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CYCLOADDITIONS OF VINYLKETENES AND ETHOXYACETYLENE

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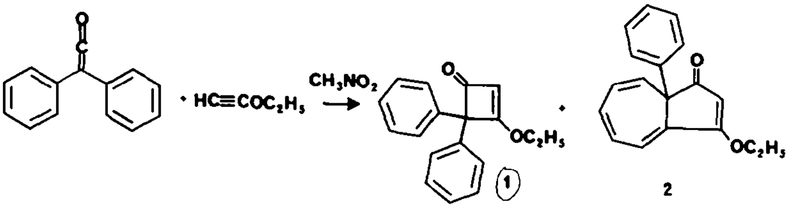
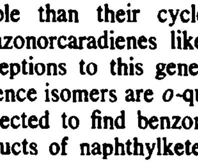
Abstract—Two major adducts are formed when diarylketenes react with ethoxyacetylene: cyclobutenones, produced by 2+2 cycloadditions characteristic of all ketenes, and norcaradienes, the unexpected products of 2+2+2 cycloadditions. Simpler vinylketenes in which the vinyl group is not incorporated in an aromatic ring yield only products derived from 2+2 cycloadditions.

2+2 Cycloadditions are characteristic reactions of ketenes.[1] Formation of cyclobutenone 1 from diphenylketene and ethoxyacetylene illustrates this generalization.[2] However, this reaction also produces similar amounts of an unexpected cycloadduct, dihydroazulenone 2.[2] Compound 2 is not formed by rearrangement of cyclobutenone 1; instead, it appears to be the result of valence isomerization of norcaradiene 3, produced directly by a concerted reaction of diphenylketene with ethoxyacetylene.[2,3] We decided to test this mechanism in the following way. Norcaradienes ordinarily are less stable than their cycloheptatriene valence isomers.[4] Benzonorcaradienes like compound 4 promised to be exceptions to this generalization, however, since their valence isomers are *o*-quinodimethanes.[4] As a result, we expected to find benzonorcaradienes among the cycloadducts of naphthylketenes and ethoxyacetylene. Here we describe the preparation of several naphthylketenes, their cycloadditions with ethoxyacetylene, and the behavior of other vinylketenes.[5]



The reaction of 1-naphthylphenylketene[6] with excess ethoxyacetylene in nitromethane (24 hr, −17°) yielded primarily a cyclobutenone, but chromatographic separation of the crude product provided a second adduct in 26% yield. The IR spectrum of this adduct contained strong bands at 1685 and 1580 cm^{-1} characteristic of 3-ethoxycyclopentenones,[2] and the similarity of the UV and NMR spectra to those reported for benzonorcaradiene 5[7] indicated that this second adduct in fact possessed structure 4. The reactions of benzonorcaradiene 4 supported this conclusion. For example, reduction with sodium borohydride produced alcohol 6, which was directly converted into ethyl Z-4-(1-naphthyl)-4-phenylbuten-3-oate (7) by the action of anhydrous hydrogen chloride (Eq 1). The sequence of reactions described in Fig. 1 accounts for this observation.



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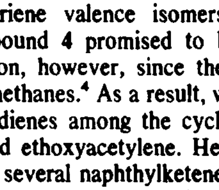

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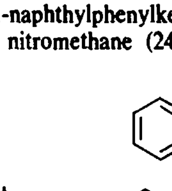

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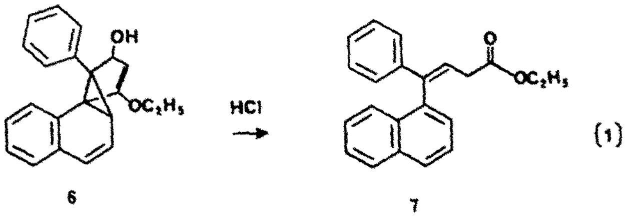
A second naphthylketene, di(2-naphthyl)ketene (8), was prepared by the method summarized in Fig. 2. The reaction of 2-naphthil (9)[8] with potassium t-butoxide in boiling benzene[9] produced t-butyl di(2-naphthyl)glycolate (10; 79%). Hydrolysis of ester 10 provided di(2-naphthyl)glycolic acid (11; 92%),[10] which was then converted into chlorodi(2-naphthyl)acetyl chloride (12; 67%) by the action of hot phosphorus pentachloride.[11] Finally, dechlorination with zinc[6] produced di(2-naphthyl)ketene (8; 89%), an orange solid. A suspension of ketene 8 in nitromethane reacted with excess ethoxyacetylene at −20° (15 hr), and a solution of the crude product in a mixture of ether and hexane slowly deposited crystals of the major adduct (37%). The IR spectrum of this compound contained strong bands at 1680 and 1585 cm^{-1} characteristic of 3-ethoxycyclopentenones,[2] and the similarity of its UV spectrum to the one reported for compound 5[7] indicated that the adduct was benzonorcaradiene 13. Unlike adduct 4, which could be recovered unchanged after sublimation at 170°, compound 13 rearranged at 160° to a phenanthrol. This product has been assigned structure 14 since an apparently similar rearrangement of adduct 2 yielded naphthol 15 (Eq 2).[2]



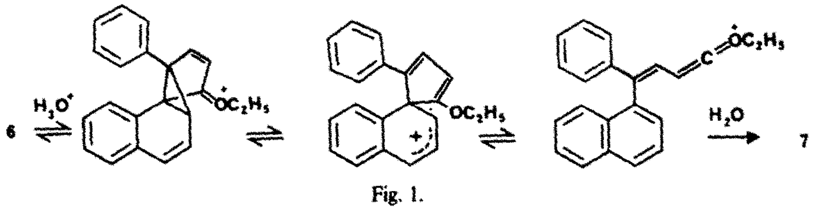


Fig. 1.

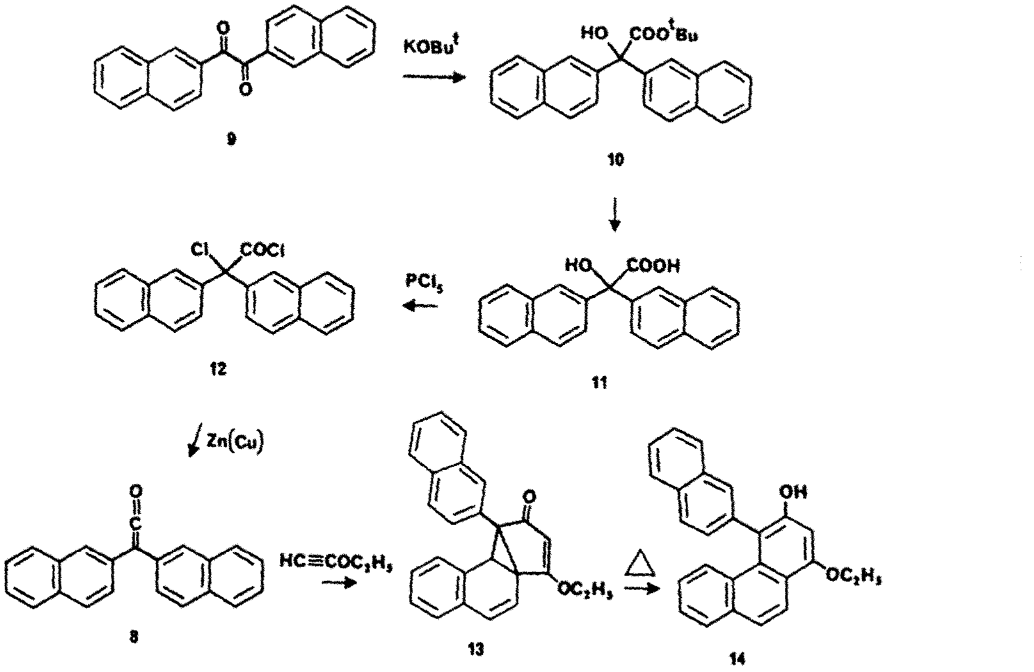
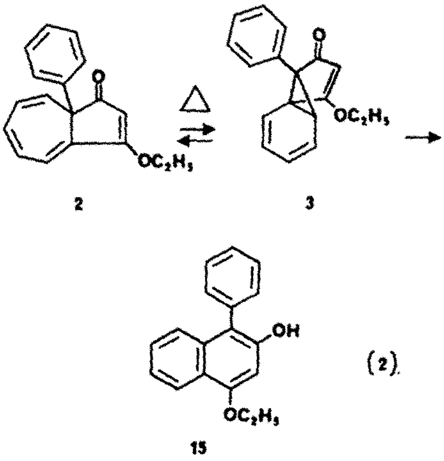


Fig. 2.

A third naphthylketene, di(1-naphthyl)ketene (**16**), was prepared by the sequence of reactions summarized in Fig. 3. Hydrolysis of the crude product from the reaction of diethyl oxalate with 1-naphthylmagnesium bromide produced di-1-naphthyl)glycolic acid (**17**; 56%),[10,12] which was efficiently converted into chlorodi(1-naphthyl)acetyl chloride (**18**; 79%) by the action of phosphorus pentachloride in cold dichloromethane. Dechlorination with zinc produced di(1-naphthyl)ketene (**16**; 84%), a yellow solid. The reaction of ketene **16** with ethoxyacetylene in nitromethane (10 hr, −20°) had a novel feature. Phenanthrol **19** (32%), presumably derived from cyclobutenone **20**, separated from a solution of the crude product in dichloromethane; and an ethereal solution of the remaining crude product slowly deposited crystals of a second adduct (13%) which melted sharply at 227.5–229.5°. The NMR spectrum of this substance at 25° in pyridine-d_5 surprised us, since it showed that the apparently pure adduct was in fact a 3.2:1 mixture of two similar benzonorcaradienes with the general structure **21**. Further study by NMR at 25° to 165° revealed that the two adducts were rapidly and reversibly interconverted at elevated temperatures ($\Delta G^{\ddagger} \sim 20$ kcal/mol). Presumably adduct **21** can adopt conformations **21a** and **21b**.[13]



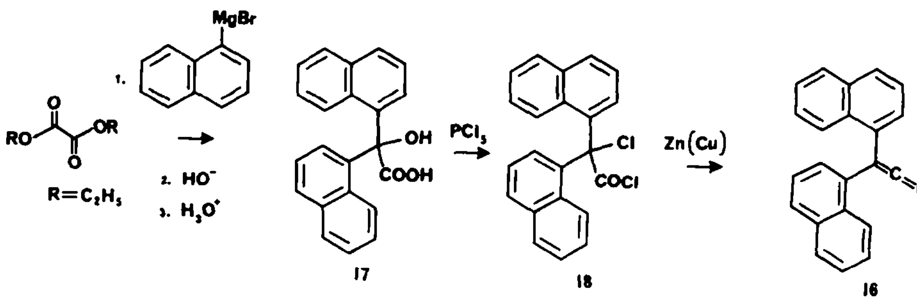
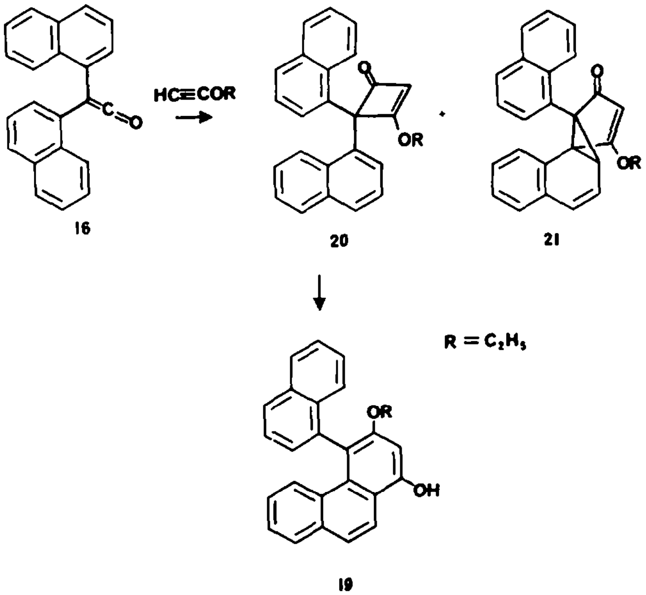
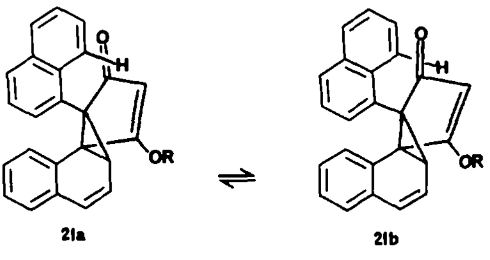
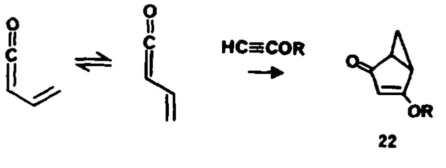


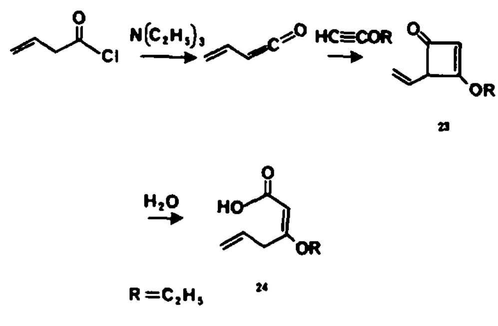
Fig. 3.





Formation of norcaradienes therefore is a characteristic feature of the cycloadditions of diarylketenes and ethoxyacetylene. Since these reactions directly involve only one of the double bonds in an aromatic ring, we wondered if simpler vinylketenes would react in the same manner (Eq 3). To test this possibility, we examined the reaction of vinylketene itself with ethoxyacetylene. When triethylamine was added to a cold (0°) ethereal solution of 3-butenoyl chloride and ethoxyacetylene,[14] triethylammonium chloride precipitated immediately. Chromatographic separation of the soluble portion of the product yielded only one mobile component, 3-ethoxy-4-vinylcyclobuten-2-one-1 (**23**; 32%), a very unstable liquid. Its reaction with water produced 3-ethoxy-2,5-hexadienoic acid (**24**).[15] Thus if vinylketene is in fact formed under these conditions, its reaction with ethoxyacetylene does not produce bicyclohexenone **22**. The reaction of 1,4-dihydro-1-naphthoyl chloride (**25**) with triethylamine in boiling ether in the presence of ethoxyacetylene yielded similar results. Chromatographic separation of the crude product provided only one mobile component. The UV spectrum of this adduct resembled the UV spectrum of phenalene,[16] and hydrolysis converted it into equal amounts of 3,4-dihydronaphthoic acid (**27**) and 3-ethoxy-phenalenone-1 (**28**). Phenalenyl ester **29**, perhaps derived from the





sequence of reactions in Fig. 4, is one of several likely structures which can be assigned to the adduct.

We attribute the failure of vinylketene itself to produce adduct 22 to two factors: unlike diarylketenes, vinylketene may adopt primarily an unreactive conformation; or the terminal C atom of the vinyl group may be incapable of bearing the same partial positive charge which develops during the 2+2+2 cycloadditions of diarylketenes.[3]

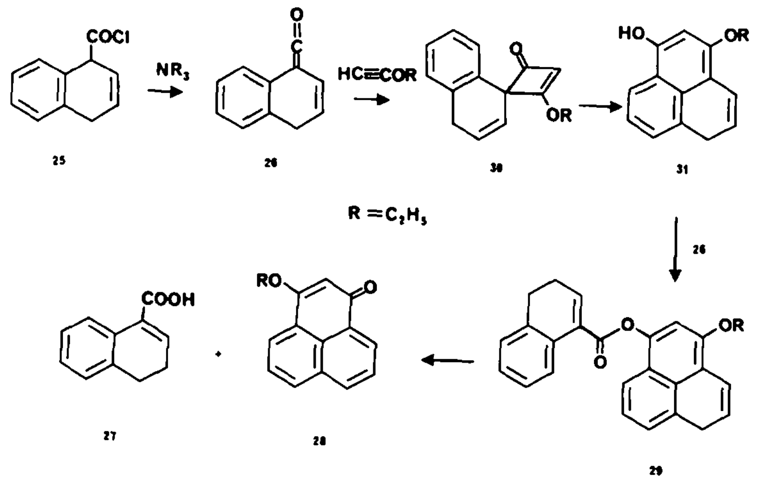


Fig. 4.

EXPERIMENTAL

All IR spectra were recorded on a Perkin–Elmer Model 137 spectrometer. Varian T-60 and HA-100 spectrometers were used to obtain ^{1}H NMR spectra. Chemical shifts are reported in ppm downfield from internal TMS (δ). An AEI MS-9 double-focusing mass spectrometer was used to obtain mass spectra (ms) at 70 eV. The ratio *m/e* and the relative intensity are reported in the form *m/e* (rel intensity). M.ps were measured on a Kofler block and are uncorrected. UV spectra were recorded on a Cary Model 14 spectrophotometer. The wavelength (λ, in nm) and the molar extinction coefficient (ε) of absorption maxima are reported in the form $\lambda_{max}(\epsilon_{max})$. Scandinavian Microanalytical Laboratories, Herlev, Denmark, performed all elemental analyses. Glassware was dried at 120° and cooled under dry N$_2$ immediately before use. Nitromethane was dried with CaCl$_2$, distilled, and stored over 4 Å molecular sieves. Benzene, hexane, and petroleum ether (b.p. 30–60°) were dried with Na wire, and ether was distilled from the sodium ketyl of benzophenone. Triethylamine was distilled twice from 1-naphthylisocyanate and once from LiAlH$_4$. Ethoxyacetylene was supplied by the Farchan Division, Story Chemical Corporation, and was redistilled immediately before use. Copper bronze was provided by British Drug Houses, Ltd. All other reagents were commercial products of the highest purity obtainable.

Cycloaddition of 1-*naphthylphenylketene and ethoxyacetylene*

Under N$_2$ at −28°, a stirred slurry of 1-naphthylphenylketene[6] (2.67 g, 10.9 mmol) in nitromethane (2.5 ml) was treated dropwise during 1.5 hr with a soln of ethoxyacetylene (1.06 g, 15.1 mmol) in nitromethane (1.5 ml). The mixture was kept at −17° for 24 hr, and then volatiles were removed by evaporation *in vacuo*. Preparative tlc (alumina, toluene) separated 4 (0.886 g, 2.82 mmol, 26%, R_f 0.2) from the residue. A sample which had been crystallized three times from a mixture of hexane and EtOAc and sublimed twice at 150° and 0.7 torr was analytically pure: m.p. 182.0–182.5°; IR (KBr) 1685, 1580 cm^{-1}; UV (EtOH) 266 (13,700); ^{1}H NMR (100 mHz, CDCl$_3$) δ 1.44 (t, 3H, J = 7 Hz), 3.26 (d, 1H, J = 5 Hz), 4.14 (m, 2H), 5.08 (s, 1H), 6.00 (d of d, 1H, J = 5, 10 Hz), 6.21 (d, 1H, J = 10 Hz), 6.7–7.7 (m, 9H); MS 315 (20), 314 (41), 286 (21), 285 (21), 258 (28), 257 (100), 228 (23), 215 (41). (Found: C, 83.85; H, 5.81. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%).

Ethyl Z-4-(1-*naphthyl*)-4-*phenylbuten*-3-*oate* (7)

A mixture of 4 (233 mg, 0.741 mmol), NaBH$_4$ (320 mg), and water (0.7 ml) in dioxane (5 ml) was stirred at 110° and after 3, 7 and 11 hr extra portions of NaBH$_4$ (320 mg) in water (0.7 ml) were added. After 17 hr the mixture was treated with water (15 ml) and stirred at 30° for 9 hr, and the hydrolyzed mixture was extracted with CH$_2$Cl$_2$. Evaporation of the extracts under reduced pressure left a residue of colorless oil, which was dissolved in a mixture of CH$_2$Cl$_2$ (15 ml) and EtOAc (2 ml). At 0°, anhyd HCl was passed through this soln for 15 min, and then solvent was removed by evaporation under reduced pressure. Tlc of the residue (silica, CCl$_4$) provided a purified sample of 7 (109 mg, 0.344 mmol, 46%, R_f 0.15), and distillation of this material at 175° and 0.1 torr yielded an analytically pure sample: IR (liquid film) 1735 cm^{-1}; UV (EtOH) 222, 245 sh, 282, 291 sh; ^{1}H NMR (100 mHz, CDCl$_3$) δ 1.18 (t, 3H, J = 7 Hz), 2.94 (d, 2H, J = 8 Hz), 4.07 (q, 2H, J = 7 Hz), 6.64 (t, 1H, J = 8 Hz), 7.1–7.9 (m, 12H); MS 316 (16), 229 (22), 228 (100). (Found: C, 83.27; H, 6.45. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37%).

t-*Butyl di*(1-*naphthyl*)*glycolate* (10)

A mixture of 9 (3.23 g, 10.4 mmol)[8] and t-BuOK (3.12 g, 27.8 mmol) in boiling benzene (45 ml) was stirred under N$_2$ for 7 hr.[9] After the mixture had been extracted with water, evaporation of the organic phase under reduced pressure left a solid residue of 10 (3.17 g, 8.24 mmol, 79%). A sample which had been crystallized twice from CCl$_4$ and once from hexane was analytically pure: m.p. 122.0–123.0°; IR (KBr) 3540, 1710 cm^{-1}; UV (EtOH) 218 (99,200), 231 (107,000), 264 (14,500), 273 (14,000); ^{1}H NMR (60 mHz, CCl$_4$) δ 1.43 (s, 9H), 4.4 (bs, 1H), 7.2–8.0

(m, 14H); MS 384 (7), 284 (34), 283 (100), 155 (100), 127 (98), 57 (67), 56 (43). (Found: C, 81.12; H, 6.33. Calcd for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29%).

Di(2-naphthyl)glycolic acid (**11**)[10]

A mixture of **10** (3.17 g, 8.24 mmol), 2,2'-oxydiethanol (20 ml), water (1 ml), and KOH (0.93 g) was stirred under N_2 at 125° for 2.5 hr[9] and then was partitioned between ether and water. Acidification of the aqueous phase precipitated **11** (2.50 g, 7.61 mmol, 92%), which was identical to authentic di(2-naphthyl)glycolic acid prepared by the method of Burtner and Cusic.[10]

Chlorodi(2-naphthyl)acetyl chloride (**12**)

An intimate mixture of **11** (13.4 g, 40.8 mmol) and PCl_5 (33.9 g, 163 mmol) was warmed under N_2 at 86° for 3 hr.[11] Poured onto ice (80 g), the oily product was converted into a solid which was filtered off, dried and extracted with a boiling mixture of benzene (100 ml) and hexane (150 ml). Evaporation of the extracts left a residue of crude **12**, which crystallized from a 10:1 mixture of hexane and benzene as a pale yellow powder (9.96 g, 27.3 mmol, 67%). A sample recrystallized twice from hexane was analytically pure: m.p. 135.0–136.5°; IR (KBr) 1800 cm^{-1}; UV (hexane) 218 (89,700), 232 (87,800); ^1H NMR (100 mHz, $CDCl_3$) δ 7.1–8.0 (m); MS 366 (13), 303 (35), 301 (100), 266 (49), 265 (88), 136 (36), 135 (47). (Found: C, 72.47; H, 4.08; Cl, 19.07. Calcd for $C_{22}H_{14}Cl_2O$: C, 72.34; H, 3.86; Cl, 19.41%).

Di(2-naphthyl)ketene (**8**)

A mixture of **12** (7.40 g, 20.3 mmol), copper bronze (0.15 g), Zn powder (1.32 g) and activated Zn (0.83 g)[17] was stirred under N_2 in boiling ether (40 ml) for 2 hr.[6] After the addition of pet. ether (125 ml, bp 30–60°) and benzene (50 ml), the mixture was filtered. Evaporation of the filtrate left an oily residue which was extracted at 40° with a mixture of pet. ether (100 ml) and benzene (55 ml). Filtration and evaporation of these extracts provided **8**, an orange solid which was used without further purification (5.32 g, 18.1 mmol, 89%). IR (CCl_4) 2100 cm^{-1}.

Cycloaddition of di(2-naphthyl)ketene and ethoxyacetylene

During 30 min, a soln of ethoxyacetylene (1.77 g, 25.3 mmol) in nitromethane (8 ml) was added dropwise under N_2 to a stirred suspension of **8** (5.32 g, 18.1 mmol) in nitromethane (90 ml) at −20°. The mixture was kept at −20° for 14.5 hr and then volatiles were removed by evaporation *in vacuo*. A soln of the oily residue in a mixture of ether (11 ml) and hexane (5 ml) at 5° slowly deposited crystals of **13** (2.45 g, 6.72 mmol, 37%). A sample which had been recrystallized three times from EtOAc was analytically pure: m.p. 122.0° (d); IR (KBr) 1680, 1585 cm^{-1}; UV (EtOH) 222 (80,600), 257 (26,600); ^1H NMR (100 mHz, $CDCl_3$) δ 1.41 (t, 3H, J = 6 Hz), 3.86 (s, 1H), 3.8–4.3 (m, 2H), 4.97 (s, 1H), 6.2–6.5 (m, 2H), 6.6–7.8 (m, 11H); MS 365 (28), 364 (100), 336 (24), 335 (21), 308 (23), 307 (73), 265 (22), 155 (26). (Found: C, 85.35; H, 5.67. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53%).

Rearrangement of benzonorcaradiene **13**

Heated neat under N_2 in a Pyrex tube at 160° for 5 hr, **13** (83.5 mg, 0.229 mmol) rearranged to **14** (82.5 mg, 0.226 mmol, 99%), a glassy solid. Crystallization from a 3:2 mixture of hexane and EtOAc provided an analytically pure sample: m.p. 164.0–167.0°; IR (KBr) 3480, 1680 cm^{-1}; UV (EtOH) 223 (90,400), 252 (32,100), 276 sh (22,100), 297 sh (11,400), 363 (3870); ^1H NMR (100 mHz, $CDCl_3$) δ 1.62 (t, 3H, J = 7 Hz), 4.27 (q, 2H, J = 7 Hz), 5.36 (s, 1H), 6.7–8.4 (m, 14H); MS 365 (42), 364 (100), 335 (27). (Found: C, 85.30; H, 5.56. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53%).

Di(1-naphthyl)glycolic acid (**17**)[10,12]

A mixture of 1-bromonaphthalene (120 g, 0.579 mol), Mg turnings (14.3 g, 0.588 mol), iodine (0.31 g) and ether (225 ml) was kept at 32° under N_2, unstirred, until an initially vigorous reaction had occurred and subsided. Then the mixture was diluted with ether (50 ml) and warmed at reflux for 1.5 hr. Benzene (315 ml) was added, and the hot mixture was treated dropwise during 30 min with a soln of diethyl oxalate (41.6 g, 0.285 mol) in ether (150 ml). The mixture was stirred at 30° for 2 hr and treated cautiously with 5N H_2SO_4 (300 ml). Evaporation of the organic phase left an oily residue which was heated with KOH (28 g) for 2 hr in boiling 95% EtOH (425 ml). The hydrolysate was diluted with water, steam-distilled (1600 ml collected) and extracted with ether. Decolorization and acidification of the aqueous phase precipitated **17** (52.7 g, 0.160 mol, 56%), which was identical to an authentic sample prepared by the method of Gomberg and Van Natta.[12]

Chlorodi(1-naphthyl)acetyl chloride (**18**)

To a stirred slurry of PCl_5 (24.2 g, 116 mmol) in CH_2Cl_2 (575 ml) at −78° under N_2, a soln of **17** (15.1 g, 46.0 mmol) in CH_2Cl_2 (575 ml) was added dropwise during 4 hr. After the mixture had been kept at −78° for 1.5 hr more and at 0° for 1.7 hr, it was extracted with cold water (0°, 915 ml), cold 0.1 N NaOH (915 ml), and twice again with cold water (915 ml portions). Evaporation of solvent under reduced pressure left a residue of crude **18**, which crystallized from a mixture of hexane (235 ml) and benzene (55 ml) in the form of glassy prisms (13.2 g, 36.1 mmol, 79%). A sample recrystallized four times from pet. ether was analytically pure: m.p. 131.0–135.0°; IR (KBr) 1780 cm^{-1}; UV (hexane) 223 (81,800), 288 (13,400); ^1H NMR (100 mHz, $CDCl_3$) δ 7.0–8.4 (m); MS 364 (8), 294 (47), 266 (35), 265 (100), 263 (42), 131.5 (34). (Found: C, 72.46; H, 3.98; Cl, 19.15. Calcd for $C_{22}H_{14}Cl_2O$: C, 72.34; H, 3.86; Cl, 19.41%).

Di(1-naphthyl)ketene (**16**)

A mixture of **18** (12.8 g, 35.0 mmol), copper bronze (0.24 g), Zn powder (2.35 g) and activated Zn (1.33 g)[17] was stirred under N_2 in boiling ether (150 ml) for 2 hr.[6] After the addition of pet. ether (75 ml, b.p. 30–60°) and benzene (75 ml), the mixture was filtered. Evaporation of the filtrate left an oily residue which was extracted at 30° with a mixture of pet. ether (60 ml) and benzene (90 ml). Filtration and evaporation of these extracts provided **16**, a yellow solid which was used without further purification (8.63 g, 29.3 mmol, 84%). IR (KBr) 2100 cm^{-1}; MS 294 (46), 266 (35), 265 (100), 263 (26).

Cycloaddition of di(1-naphthyl)ketene and ethoxyacetylene

A soln of ethoxyacetylene (0.876 g, 12.5 mmol) in nitromethane (7 ml) was added dropwise under N_2 during 20 min to a stirred soln of **16** (2.85 g, 9.68 mmol) in nitromethane (100 ml) at −27°. The mixture was kept at −20° for 10 hr, and then volatiles were removed by evaporation *in vacuo*. From a soln of the residue in CH_2Cl_2 (10 ml), **19** precipitated as a white powder (1.12 g, 3.07 mmol, 32%). A sample recrystallized twice from a mixture of MeOH and CH_2Cl_2 was analytically pure: m.p. 231.5–235.0°; IR (KBr) 3300, 1590 cm^{-1}; UV (EtOH) 226 (86,900), 248 (40,100), 282 (18,300), 311 (12,300), 349 (3700), 367 (3600); ^1H NMR (100 mHz, pyridine-d_5) δ 0.78 (t, 3H, J = 6 Hz), 3.82 (q, 2H, J = 6 Hz), 6.6–8.9 (m, 15H); MS 365 (30), 364 (100), 336 (36), 335 (24), 289 (25), 276 (22). (Found: C, 85.36; H, 5.54. Calcd for $C_{26}H_{20}O_2$: C 85.69; H 5.53%).

Evaporation of CH_2Cl_2 from the supernatant left a residue which was redissolved in ether (4 ml). This soln slowly deposited crystals of **21** (0.472 g, 1.30 mmol, 13%). A sample recrystallized twice from a mixture of MeOH and CH_2Cl_2 was analytically pure: m.p. 227.5–229.5°; IR (KBr) 1685, 1585 cm^{-1}; UV (hexane) 219 (68,500), 271 (16,900); ^1H NMR (100 mHz, pyridine-d_5) δ 1.29 (t, 3H, J = 7 Hz), 3.48 (t, 1H, J = 2.5 Hz), 3.9–4.3 (m, 2H), 5.44 (s, 1H), 6.33 (d, 2H, J = 2.5 Hz), 6.5–8.7 (m, 11H); δ 1.30 (t, 3H, J = 7 Hz), 3.67 (t, 1H, J = 2.5 Hz), 3.9–4.3 (m, 2H), 5.36 (s, 1H), 5.91 (d, 2H, J = 2.5 Hz), 6.5–8.7 (m, 11H); MS 365 (31), 364 (98), 336 (30), 335 (32), 308 (31), 307 (100), 289 (36), 265 (56), 263 (35), 127 (38). (Found: C, 85.50; H, 5.52. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53%).

Cycloaddition of vinylketene and ethoxyacetylene

Under N_2 at 0°, a stirred soln of 3-butenoyl chloride (538 mg, 5.15 mmol)[18] and ethoxyacetylene (734 mg, 10.5 mmol) in ether (20 ml) was treated dropwise during 1 hr with a soln of triethylamine (565 mg, 5.58 mmol) in ether (8 ml). Filtration then removed triethylammonium chloride, and evaporation of the filtrate under reduced pressure left a residue of undistillable oil. Preparative tlc (silica, 1:1 EtOAc/cyclohexane) separated only one mobile component, **23** (226 mg, 1.64 mmol, 32% R_f 0.7). IR (liquid film) 1765, 1600 cm^{-1}; UV (hexane) 247; ^{1}H NMR (100 mHz, CCl_4) δ 1.38 (t, 3H, J = 6 Hz), 3.47 (d of t, 1H, J = 3, 0.5 Hz), 3.85 (q, 2H, J = 6 Hz), 4.94 (s, 1H), 5.0–5.3, 5.6–6.1 (m, 3H); MS 138 (72), 110 (52), 69 (100), 68 (33).

3-*Ethoxy*-2,5-*hexadienoic acid* (**24**)

Under N_2 at 0°, a stirred soln of 3-butenoyl chloride (510 mg, 4.88 mmol)[18] and ethoxyacetylene (814 mg, 11.6 mmol) in ether (20 ml) was treated dropwise during 0.5 hr with a soln of triethylamine (541 mg, 5.35 mmol) in ether (8 ml). Triethylammonium chloride was removed by filtration, and the filtrate was stirred with 0.1N HCl (50 ml) for 22 hr at 28°. Evaporation of the ethereal phase left a residue from which preparative tlc (silica, CCl_4) separated **24** (81 mg, 0.52 mmol, 11%, R_f 0.4). A sample crystallized once from a mixture of hexane and EtOAc and sublimed at 70° and 0.1 torr was analytically pure: m.p. 93.5–94.0°; IR (CH_2Cl_2) 3300–2400, 1685, 1600 cm^{-1}; UV (EtOH) 231 (14,300); ^{1}H NMR (100 mHz, $CDCl_3$) δ 1.38 (t, 3H, J = 6 Hz), 3.52 (d of t, 2H, J = 7, 1 Hz), 3.86 (q, 2H, J = 6 Hz), 5.02 (s, 1H), 5.0–6.1 (m, 3H), 11.0–11.8 (bs, 1H); MS 156 (33), 110 (40), 109 (40), 87 (100), 82 (64), 69 (95), 68 (31). (Found: C, 61.61; H, 7.75. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75%).

1,4-*Dihydro*-1-*naphthoyl chloride* (**25**)

During 20 min a soln of oxalyl chloride (630 mg, 4.96 mmol) in benzene (5 ml) was added dropwise under N_2 to a stirred soln of 1,4-dihydro-1-naphthoic acid (707 mg, 4.06 mmol)[19] in benzene (7.5 ml) at 5°. After the mixture had been kept at 25° for 4 hr, evaporation of solvent under reduced pressure left a residue of **25**, which was used without further purification (770 mg, 4.00 mmol, 98%). IR (liquid film) 1790 cm^{-1}; UV (hexane) end absorption; ^{1}H NMR (60 mHz, CCl_4) δ 3.2–3.5 (m, 2H), 4.67 (q, 1H), 5.7–6.4 (m, 2H), 7.0–7.2 (m, 4H).

Cycloaddition of ketene **26** *and ethoxyacetylene*

A mixture of **25** (389 mg, 2.02 mmol) and ethoxyacetylene (833 mg, 11.9 mmol), stirred under N_2 in boiling ether (20 ml), was treated during 50 min with a soln of triethylamine (242 mg, 2.39 mmol) in ether (10 ml). Filtration then removed triethylammonium chloride (241 mg, 1.75 mmol, 87%) and evaporation of the filtrate left a residue of viscous liquid. Preparative tlc (silica, 1:3 ether/pet. ether) separated only one significant mobile component, **29** (111 mg, 0.290 mmol, 29%, R_f 0.3). IR (CCl_4) 1745, 1650, 1590 cm^{-1}; UV (hexane) 244 (33,000), 312 (7500), 325 (7800), 343 (6200), 361 (7800), 381 (5300); ^{1}H NMR (100 mHz, CCl_4) δ 1.46 (t, 3H, J = 6 Hz), 2.3–2.6 (m, 2H), 2.6–3.0 (m, 2H), 4.0 (bs, 2H), 4.10 (q, 2H, J = 6 Hz), 5.7–6.6 (m, 2H), 6.7–8.1 (m, 8H), 7.56 (t, 1H, J = 2 Hz); MS 382 (3), 155 (48), 153 (44), 152 (31), 129 (100), 128 (56), 127 (49).

A soln of **29** (36 mg, 0.094 mmol) and KOH (50 mg) in 95% EtOH (5 ml) was kept at 25° for 13 hr and was then partitioned between water and ether. Acidification of the aqueous phase precipitated **27** (12 mg, 0.069 mmol, 73%), identical to an authentic sample prepared by the method of Kamm and McClugage.[20] Evaporation of the organic phase left a residue of **28** (12 mg, 0.054 mmol, 57%). A sample sublimed at 120° and 0.2 torr, crystallized once from a mixture of hexane and EtOAc and resublimed was analytically pure: m.p. 148.5–149.5°; IR (KBr) 1630, 1580 cm^{-1}; UV (EtOH) 206 sh (36,000), 225 sh (23,000), 245 (23,400), 328 (12,400), 353 (11,400); ^{1}H NMR (100 mHz, $CDCl_3$) δ 1.53 (t, 3H, J = 6 Hz), 4.13 (q, 2H, J = 6 Hz), 5.99 (s, 1H), 7.2–8.6 (m, 6H); MS 224 (78), 196 (100), 168 (26), 155 (33), 139 (41). (Found: C, 80.05; H, 5.44. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39%).

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