oil was cooled and added to ethanol, and the crystals were collected by filtration. The yield of **17** was 72 g (60%): mp 113–114°; ir (KBr) 6.0 and 6.18 μ; nmr ($CDCl_3$) δ 2.27 (s, 3) and 6.4–8.0 (m, 14).

Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.13; H, 5.84; N, 4.59.

4,4-Dimethyl-1,5-diphenyl-2-*p*-tolyl-6-oxa-2-azabicyclo[3.1.0]-hexan-3-one (18).—Dimethylketene (7.7 g, 0.11 mol) was added in two portions to a solution of 30 g (0.1 mol) of **17** in 250 ml of ether. The temperature rose to 34°, and product began to separate after about 0.5 hr. The mixture, stirred overnight and filtered, gave 26 g (71%) of **18**: mp 183–184°; ir (KBr) 5.75 μ; nmr ($CDCl_3$) δ 1.21 (s, 3), 1.43 (s, 3), 2.05 (s, 3), and 6.8–7.5 (m, 14).

Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27; N, 3.79. Found: C, 81.26; H, 6.41; N, 3.51.

3-Benzoyl-2,2-dimethyl-3-phenyl-*p*-hydracrylotoluidide (19).—**18** (5 g, 0.014 mol) was combined with 75 ml of aqueous 10% HCl and the mixture refluxed with stirring for 4 hr. An ir spectrum of the crude material showed a band at 5.73 μ (starting material). The solid was dried, ground in a mortar, and refluxed for an additional 2 hr in 75 ml of aqueous 10% HCl. Filtration of the cooled solution gave 4.6 g (88%) of crude **19**. An analytical sample was recrystallized from xylene: mp 216–217°; ir (Nujol) 6.0 μ; nmr ($CDCl_3$, CD_3SOCD_3) δ 1.02 (s, 3), 1.60 (s, 3), 2.24 (s, 3), 5.17 (s, 1), 7.45 (m, 2), and 6.6–7.3 (m, 12).

Anal. Calcd for $C_{25}H_{25}NO_3$: C, 77.49; H, 6.50; N, 3.61. Found: C, 77.49; H, 6.58; N, 3.30.

19 was also obtained by treatment of **8** with *p*-toluidine. **8** (14 g, 0.05 mol) and 5.35 g (0.05 mol) of *p*-toluidine were combined and heated at 100° for 1 hr. The ir spectrum showed a new band at 6.0 μ. An additional 0.05 mol of *p*-toluidine was added and the mixture heated at 150° for 2 hr. The oil was cooled and treated with cyclohexane to give 5.9 g (31%) of **19**.

Registry No.—**3**, 29689-76-7; **8**, 29689-77-8; **9**, 29689-78-9; **10**, 29689-79-0; **11**, 29689-80-3; **12**, 29689-81-4; **13**, 29689-82-5; **14**, 29689-83-6; **16a**, 29689-84-7; **16b**, 29689-85-8; **17**, 29689-86-9; **18**, 29784-79-0; **19**, 29784-80-3; dimethylketene, 598-26-5.

Some Reactions of Tetramethylallene

JAMES C. MARTIN,* PHILIP L. CARTER, AND JAMES L. CHITWOOD

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company,
Kingsport, Tennessee 37662

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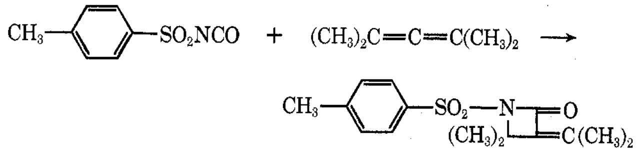
Tetramethyllallene (TMA) reacted with sulfonyl isocyanate *via* a 2 + 2 cycloaddition to give the azetidinone **1**. Trichloroacetyl isocyanate and TMA reacted *via* a 4 + 2 cycloaddition to give **2**, which rearranged readily to the acyclic product **3**. TMA reacted thermally with acrylonitrile to give a mixture of the cyclobutane **4** and the acyclic diene **5**. Dimethyl acetylenedicarboxylate and TMA reacted to afford a mixture of the isomeric trienes **9** and **10**.

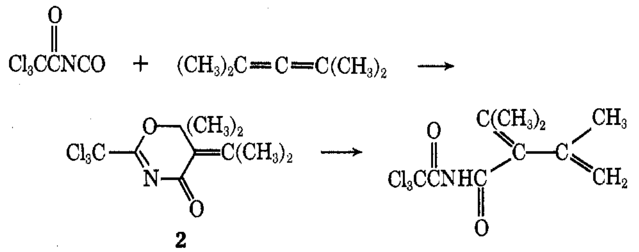
The purpose of this paper is to report some of the reactions of tetramethylallene (TMA) with activated isocyanates, electron-deficient olefins, and acetylenes.

TMA undergoes facile cycloaddition reactions with heterocumulenes. The reactions of TMA with dimethylketene and diphenylketene have been reported.[1] Moriconi and Kelly[2,3] have reported the cycloaddition of chlorosulfonyl isocyanate to TMA and other allenes. In agreement with Moriconi's work, we found that activated isocyanates react readily with TMA. *p*-Tolylsulfonyl isocyanate and TMA, when warmed in benzene, gave 3-isopropylidene-4,4-dimethyl-1-(*p*-tolylsulfonyl)-2-azetidinone (**1**) in 67% yield.



1

Interestingly, replacement of the *p*-tolylsulfonyl moiety by a trichloroacetyl group results in facile formation of **2**, a 1,4 cycloadduct of a type not available from sulfonyl isocyanates. The reaction between trichloroacetyl isocyanate and TMA in carbon tetrachloride at ambient temperature was followed by nmr. The complete conversion to **2** required about 18 hr and was evidenced by the disappearance of the TMA singlet and the appearance of three singlets characteristic of the methyl groups of **2**.



2 3

After 9 days at room temperature, **2** had completely rearranged to **3**, as evidenced by the disappearance of the spectrum of **2** and the appearance of a new spectrum characteristic of **3**. A preparative run gave **3** in 82% yield.

The thermal reaction of TMA with electron-deficient olefins was reported to yield six-membered-ring products, resulting from a preliminary isomerization of the allene to 2,4-dimethyl-1,3-pentadiene (**7**) followed by a Diels–Alder reaction.[4] Instead, we found that the reaction of TMA and acrylonitrile at 150° gave a 73% conversion to a 3:2 mixture of 3-isopropylidene-2,2-dimethylcyclobutanecarbonitrile (**4**) and 4-isopropenyl-5-methyl-4-hexenenitrile (**5**). None of the reported product (**6**) was found, but, when TMA was deliberately isomerized to the conjugated diene **7** and then heated with acrylonitrile, the cyclohexene **6** was the exclusive product.

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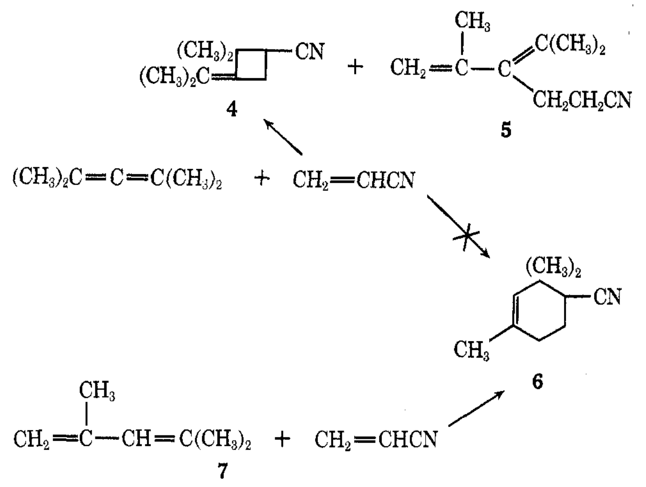
[1] J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965).

[2] E. J. Moriconi and J. F. Kelly, *J. Amer. Chem. Soc.*, **88**, 3657 (1966).

[3] E. J. Moriconi and J. F. Kelly, *J. Org. Chem.*, **33**, 3036 (1968).

[4] D. R. Taylor and D. B. Wright, *Chem. Commun.*, 434 (1968).



The identities of **4** and **5** were assigned on the basis of their nmr and ir spectra. Compound **5** showed no maximum in its ultraviolet spectrum. Precedent for this absence is found in the work of Criege and Noll,[5] who observed that certain isomers of polymethylated 1,3-butadienes had no uv maximum.

The addition of TMA to dimethyl acetylenedicarboxylate occurred readily in a variety of solvents at temperatures of 80–110°.[6] In each solvent, most of the volatile material obtained consisted of two 1:1 adducts, dimethyl (1-isopropylidene-2-methylallyl)fumarate (**8**) and dimethyl (1-isopropylidene-2-methylallyl)maleate (**9**).[7] The combined yields of **8** and **9** varied between 25 and 50% (see Table I). In addition to **8** and **9**, these reactions yielded red, high-boiling residues whose spectral data indicated them to be 1:2 adducts from TMA and dimethyl acetylenedicarboxylate. The ratios of **8** and **9** were solvent dependent, varying from 85:15 in toluene to 35:65 in acetonitrile (see Table I); however, the reaction rate was relatively independent of solvent polarity.

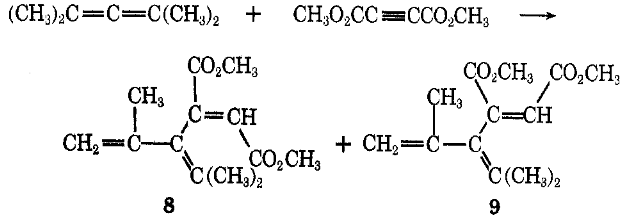
TABLE I

REACTION CONDITIONS AND PRODUCT COMPOSITIONS FOR THE ADDITION OF TMA TO DIMETHYL ACETYLENEDICARBOXYLATE

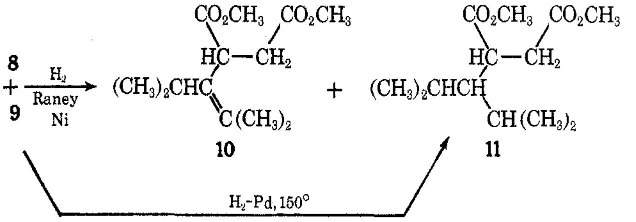
Solvent	Temp, °C	Reaction time, hr	Yield of 1:1 adduct isolated, %	9/8 ratio
No solvent	100–120	4	35	65/35
Toluene	110	7	47	85/15
Benzene	80	42	35	73/27
Benzene	25	25 days	Not isolated	47/53
Tetramethylallene[a]	100	3	45	75/25
Cumene	110	5	35	70/30
Acetonitrile	82	24	57	35/65
Carbon tetrachloride	77	46	58	38/62

[a] 1 *M* in dimethyl acetylenedicarboxylate.

Structural assignments for **8** and **9** were made on the basis of spectral data and hydrogenation results. The individual isomer assignments of **8** and **9** were based upon a comparison of the chemical shift values of the vinyl hydrogen adjacent to the carboxylate group with those of dimethyl fumarate and dimethyl maleate.



The hydrogenation of a mixture of **8** and **9** to dimethyl (1-isopropyl-2-methylpropyl)succinate (**11**) proved to be difficult, requiring 5% palladium on carbon at 150° and 100 atm. There was very little hydrogen uptake with 5% palladium on carbon at 2.7 atm and room temperature. Hydrogenation over Raney nickel at 150° and 100 atm gave a mixture of dimethyl (1-isopropyl-2-methylpropenyl)succinate (**10**) and **11**. This mixture was resistant to further hydrogenation. Pure



8 gave mostly **11** (85%) upon hydrogenation over Raney nickel, and pure **9** gave approximately equal amounts of **10** and **11**. It is apparent from these results that the tetrasubstituted double bond is hydrogenated over Raney nickel only when the double bond between the carboxylates is in place, perhaps by a 1,4 addition of hydrogen.

Experimental Section

3-Isopropylidene-4,4-dimethyl-1-(*p*-tolylsulfonyl)-2-azetidinone (1).—A solution of 19.7 g (0.1 mol) of *p*-tolylsulfonyl isocyanate and 9.6 g (0.1 mol) of TMA[8] in 30 ml of benzene was heated for 12 hr on a steam bath. The solvent was evaporated at room temperature to give 29.1 g of crystalline residue. Recrystallization from ethyl alcohol yielded 19.6 g (67%) of **1**: mp 131–133°; ir (KBr) 5.70 and 5.90 μ; nmr (CH_2Cl_2) δ 1.59 (s, 6), 1.74 (s, 3), 1.99 (s, 3), 2.39 (s, 3), and 7.60 (typical aromatic AA′, BB′ pattern, 4).

Anal. Calcd for $C_{15}H_{19}NO_3S$: C, 61.4; H, 6.5; N, 4.8; S, 10.9. Found: C, 61.6; H, 6.5; N, 4.7; S, 10.9.

2-Isopropenyl-3-methyl-*N*-(trichloroacetyl)crotonamide (3).—A solution of 3.0 g (0.03 mol) of TMA and 5.7 g (0.03 mol) of trichloroacetyl isocyanate in 10 ml of benzene was stirred under an atmosphere of nitrogen without any noticeable evolution of heat. After standing at room temperature under nitrogen for 9 days, the mixture contained no isocyanate as evidenced by its infrared spectrum. Removal of the solvent *in vacuo* left a low-melting, solid residue. This solid was recrystallized twice from pentane and once from hexane to give 7.0 g (82%) of **3**: mp 61–62°; ir (KBr) 5.63, 5.90, and 6.20 μ; nmr (CCl_4) δ 1.91 (s, 3), 2.06 (s, 3), 1.92 (s, 3, $C{=}CCH_3$ shows fine splitting but is overlapped by peak at 1.91), 5.14 (s, 1), 5.43 (s, 1), and 9.63 (s, 1).

Anal. Calcd for $C_{10}H_{12}Cl_3NO_2$: C, 42.2; H, 4.3; N, 4.9; Cl, 37.4. Found: C, 42.0; H, 4.4; N, 4.7; Cl, 37.4.

A slight excess of trichloroacetyl isocyanate was added to TMA and carbon tetrachloride in an nmr tube. The mixture was

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[5] R. Criege and K. Noll, *Justus Liebigs Ann. Chem.*, **627**, 3 (1959).

[6] Kiefer and Okamura reported recently that TMA and dimethyl fumarate or maleate gave exclusively the diene-type product analogous to **5**: E. F. Kiefer and M. Y. Okamura, *J. Amer. Chem. Soc.*, **90**, 4187 (1968).

[7] Varying amounts of two other components were detected. Generally their combined areas represented 15% or less of the volatile material. They were not identified.

[8] J. C. Martin (to Eastman Kodak Co.), U. S. Patent 3,131,234 (1964).

scanned periodically for several days. After 18 hr the methyl peak at δ 1.60 (TMA) had disappeared, and peaks at δ 1.79 (s, 6), 2.04 (s, 3), and 2.06 (s, 3) characteristic of 5,6-dihydro-5-isopropylidene-6,6-dimethyl-2-(trichloromethyl)-4*H*-1,3-oxazin-4-one (**2**) appeared. The infrared spectrum of the solution at this time showed maxima at 5.68, 5.87, and 6.16 μ, which are characteristic of **2**. After the solution had stood 2 days at room temperature, the nmr spectrum indicated the start of the decay of **2** to **3**. This process was substantially complete after 9 days.

3-Isopropylidene-2,2-dimethylcyclobutanecarbonitrile (4) and 4-Isopropenyl-5-methyl-4-hexenenitrile (5).—A mixture of 50 g (0.5 mole) of TMA, 52 g (1.0 mol) of acrylonitrile, 0.5 g phenothiazine, and 3 g of potassium carbonate was heated in a stainless steel rocking autoclave at 150° for 24 hr. The reaction mixture was filtered, and the filtrate was distilled through a 6-in. Vigreux column to give 52.5 g (73%) of material, bp 69–72° (4 mm). Glpc (Carbowax on Chromosorb at 140°) showed two closely associated peaks (**4** and **5**) in the area ratio of 3 to 2. Analytical samples were isolated by glpc to give **4** and **5**.

4: ir (neat) 4.45 μ (no absorption near 6.0 μ); nmr (CCl_4) δ 1.28 (s, 3), 1.35 (s, 3), 1.45 (t, 3, $J = 1.0$ Hz), 1.56 (t, 3, $J = 1.4$ Hz), and 2.70 (m, 3).

Anal. Calcd for $C_{10}H_{15}N$: C, 80.5; H, 10.1; N, 9.4. Found: C, 80.2; H, 10.4; N, 9.2.

5: ir (neat) 6.13 and 11.1 μ; nmr (CCl_4) δ 1.51 (q, 3), 1.68 (s, 6), 2.28 (m, 4), 4.55 and 4.59 (2 quartets, $\mathbf{H}^1H^2C{=}C(CH_3{}^3)$–, $J_{1,2} = 2.4$ Hz and $J_{1,3} = 1.0$ Hz), and 4.90 and 4.92 (2 quartets, $H^1\mathbf{H}^2C{=}C(CH_3{}^3)$–, $J_{1,2} = 2.4$ Hz, $J_{2,3} = 1.4$ Hz, 1).

Anal. Calcd for $C_{10}H_{15}N$: C, 80.5; H, 10.1; N, 9.4. Found: C, 80.5; H, 10.1; N, 9.3.

2,2,4-Trimethyl-3-cyclohexene-1-carbonitrile (6).—A mixture of 40.0 g (0.416 mol) of 2,4-dimethyl-1,3-pentadiene (**7**),[9] 44 g (0.832 mol) of acrylonitrile, and 0.5 g of phenothiazine was heated in an autoclave at 150° for 12 hr. Distillation through an 8-in. packed column gave 19.1 g (31%) of **6**: bp 48° (12 mm); nmr (CCl_4) δ 1.13 (s, 6), 1.64 (s, 3), 1.98 (m, 4), 2.44 (m, 1), and 5.07 (finely split singlet, 1).

Dimethyl (1-Isopropylidene-2-methylallyl)fumarate (8) and Dimethyl (1-Isopropylidene-2-methylallyl)maleate (9).—The general procedure used for running the addition reaction of TMA and dimethyl acetylenedicarboxylate follows. Details are given in Table I.

A solution containing 16.0 g (0.16 mol) of TMA and 21.3 g (0.15 mol) of dimethyl acetylenedicarboxylate in 300 ml of solvent was maintained at a constant temperature, usually the reflux temperature.[10] The disappearance of dimethyl acetylenedicarboxylate was monitored by glpc (5% QF-1 silicone on Chromosorb P), and the reaction was allowed to proceed to completion. The solvent and excess TMA were removed at reduced pressure.

The dark red residue was distilled through a 10-in. Vigreux column to give a 35–58% yield of volatile material, bp 85–90° (0.6 mm). The volatile material contained compounds **8** and **9** and varying amounts of two minor components which were not identified. Analytical samples of compounds **8** and **9** were obtained by preparative glpc (QF-1).

8: ir (neat) 3.25, 5.79, and 11.15 μ; nmr (CCl_4) δ 1.58 (s, 3), 1.80 (complex, 6), 3.65 (s, 3), 3.72 (s, 3), 4.80 (m, 1), 4.95 (m, 1), and 6.72 (s, 1); mass spectrum (70 eV) *m/e* base peak 119, molecular ion 238.

Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.61; H, 7.42.

9: ir (neat) 3.25, 5.80, and 11.15 μ; nmr (CCl_4) δ 1.8 (complex, 9), 3.68 (s, 3), 3.72 (s, 3), 4.70 (m, 1), 5.05 (m, 1), and 5.80 (s, 1); mass spectrum (70 eV) *m/e* base peak 119, molecular ion 238.

Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.76; H, 7.53.

The nmr spectra (CCl_4) of the residues showed approximately equal area patterns centered at δ 3.7 and δ 1.7. In the nmr spectra of the residues from the reaction in cumene, however, these two patterns were accompanied by a third absorption centered at δ 7.3 with relative areas of 4 (δ 7.3):3 (δ 3.7):12 (δ 1.7). The ir (neat) of the residue showed intense bands at 5.80 and 8.00 (broad) μ.

Hydrogenation of Adducts 8 and 9.—A 22.1-g (0.093-mol) portion of **8** and **9** (ratio of **8** to **9** = 36:64) was dissolved in 200 ml of reagent grade cyclohexane and hydrogenated over 0.5 g of palladium on carbon at 2.7 atm for 8 hr. There was little hydrogen uptake during this time and little change in the glpc trace. The catalyst was removed by filtration, and hydrogenation was attempted with 5.0 g of Raney nickel (alcohol washed) at 150° and 100 atm for 3 hr. The catalyst was removed by filtration and the solvent by rotary evaporation at reduced pressure. Two major components were obtained, each with a different glpc retention time (QF-1) from either **8** or **9**. Distillation gave 15.7 g of a mixture of dimethyl (1-isopropyl-2-methylpropenyl)succinate (**10**) and dimethyl (1-isopropyl-2-methylpropyl)succinate (**11**), bp 86.5–88.0° (0.7 mm), in the ratio of 59 to 41. Pure samples were separated by glpc.

10: ir (neat) 5.75 μ; nmr ($CDCl_3$) δ 0.8–1.4 (complex, 6), 1.53 (s, 3), 1.66 (s, 3), 2.0–3.9 (complex, 4), 3.60 (s, 3), and 3.65 (s, 3); mass spectrum (70 eV) *m/e* base peak 169, molecular ion 242. High-resolution mass spectrum (single peak by glpc). Calcd for $C_{13}H_{22}O_4$: 242.1518. Found: 242.1520.

11: ir (neat) 5.78 μ; nmr ($CDCl_3$) δ 0.9 (complex, 12), 1.4–3.1 (complex, 6), and 3.62 (s, 6); mass spectrum (70 eV) *m/e* base peak 114, no molecular ion.

Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90. Found: C, 64.02; H, 9.76.

A sample of the mixture of **10** and **11** was hydrogenated again over Raney nickel at 150° and 100 atm for 6 hr. The ratio of **10** to **11** remained constant. A cyclohexane solution of **8** and **9** from a Raney nickel hydrogenation was hydrogenated over 5% palladium on carbon at 150° and 100 atm for 6 hr. The product was shown to be **11** by glpc retention time and comparison of ir spectra.

Hydrogenation of Adduct 8.—A 2.0-g portion of pure **8** was obtained by preparative glpc. This sample was dissolved in 200 ml of cyclohexane and hydrogenated over Raney nickel at 150° and 100 atm for 3 hr. Analysis by glpc showed 15% **10** and 85% **11**.

Hydrogenation of Adduct 9.—A 1.5-g portion of pure **9** was obtained by preparative glpc. The sample was dissolved in 200 ml of cyclohexane and hydrogenated over Raney nickel at 150° and 100 atm for 3 hr. Analysis by glpc showed approximately equal amounts of **10** and **11**.

Registry No.—**1**, 29689-67-6; **3**, 29689-68-7; **5**, 29689-69-8; **6**, 19788-20-6; **8**, 29689-71-2; **9**, 29689-72-3; **10**, 29689-73-4; **11**, 29689-74-5; TMA, 1000-87-9.

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[9] Prepared according to ref 4.

[10] To avoid the isomerization of TMA to 2,4-dimethyl-1,3-pentadiene, either the glassware was washed with ammonium hydroxide solution or a pellet of sodium hydroxide was added to the reaction mixture.