showing a correct analysis for $C_{18}H_{22}$. Its infrared spectrum was identical with the authentic sample; infrared maxima (liquid film): 3080, 3050, 2950, 2880, 1615, 1500, 1455, 1032, 905, 746, and 697 cm.$^{-1}$. A minor fraction, $n^{24}\mathrm{D}$ 1.5453 (0.3 g.), appeared to be isomeric diphenylhexane(s); infrared maxima (liquid film): 1380 cm.$^{-1}$.

G.l.c. (PEG 20,000) analysis of the lower boiling fraction gave three peaks in the ratio of 1:14:26. The components were separated by preparative g.l.c. (PEG 20,000, 200°; N_2, 120 cc./min.) and were identified as described below to be *n*-hexylbenzene, 1,4-dimethyltetralin, and 1-ethyltetralin, respectively.

When the reaction was conducted at 80–83° for 6 hr., distillation of the reaction products gave two fractions: b.p. 111–112° (26 mm.), 6.6 g., and b.p. 135–148° (1.5 mm.), 3.1 g.

A sample (1 g.) of the higher boiling fraction was purified by chromatography on an alumina column to afford 0.5 g. of pure 1,6-diphenylhexane, $n^{25}\mathrm{D}$ 1.5437, which showed a correct analysis for $C_{18}H_{22}$, and 0.5 g. of isomeric diphenylhexane(s), $n^{25}\mathrm{D}$ 1.5446; infrared maxima absorption (liquid film): 1380 cm.$^{-1}$.

G.l.c. of the lower boiling fraction gave three peaks: *n*-hexylbenzene, 1,4-dimethyltetralin, and 1-ethyltetralin in the ratio of 14:6.2:29.

The *n*-hexylbenzene fraction showing a correct analysis for $C_{12}H_{18}$ had an infrared spectrum which was identical with that of authentic sample[7]; infrared maxima (liquid film): 2970, 2880, 2810, 1610, 1500, 1450, 1380, 1030, 745, 725, and 700 cm.$^{-1}$.

The 1,4-dimethyltetralin fraction showed a correct analysis for $C_{12}H_{16}$ had an infrared spectrum which was identical with that of authentic 1,4-dimethyltetralin[8]; infrared maxima (liquid film): 3130, 3060, 2990, 2910, 1960, 1930, 1850, 1815, 1715, 1615, 1590, 1500, 1470, 1450, 1380, 1330, 1025, 780, and 750 cm.$^{-1}$. Dehydrogenation of this fraction (0.1 g.) by heating with 0.04 g. of sulfur at 230–240° for 2 hr. gave 1,4-dimethylnaphthalene which was identified in its picrate form, m.p. 142° (lit.[8] m.p. 143°), showing a correct analysis for $C_{18}H_{15}N_3O_7$.

The 1-ethyltetralin fraction also showing a correct analysis for $C_{12}H_{16}$ had an infrared spectrum which was identical with the one of authentic 1-ethyltetralin[9]; infrared maxima (liquid film): 3130, 3070, 2990, 2910, 1960, 1930, 1850, 1810, 1610, 1590, 1500, 1460, 1380, 750, and 730 cm.$^{-.1}$

***trans*-1,2-Dichlorocyclohexane**, b.p. 80–82° (25 mm.), $n^{21.5}\mathrm{D}$ 1.4898, was prepared by the method of Kharasch and Brown[18] from cyclohexene and sulfuryl chloride and its *trans* configuration was established by comparison of infrared data with published ones.[19] This preparation gave a single peak on g.l.c.

***cis*-1,2-Dichlorocyclohexane.**—The reaction of 2-chlorocyclohexanol[20] with thionyl chloride in the presence of pyridine according to the method of Stevens and Grummit[21] gave a mixture of *cis*- and *trans*-1,2-dichlorocyclohexanes (g.l.c. showed two peaks in the ratio of 3:1), from which pure *cis* isomer was obtained by repeated fractionation, b.p. 89–92° (17 mm.), $n^{20.5}\mathrm{D}$ 1.4960. This sample gave a single peak on g.l.c., the retention time being 1.93 relative to *trans*-1,2-dichlorocyclohexane.

***cis*- and *trans*-1,4-Dichlorocyclohexanes.**—This mixture, b.p. 72–80° (12 mm.), was prepared by the method of Kwestroo, Meijer, and Havinga,[22] and g.l.c. showed two major peaks with retention times of 1.25 and 1.33 relative to *trans*-1,2-dichlorocyclohexane. Upon cooling, the crystalline *trans*-1,4-dichlorocyclohexane, m.p. 102° (lit.[13] m.p. 102–102.8°), was obtained and its relative retention time on g.l.c. was observed as 1.33.

Izomerization of *trans*-1,2-Dichlorocyclohexane.—A mixture of 50 g. of *trans*-1,2-dichlorocyclohexane, 8.9 g. of aluminum chloride, and 150 ml. of carbon disulfide was stirred at room temperature for 10 hr. The dark reaction product was decomposed with ice–water and acidified with hydrochloric acid; the solvent was removed by steam distillation. The residue was taken up in benzene and the benzene layer was washed and dried ($CaCl_2$). Evaporation of benzene followed by distillation *in vacuo* gave a colorless oil, b.p. 58–60° (9 mm.), $n^{21}\mathrm{D}$ 1.4907, which weighed 28.2 g. and showed a correct analysis for $C_6H_{10}Cl_2$.

The g.l.c. data are given in Table I and the n.m.r. spectrum (recorded on Varian-A60 in carbon tetrachloride solution using tetramethylsilane as an internal reference) had two multiplets whose chemical shifts were 1.5–2.5 and 3.8–4.5 p.p.m., respectively. No methyl signal was observed.

In another run, the corresponding fraction (26.4 g.), b.p. 60–77° (12 mm.), was redistilled and the lowest boiling fraction, b.p. 65–69° (11 mm.), was cooled at −35° in a solution of 50 ml. of *n*-pentane. Thus *ca.* 1 g. of colorless crystals melting at 102–102.5° after recrystallization from ethanol was obtained. Mixture melting point with authentic *trans*-1,4-dichlorocyclohexane showed no depression and the infrared spectra were superimposable.

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[18] M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 3432 (1939).

[19] P. Laeboe, J. J. Lothe, and K. Lunde, *Acta Chem. Scand.*, **11**, 1677 (1957).

[20] M. S. Newman and C. A. VanderWerf, *J. Am. Chem. Soc.*, **67**, 235 (1945).

[21] H. C. Stevens and O. Grummit, *ibid.*, **72**, 4876 (1952).

[22] W. Kwestroo, F. A. Meijer, and E. Havinga, *Rec. trav. chim.*, **73**, 717 (1954).

A Novel Telomerization Process

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Reaction of oxalyl chloride with olefins is reported to occur only in the case of certain di- and trisubstituted ethylenes.[1,2] These particular reactions result in replacement of an ethylenic hydrogen with the chloroformyl group and apparently occur by an ionic mechanism. Although oxalyl chloride undergoes homolytic decomposition under relatively mild conditions,[3] there are no reports of a free-radical addition to the carbon–carbon double bond.

A Co^{60}-catalyzed reaction between ethylene and oxalyl chloride was discovered in these laboratories during the course of a general investigation of radiation promoted telomerizations. In the first of several preliminary experiments, an equimolar mixture of oxalyl chloride and ethylene (500 p.s.i.) was irradiated 41 hr. at 10^5 rep/hr. and 25°. Analysis (g.l.p.c.) indicated two major products: the 1:1 ($G = 20$) and 2:1 ($G = 70$) telomers $Cl(C_2H_4)_nCOCl$; other products including the 3:1 telomer were formed, but these totaled less than 1% of the combined 1:1 and 2:1 telomer yields. Surprisingly, and in contrast to the broad distribution of products predicted for a "normal" telomerization,[4] the 2:1 telomer was the sole major product at low (*e.g.*, <1:20) oxalyl chloride–ethylene mole ratios. No measurable "dark" reaction was observed and the catalytic effect of radiation was completely nullified by small amounts (*e.g.*, 1%) of molecular oxygen.

These results indicate a short-chain free-radical process in which the 2:1 radical intermediate is subject to an abnormally high incidence of chain transfer. If the chain carrier is assumed to be the chloroxalyl radical, ·COCOCl, then the principal features of the process can be explained by the following sequence of reactions. One addition step (1) followed by chain transfer (2) leads to a nonisolable α-keto acid chloride,

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[1] M. S. Kharasch, S. S. Kane, and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 333 (1942).

[2] F. Bergmann, *et al.*, *ibid.*, **70**, 1612 (1948).

[3] (a) M. S. Kharasch and H. C. Brown, *ibid.*, **64**, 329 (1942); (b) F. Runge, *Z. Elektrochem.*, **56**, 779 (1952); (c) M. T. Ahmed and A. J. Swallow, *J. Chem. Soc.*, 3918 (1963).

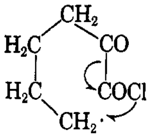
[4] See C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 6.

$$\cdot COCOCl + C_2H_4 \longrightarrow \cdot C_2H_4COCOCl \quad (1)$$

$$\cdot C_2H_4COCOCl + ClCOCOCl \longrightarrow (ClC_2H_4COCOCl) + \cdot COCOCl \quad (2)$$

$$(ClC_2H_4COCOCl) \xrightarrow[-CO]{} ClC_2H_4COCl \quad (3)$$

$$\cdot C_2H_4COCOCl + C_2H_4 \longrightarrow \cdot(C_2H_4)_2COCOCl \quad (4)$$



$$\xrightarrow[-CO]{} Cl(C_2H_4)_2CO\cdot \quad (5)$$

$$Cl(C_2H_4)_2CO\cdot + ClCOCOCl \longrightarrow Cl(C_2H_4)_2COCl + \cdot COCOCl \quad (6)$$

which should readily lose CO (from C-1)[5] to form the 1:1 product (3).[6] A facile intramolecular transfer of chlorine *via* a cyclic intermediate (5) is postulated to account for the termination of chain growth at $n = 2$.[7] The acyl radical formed in eq. 5 might undergo several different reactions but related studies suggest that chain transfer (6) would predominate.[8]

This mechanism predicts a simple relationship at low conversions between the 1:1 and 2:1 yield ratio, the chain-transfer constant $C_1 = k_2/k_4$, and the relative concentrations of telogen and olefin (R), *viz.*

$$\frac{1:1 \text{ yield}}{2:1 \text{ yield}} \simeq \frac{d[1:1]}{d[2:1]} = \frac{k_2[(COCl)_2]}{k_4[C_2H_4]} = C_1R$$

The same relationship would apply to a conventional telomerization in which C_2 is large yet finite, and it would be inaccurate only to the extent that $C_2R/C_2R + 1$ differs from unity. Table I summarizes several low to moderate conversion experiments which demonstrate that C_1 is essentially invarient with R (range: 0.6–2), also, that C_2 is large both numerically and in comparison to C_1 and C_3. The pronounced decrease, some two orders of magnitude, in the value of the chain-transfer constant between $n = 2$ and $n = 3$ seemingly reflects the relative ease with which rearrangement (5) occurs, and is in marked contrast with the slight to moderate increases generally observed for telomerizations in which only bimolecular-type transfer steps are involved.[9]

Carbon monoxide equivalent to 99% of the combined yields of the 1:1, 2:1, and 3:1 telomers was found in the gaseous product of run 5, Table I. The equivalence in yields is interpreted to mean that reaction 3 was complete prior to work-up and analysis of the telomers. Although some carbon monoxide may be formed by direct decomposition of oxalyl chloride, the co-product, phosgene, can be ruled out as the principal telogen.[10]

Even though the oxalyl chloride–ethylene reaction can apparently be regulated so as to produce selectively either of two potentially useful acid chlorides, presently it does not qualify as a reliable synthetic tool. This conclusion is based on the wide variation in G experienced in the series of experiments, Table I.

Experimental

Reagents.—Eastman White Label oxalyl chloride was fractionated through an all-glass column. A center-cut fraction (80%) was collected and stored under argon in darkness. The ethylene used was Phillips research grade with an indicated purity of 99.94 mole %.

Irradiation.—The telomerizations were carried out in glass-lined, magnetically stirred 316 stainless autoclaves with net capacities of 70 ml. Oxalyl chloride (25.0 ml. in the experiments, Table I) was charged to the reactors under argon and then degassed twice by the freeze-pump technique. Accurately measured quantities of ethylene were pressured into the stirred reactors at 25°. Equilibrium (saturation) pressures ranged from 627 (runs 1 and 2) to 395 p.s.i. (runs 7 and 8). The amounts of ethylene in solution as calculated from density–pressure–volume measurements (a thin deposit on the wall of the liner defined the volume of the liquid phase) ranged from 88% of the charge at the highest pressure to 69% at the lowest pressure.

Irradiations with the Co^{60} source were performed under water at ambient temperature (approximately 25°). Average dose rates in reaction volumes were determined by sodium formate (0.2 M) dosimetry.[11]

Identification and Analysis of Products.—This was accomplished with the aid of a gas chromatograph equipped with a silicone-on-glass column and with detectors suitable for measuring concentrations as low as 10 p.p.m. The telomer acid chlorides as well as the corresponding ethyl esters were identified with authentic standards (see below) through their g.l.p.c. retention times. Only the 2:1 ester was isolated (distillation) and identified as the neat liquid. Several unidentified liquid components were detected by g.l.p.c. but these never totaled more than about 1 wt.% of all products.

Telomer yields for the experiments (Table I) were based on quantitative treatment of the liquid products with excess ethanol and g.l.c.p. analysis of the resulting alcohol–ester solutions. A control run employing a synthetic mixture of acid chlorides with composition corresponding to that indicated for the product run 3 gave the following recoveries (%): 1:1 (106), 2:1 (100), and 3:1 (102). The moles of gas recovered in the various experiments corresponded to 99 ± 3% of the amounts charged. In run 5, 0.0303 mole of carbon monoxide was found (mass spectrometry) in the gaseous product and the liquid product yielded 0.0307 mole of telomers.

Standards.—Ethyl oxalate, 2-chloropropionyl chloride, and ethyl 2-chloropropionate, all >99 wt. % pure by g.l.p.c., were obtained from commercial sources. Pure 2:1 and 3:1 ethylene–carbon tetrachloride telomers were hydrolyzed with aqueous sulfuric acid and after purification the resulting ω-chloro acids were treated with oxalyl chloride to give 5-chloropentanoyl chloride,

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(5) The decomposition and its course are predicated on the basis of properties indicated for pyruvyl chloride [see P. Carré and P. Jullien, *Compt. rend.*, **202**, 1521 (1936)] and ethyl α-C^{14}-pyruvate [M. Calvin and R. M. Lemmon, *J. Am. Chem. Soc.*, **69**, 1232 (1947)].

(6) Kharasch and Brown[3a] discounted the possibility that α-keto acid chlorides are intermediates in free-radical substitution reactions of oxalyl chloride primarily because of their failure to obtain either pyruvyl chloride or acetyl chloride from pyruvic acid and oxalyl chloride. An earlier publication by Carré and Jullien,[5] indicating that these acid chlorides were present in the products of the reaction of pyruvic acid and thionyl chloride, was apparently overlooked.

(7) The proposal by Kharasch and Brown[3a] that alkyl radicals attack oxalyl chloride at the carbon–carbon bond rather than at the carbon–chloride bond suggests that the chain carrier in the present reaction is ·COCl and that the radical $\cdot(C_2H_4)_2COCl$ undergoes intramolecular rearrangement as in eq. 5; however, aliphatic acid chlorides are evidently quite stable under free-radical conditions and therefore such rearrangement does not seem likely.

(8) The high reactivity of acyl radicals in chain-transfer reactions is illustrated by the selective formation of telomers $A(C_2H_4)_nCOB$ from ethylene, certain chain-transfer agents (AB), and carbon monoxide, n being generally low compared with values for telomerizations of AB and ethylene alone [see R. E. Foster, *et al.*, *ibid.*, **78**, 5606 (1956)]. Preliminary results from a current study of the radiation-catalyzed reaction in which AB = CCl_4 provide further evidence of this high reactivity. For example, irradiation (dose: 2–3 × 10^6 rep) of a 1:1:2.7 C_2H_4–CCl_4–CO mixture at 30° and 2600 p.s.i. gave a product containing 88 wt. % 1:1 and 2:1 acid chlorides (mole ratio 1:1–2:1 = 11.5; yield = 25 mole %). More than 95 mole % of the titratable acid present in the product was accounted for as the 1:1 and 2:1 acid chlorides. Other possible reactions of the acyl radicals such as addition to ethylene or decarbonylation are apparently of little importance, even in the absence of added carbon monoxide.

(9) *Cf.* ref. 4; also F. W. Mellows and M. Burton, *J. Phys. Chem.*, **66**, 2164 (1962).

(10) Mixtures of liquid and solid products which are presumably high molecular weight telomers [see Japanese Patent 7880 (1963); *Chem. Abstr.*, **59**, 13828 (1964)] were obtained on irradiation of dense 0.5–1.5:1 phosgene–ethylene mixtures. *Only trace amounts of the 1:1 (G <0.5), 2:1 (G ~2–4),* and 3:1 (*G* ~2) telomers were found in these products.

(11) T. J. Hardwick and W. S. Guentner, *J. Phys. Chem.*, **63**, 896 (1959).

TABLE I

RADIATION-CATALYZED OXALYL CHLORIDE–ETHYLENE TELOMERIZATION AT 25°

Run no.[a]	$\frac{[(COCl)_2]_0}{[C_2H_4]_0}$ (mole ratio)[b]	Telomer yield (mole % on telogen)			G (telomers)[c]	C_n[d]		
		1:1	2:1	3:1		n = 1 (k_2/k_4)	n = 2	n = 3
1	0.59	0.60	4.68	0.06	500	0.21 (0.22)	~120	~6
2	0.60	..	...	...	~100	.. (0.21)[e]	...	...
3	1.1	2.9	10.2	0.08	1400	0.26 (0.26)	~110	~7
4	1.1	...	...	...	~50	..	...	...
5[f]	1.1	2.1	8.60	0.07	220	0.22 (0.22)	~110	~7
6[g]	1.1	0	0	0	0	..	...	...
7	1.9	4.2	9.55	0.02	1500	0.23 (0.23)	~180	~0.3
8	1.9	...	...	...	~50	..	...	...

[a] Dose rate in each run = 1.5 × 10^4 rep (in water); dosage = 0.63 *M* rep except in runs 5 (3.2 *M* rep) and 6 (2.4 *M* rep). [b] For liquid phase. [c] Based on uncorrected radiation dosages. [d] See ref. 4 for formula. [e] Only 1:1–2:1 yield ratio was determined. [f] Recovered 0.99 mole of carbon monoxide/mole of telomers. [g] Starting mixture contained 1 mole % oxygen.

b.p. 63–64° (4 mm.), lit.[12] b.p. 56–58° (2.5 mm.), neut. equiv. 77.5 (calcd. 77.5), and likewise 7-chloroheptanoyl chloride, b.p. 82° (2 mm.), neut. equiv. 91.0 (calcd. 91.5). Reaction of the acid chlorides with ethanol gave, after distillation, 99+ wt. % pure samples of ethyl 5-chloropentanoate, b.p. 83.5–84.5° (8 mm.), $n^{25}D$ 1.4339, lit.[13] b.p. 83.5–85° (8 mm.), $n^{20}D$ 1.4355, and ethyl 7-chloroheptanoate, b.p. 91.5° (2 mm.), $n^{25}D$ 1.4391.

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[12] N. Clark and A. Hams, *J. Biochem.*, **55**, 839 (1953).

[13] L. Cheney and J. R. Piening, *J. Am. Chem. Soc.*, **67**, 731 (1947).

The Isolation of a Cyclic Intermediate in the Ketone–Alkoxyacetylene Reaction

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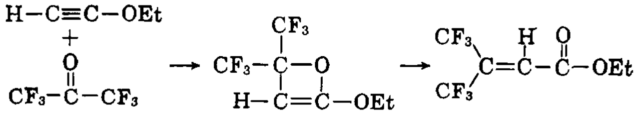
Ketones react with alkoxyacetylenes in the presence of boron trifluoride catalyst to give α,β-unsaturated esters in high yield.[1] The formation of an oxete as a cyclic intermediate has been postulated for this reaction,[1] but such an intermediate has not been isolated previously.

We have found that hexafluoroacetone (I) reacts vigorously and exothermically with ethoxyacetylene without added catalyst. When the reaction is conducted at room temperature, ethyl β,β-bis(trifluoromethyl)acrylate (III) is formed. If the reaction is carried out at lower temperatures, however, the intermediate oxete II can be isolated and characterized. This oxete II slowly isomerizes to the ester III if stored at room temperature for a few days. This rearrangement is exothermic and becomes rapid at about 70°.



I II III

Experimental[2]

2-Ethoxy-4,4-bis(trifluoromethyl)-2-oxete.—Hexafluoroacetone, 10.5 ml. measured at −78° (0.1 mole), was slowly distilled into a flask that contained 7.0 g. (0.1 mole) of freshly distilled ethoxyacetylene precooled to −78°. Strong cooling was maintained during the entire addition. The dark reaction mixture was distilled at reduced pressure to give 20.1 g. (85% yield) of 2-ethoxy-4,4-bis(trifluoromethyl)-2-oxete as a colorless oil, b.p. 29–30° (8 mm.), $n^{25}D$ 1.3331. The F^{19} n.m.r. spectrum showed a singlet at 10.7 p.p.m., and the proton n.m.r. spectrum showed a singlet at 4.60 p.p.m. in addition to resonance lines attributed to the ethyl group. The infrared spectra contained a band at 5.93 for C=C and at 3.14 μ for ≡CH.

Anal. Calcd. for $C_7H_6F_6O$: C, 35.61; H, 2.57; F, 48.28. Found: C, 35.41; H, 2.87; F, 48.22.

Ethyl β,β-Bis(trifluoromethyl)acrylate.—A sample of 2-ethoxy-4,4-bis(trifluoromethyl)-2-oxete that had been stored at room temperature for 2 weeks was found to have isomerized quantitatively to ethyl β,β-bis(trifluoromethyl)acrylate, b.p. 126–127°, $n^{25}D$ 1.3382.[3] The infrared spectrum of this ester contained bands at 5.96 (C=C) and 5.72 μ (C=O). The F^{19} n.m.r. spectrum showed two quartets (*J* = 8 c.p.s.) centered at −4.61 and −0.18 p.p.m. The proton n.m.r. spectrum contained a singlet at 7.22 p.p.m. in addition to resonance lines attributed to the ethyl group.

Anal. Calcd. for $C_7H_6F_6O_2$: C, 35.61; H, 2.57; F, 48.28. Found: C, 34.45; H, 2.73; F, 48.07.

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[1] H. Vieregge, H. J. T. Bos, and J. F. Arens, *Rec. trav. chim.*, **78**, 664 (1959).

[2] Fluorine n.m.r. spectra were obtained with a Varian Associates high-resolution n.m.r. spectrometer operating at 56.4 Mc./sec. Spectra were calibrated in terms of higher field displacement in p.p.m. from the F^{19} resonance of 1,2-difluorotetrachloroethane used as an external reference. Proton resonance spectra were obtained with a Varian Associates A-60 spectrometer. Spectra were calibrated in terms of lower field displacement in p.p.m. from the proton resonance of tetramethylsilane used as an internal reference.

[3] I. L. Knunyants and Yu. A. Cherburkov [*Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2162 (1960)] report b.p. 128° (747 mm.) and $n^{20}D$ 1.3414 for this compound, which was prepared by the esterification of the corresponding acid.

(+)- and (−)-(Isopropylidenaminooxy)propionic Acid

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In 1955 Newman and Lutz[1] introduced optically active α-(2,4,5,7-tetranitro-9-fluorenylidenaminooxy)propionic acid, subsequently abbreviated TAPA,[2] for the resolution of polycyclic aromatic hydrocarbons which do not possess a functional group capable of salt formation with an optically active acid or base. This compound consists of the complexing agent, tetranitro-

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[1] M. S. Newman and W. B. Lutz, *J. Am. Chem. Soc.*, **78**, 2469 (1956).

[2] M. S. Newman and D. Lednicer, *ibid.*, **78**, 4765 (1956).