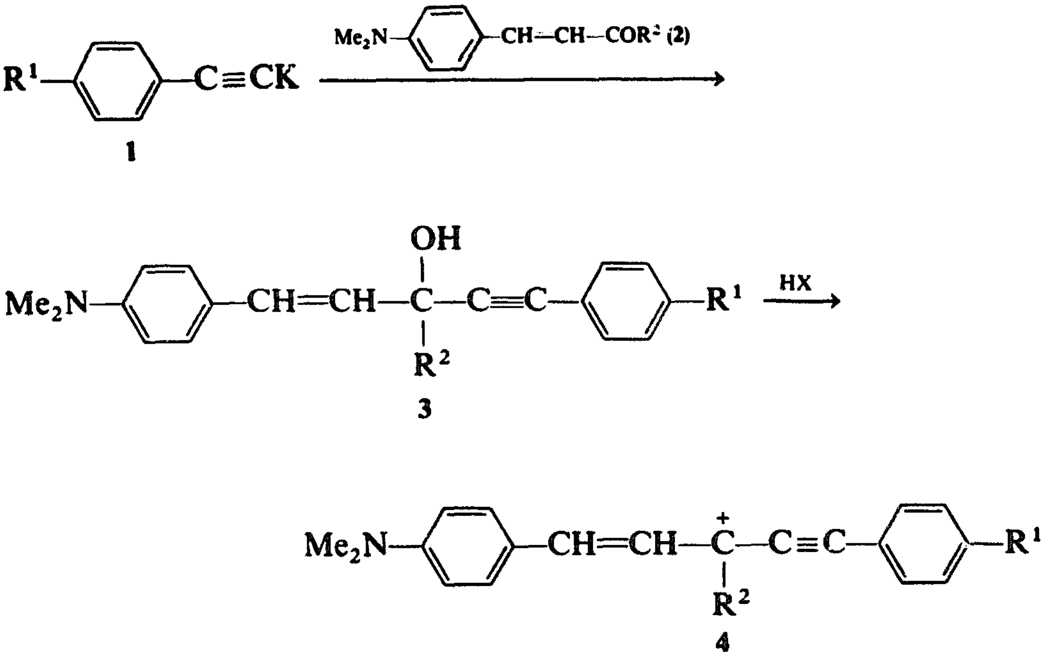
Dyes and Pigments 0143-7208/88/$03·50



5

$R = Ph$, $-C{\equiv}C-Ph$, $-C{\equiv}C-C_6H_5-NMe_2$-*p*, etc.

nologues.[4] We report here the synthesis and the visible absorption spectra of the substituted (ethynyl) (vinyl) carbenium ions [(4), diphenylmethane and triphenylmethane dye ethynovinylogues] and related dyes,[5,6] e.g., (phenyl) (*p*-dimethylaminophenyl) (*p*-dimethyl-aminophenylethynyl)carbenium ion (7). The light absorption characteristics of the monocations (4c and 4d) in the presence of a large molar excess of an acid are also reported.

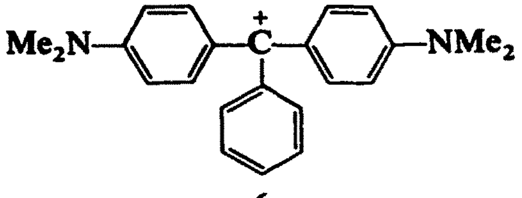


	R1	R2
a	H	*t*-Bu
b	H	Ph
c	Me2N	*t*-Bu
d	Me2N	Ph

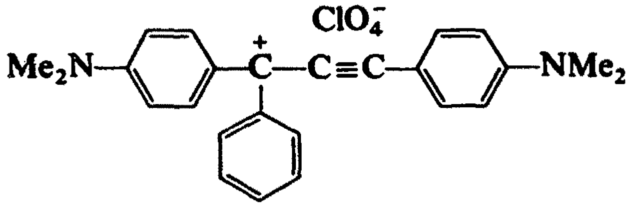
Scheme 1

2 RESULTS AND DISCUSSION

The precursors (**3**) were prepared as outlined in Scheme 1 by reaction of the ketones (**2**) with the potassium *p*-substituted phenylacetylenes (**1**).[2,3] The isolated alcohols were treated with perchloric acid to give the dyes (**4**) as crystals. Similarly, the dye **7** was prepared from the alcohol **3**, which was synthesized by the reaction of lithium *p*-dimethylaminophenylacetylide[7] with phenyl *p*-dimethylaminophenyl ketone.



6



7

The longest-wavelength absorption maxima of the dyes are shown, together with comparative data for Malachite Green (**6**),[8] in Table 1. The dyes **4c** and **4d**, being able to delocalize the positive charge, absorb in the near-IR and it is of particular interest to note the remarkable red shift when comparing dye **4d** with dyes **6** and **7** (Table 1). Compound **7** (λ_{max} 727 nm) is also bathochromic with respect to the corresponding vinylogue (λ_{max} 715 nm).[9] The composition of the ion-pair obtained from **3** by treatment with trifluoroacetic acid in CH_2Cl_2 was studied by the continuous-variations method and found to be 1:1 (monocation–CF_3CO_2) (Fig. 1). It is thus

TABLE 1

Light Absorption Properties of 4 and Related Dyes

Dye	$\lambda_{max}(CH_2Cl_2)$ *(nm)*	*log* ε *(dm³ mol⁻¹ cm⁻¹)*
4a	530	4·68
4b	568	4·47
4c	760	4·42
4d	814	4·86
Malachite Green[a]	621	4·11
7	727	4·93

[a] In 98% acetic acid.[8]

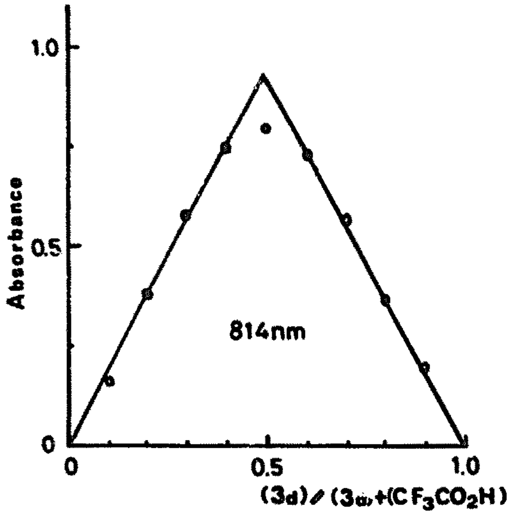


Fig. 1. Composition ratio of ion-pair.

apparent that no protonation occurs in the monocations **4a** and **4b**. On the other hand, in the presence of a large excess of acid (100–2000-fold), **4c** and **4d** undergo successively protonation on either of the two dimethylamino groups to yield the dications, which show significant blue shifts (**4c**: $\lambda_{max} = 760 \rightarrow 496$ nm; **4d**: $\lambda_{max} = 814 \rightarrow 548$ nm). With such a protonation, a hypsochromic effect should be observed as the result of the loss of conjugation of the lone electron pair of the protonated dimethylamino group with the rest of the molecule. The effect of acid on the absorption

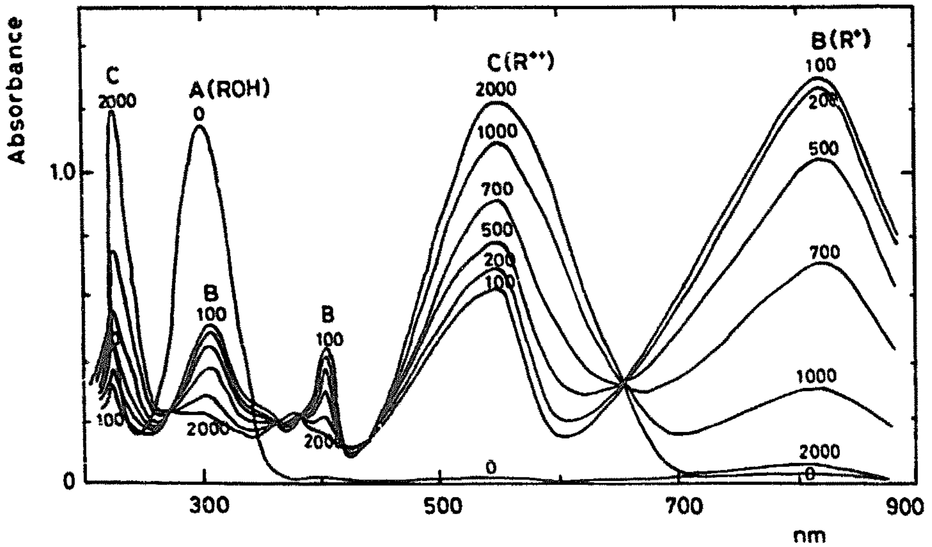


Fig. 2. Effect of trifluoroacetic acid concentration on absorption spectra of **3d** in CH_2Cl_2. A, **3d** (1 cm path length, $5{\cdot}08 \times 10^{-5}$ mol dm^{-3}; B, monocation derived from **3d**; C, dication. The numbers on the peaks denote molar excess ratios of the acid to **3d**.

spectra of **4d** is shown in Fig. 2, in which isosbestic points are observed, indicating the presence of an equilibrium between **4d** and the corresponding dication. Dilution of the above solution with CH_2Cl_2 reproduces gradually the spectra corresponding to the monocation. Isolation of the dications have not yet been successful.

Results of the application in diode-laser high-density recording will be reported, with those of other dye ethynologues, separately.

3 EXPERIMENTAL

All melting points are uncorrected. UV–visible spectra were recorded on Shimadzu UV-265F and Hitachi 210 spectrophotometers, IR spectra on a JASCO IRA 2 spectrophotometer, ^{1}H-NMR spectra on a JEOL FX 90Q spectrometer using TMS as the internal standard and mass spectra on a JEOL instrument. All new compounds gave satisfactory elemental analyses.

3.1 Preparation of *p*-dimethylaminobenzylidene ketones (2)

3.1.1 p-*Dimethylaminobenzylideneacetophenone* (**2**, $R^2 = C_6H_5$)
p-Dimethylaminobenzaldehyde (1·00 g, 6·7 mmol), acetophenone (1·20 g, 10 mmol), a 40% solution of NaOH in H_2O–EtOH (4:1, 2 ml) and EtOH (10 ml) were mixed for 2 h at room temperature. The reaction mixture was poured onto water (100 ml). The product was recrystallized from MeOH to give 0·90 g (54%) of **2** ($R^2 = C_6H_5$), m.p. 114°C;reported m.p. (CH_2Cl_2) 114°C.[10] ν_{max}(IR): 1645 (C=O), 990 (C=C, *trans*) cm^{-1}. Mass spectrum: 251 (M^+). NMR ($CDCl_3$): 3·03 (s, 6H, NMe_2); 6·67 (d, 2H, $J = 9$ Hz, ArH); 7·41–7·83 (m, 7H, 5ArH + CH=CH); 7·91–8·07 (m, 2H, ArH).

3.1.2 p-*Dimethylaminobenzylidenepinacolone* (**2**, R^2 = t-*Bu*)
Yield 57%, m.p. 76–77°C. ν_{max}(IR): 1675 (C=O), 990 (CH=CH, *trans*) cm^{-1}. Mass spectrum: 231 (M^+). NMR ($CDCl_3$): 1·22 (s, 9H, *t*-Bu); 2·96 (s, 6H, NMe_2); 6·60 (d, 2H, $J = 9$ Hz, ArH); 6·85 (d, 1H, $J = 15$ Hz, CH=); 7·41 (d, 2H, $J = 9$ Hz, ArH); 7·63 (d, 1H, $J = 15$ Hz, CH=).

3.2 Preparation of alcohols (3a, 3b, 3c and 3d): general method

Reaction of potassium phenylacetylides (**1**, $R^1 = H$, NMe_2;[2,3,7] 3 mmol) with the corresponding ketones (**2**; 3 mmol) in THF (40 ml) at −5°C for 3 h gave the alcohols **3**, as follows.

3a: Yield 81%, m.p. 112–115°C (ether). ν_{max}(IR): 3050–3200 (OH), 2310 (C$\equiv$C), 1605 (C$=$C) cm^{-1}. Mass spectrum: 333 (M$^+$). λ_{max}($\mathrm{CH_2Cl_2}$): 303 nm (ε_{max} 28 000 dm^3 mol^{-1} cm^{-1}). NMR ($\mathrm{CDCl_3}$): 1·16 (s, 9H, *t*-Bu); 2·15 (s, 1H, OH); 2·96 (s, 6H, $\mathrm{NMe_2}$); 6·21 (d, 1H, $J = 15$ Hz, CH$=$); 6·69 (d, 2H, $J = 9$ Hz, ArH); 6·87 (d, 1H, $J = 15$ Hz, CH$=$); 7·26–7·40 (m, 7H, ArH).

3b: Yield 65%, m.p. *c.* 120°C (decomp.) ($\mathrm{CH_2Cl_2}$). ν_{max}(IR): 3050–3200 (OH), 2200 (C$\equiv$C), 1605 (C$=$C) cm^{-1}. Mass spectrum: 353 (M$^+$). λ_{max}($\mathrm{CH_2Cl_2}$): 308 nm (ε_{max}24 800 dm^3 mol^{-1} cm^{-1}). NMR ($\mathrm{CDCl_3}$): 2·69 (s, 1H, OH); 2·94 (s, 6H, $\mathrm{NMe_2}$); 6·23 (d, 1H, $J = 15$Hz, CH$=$); 6·66 (d, 2H, $J = 9$Hz, ArH); 6·94 (d, 1H, $J = 15$ Hz, CH$=$); 7·24–7·83 (m, 12H, ArH).

3c: Yield 31%, m.p. 135–137°C (ether). ν_{max}(IR): 3100–3500 (OH), 2220 (C$\equiv$C), 1610 (C$=$C), 970 (CH$=$CH, *trans*) cm^{-1}. Mass spectrum: 376 (M$^+$). λ_{max}($\mathrm{CH_2Cl_2}$): 290 nm (ε_{max}49 300 dm^3 mol^{-1} cm^{-1}). NMR ($\mathrm{CDCl_3}$)·1·16(s, 9H, *t*-Bu); 2·08 (s, 1H, OH); 2·97 (s, 12H, $\mathrm{2NMe_2}$); 6·20 (d, 1H, $J = 15$ Hz, CH$=$); 6·62 (d, 2H $J = 9$ Hz, ArH); 6·67 (d, 2H, $J = 9$ Hz, ArH); 6·89 (1H, d, $J = 15$ Hz, CH$=$); 7·32 (d, 2H, $J = 9$ Hz, ArH); 7·36 (d, 2H, $J = 9$ Hz, ArH).

3d: Yield 38%, m.p. 131–133°C ($\mathrm{CH_2Cl_2}$–ether). ν_{max}(IR): 3050–3250 (OH), 2220 (C$\equiv$C), 1605 (C$=$C), 940 (CH$=$CH, *trans*) cm^{-1}. Mass spectrum: 396 (M$^+$). λ_{max}($\mathrm{CH_2Cl_2}$): 304 nm (ε_{max}45 600 dm^3 mol^{-1} cm^{-1}). NMR ($\mathrm{CDCl_3}$): 2·65 (s, 1H, OH); 2·93 (s, 6H, $\mathrm{NMe_2}$); 2·96 (s, 6H, $\mathrm{NMe_2}$); 6·24 (d, 1H, $J = 16$ Hz, CH$=$); 6·62 (d, 2H, $J = 9$ Hz, ArH); 6·64 (d, 2H, $J - 9$ Hz, ArH); 6·92 (d, 1H, $J = 16$ Hz, CH$=$); 7·24–7·47 and 7·69–7·80 (m, 9H, ArH).

3.3 Preparation of dyes (4a, 4b, 4c, and 4d): general method

4d: Perchloric acid (60%, 27 μl) was added to a solution of **3d** (0·10 g, 0·25 mmol) in $\mathrm{CH_2Cl_2}$–EtOH [1 : 2 (v/v), 15 ml] at 0°C. After stirring for 30 min the mixture was evaporated *in vacuo*. The resultant crystals were filtered and washed thoroughly with ether, yield 0·10 g (83%), m.p. *c.* 175°C (decomp.). ν_{max}(IR): 2104 (C$\equiv$C), 1600 (C$=$C), 1070–1100 ($\mathrm{ClO_4}$) cm^{-1}. Mass spectrum: 379 (M$^+$ $-$ $\mathrm{ClO_4^-}$). λ_{max}($\mathrm{CH_2Cl_2}$): 311 (18 700), 409 (16 200), 548 (22 900), 814 nm (ε_{max} 47 300 dm^3 mol^{-1} cm^{-1}). NMR ($\mathrm{CDCl_3}$): 3·24 (s, 6H, $\mathrm{NMe_2}$); 3·52 (s, 6H, $\mathrm{NMe_2}$); 6·60–8·10 (m, 15H, CH$=$CH + ArH).

4a: Yield 8%, m.p. *c.* 190°C (decomp). ν_{max}(IR): 2180 (C$\equiv$C), 1070–1090 ($\mathrm{ClO_4}$) cm^{-1}. Mass spectrum: 316 (M$^+$ $-$ $\mathrm{ClO_4^-}$). λ_{max}($\mathrm{CH_2Cl_2}$): 314 (6100), 530 nm (ε_{max}47 800 dm^3 mol^{-1} cm^{-1}). NMR ($\mathrm{CDCl_3}$): 1·59 (s, 9H, *t*-Bu); 3·65 (s, 6H, $\mathrm{NMe_2}$); 6·92–8·24 (m, 11H, CH$=$CH + ArH).

4b: Yield 18%, m.p. *c.* 120°C (decomp). ν_{max}(IR): 2150 (C≡C), 1600 (C═C), 1060–1090 (ClO_4). Mass spectrum: 336 ($M^+ - ClO_4^-$). λ_{max}(CH_2Cl_2); 568 nm (ε_{max} 29 600 dm^3 mol^{-1} cm^{-1}). NMR (acetone-d_6): 3·78 (s, 6H, NMe_2); 6·70–8·45 (m, 16H, CH═CH + ArH).

4c: Yield 63%, m.p. *c.* 120°C (decomp). ν_{max}(IR): 2150 (C≡C), 1600 (C═C), 1000–1170 (ClO_4). Mass spectrum: 359 ($M^+ - ClO_4^-$). λ_{max}(CH_2Cl_2): 300 (14 500), 378 (9580), 464 (12 700), 492 (13 200), 760 nm (ε_{max}26 900 dm^3 mol^{-1} cm^{-1}). NMR (CD_2Cl_2): 1·40 (s, 9H, *t*-Bu); 3·09 (s, 6H, NMe_2); 3·52 (s, 6H, NMe_2); 6·60–8·30 (m, 10H, CH═CH + ArH).

3.4 Preparation of (phenyl) (*p*-dimethylaminophenyl) (*p*-dimethylaminophenylethynyl) perchlorate (7)

3.4.1 Stage 1: (phenyl) (p-dimethylaminophenyl) (p-dimethylaminophenylethynyl)methyl alcohol (precursor of 7)

A mixture of phenyl *p*-dimethylaminophenyl ketone (0·72 g, 3·2 mmol) and lithium *p*-dimethylaminophenylacetylide, prepared from *p*-dimethylaminophenylacetylene (0·50 g, 3·4 mmol) with *n*-BuLi (3·2 mmol) in THF (110 ml), was stirred at −15°C overnight and worked up in the usual way. The solid obtained was recrystallized from benzene to give colourless crystals (0·75 g, 63%), m.p. 125–127°C. ν_{max}(IR): 3150 (OH), 2200 (C≡C), 1600 (C═C) cm^{-1}. Mass spectrum: 370 (M^+). NMR ($CDCl_3$): 2·72 (s, 1H, OH); 2·92 (s, 6H, NMe_2); 2·95 (s, 6H, NMe_2); 6·62 (d, 2H, $J = 8$ Hz, ArH); 6·64 (d, 2H, $J = 8$ Hz, ArH); 7·24–7·80 (m, 9H, ArH).

3.4.2 Stage 2: Compound 7

To a solution of the above alcohol (40 mg, 0·1 mmol) in benzene (30 ml) was added perchloric acid (60%, 5 drops). The mixture was stirred for 2 h. The resulting solid was decanted and recrystallized from acetone–EtOH (1:1, v/v) to give green crystals (24 mg, 52%), m.p. *c.* 164°C (decomp). ν_{max}(IR): 2120 (C≡C), 1598 (C═C), 1090 (ClO_4) cm^{-1}. Mass spectrum: 345 ($M^+ - ClO_4^-$). λ_{max} (CH_2Cl_2): 482 (20 200), 727 nm (ε_{max} 96 800 dm^3 mol^{-1} cm^{-1}). NMR (acetone-d_6): 3·22 (s, 6H, NMe_2); 3·66 (s, 6H, NMe_2); 6·91 (d, 2H, $J = 9$ Hz, ArH); 7·33 (d, 2H, $J = 9$ Hz, ArH); 7·62–7·79 (m, 7H, ArH); 8·11 (d, 2H, $J = 9$ Hz, ArH).

ACKNOWLEDGEMENTS

We are grateful to Professor (Emeritus) Masazumi Nakagawa (Osaka University) for useful discussions. The financial support of the Grant-in-Aid for Scientific Research (No. 62470035) from the Ministry of Education, Science and Culture of Japan is gratefully acknowledged.

REFERENCES

1. Umehara, M., Abe, M. & Oba, H., *J. Synth. Org. Chem. Jpn*, **43** (1985), 334 and references cited therein.
2. Akiyama, S., Nakatsuji, S., Nakashima, K. & Watanabe, M., *J. Chem. Soc., Chem. Commun.* (1987), 710.
3. Akiyama, S., Nakatsuji, S., Nakashima, K. & Watanabe, M., *J. Chem. Soc., Chem. Commun.* (1987), 1240.
4. Nakatsuji, S., Nakashima, K., Yamamura, K. & Akiyama, S., *Tetrahedron Lett.*, **25** (1984), 5143.
5. Akiyama, S., Yoshida, K., Hayashida, M., Nakashima, K., Nakatsuji, S. & Iyoda, M., *Chem. Lett.* (1981), 311.
6. Nakatsuji, S., Okamoto, N., Nakashima, K. & Akiyama, S., *Chem. Lett.* (1986), 329.
7. Akiyama, S., Nakatsuji, S., Yoshida, K., Nakashima, K., Hagiwara, T., Tsuruta, H. & Yoshida, T., *Bull. Chem. Soc. Jpn*, **56** (1983), 6361.
8. Barker, C. C., Bride, M. H., Hallas, G. & Stamp, A., *J. Chem. Soc.* (1961), 1285.
9. Dufraisse, C., Étienne, A. & Barbieri, P., *Compt. Rend.*, **232** (1951), 1977.
10. Nielsen, A. T. & Houlihan, W. J., *Org. React.*, **16** (1968), 1.